

A11101 955046

A UNITED STATES
DEPARTMENT OF
COMMERCE
PUBLICATION



NBS
PUBLICATIONS

NSRDS—NBS 37



JANAF Thermochemical Tables

Second Edition

U.S.
DEPARTMENT
OF
COMMERCE
National
Bureau
of
Standards

OCT 6 1971

162031

UNITED STATES DEPARTMENT OF COMMERCE • MAURICE H. STANS, *Secretary*

U.S. NATIONAL BUREAU OF STANDARDS • LEWIS M. BRANSCOMB, *Director*

JANAF Thermochemical Tables

SECOND EDITION

D. R. Stull and H. Prophet

Project Directors

Office of Standard Reference Data
National Bureau of Standards
Washington, D.C. 20234



NSRDS—NBS, 37.

t. manual reference
Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37, 1141 pages (June 1971)

CODEN: NSRDA

Issued June 1971

JANAF THERMOCHEMICAL TABLES

Second Edition

Superseding PB 168-370 and addenda 1, 2 and 3.

Prepared under
Air Force Contracts
F04611-67-C-0009
F04611-70-0028

by

The following personnel of the Dow Chemical Company:

D. R. Stull and H. Prophet, Project Directors

J. Chao,	1961-69	A. N. Syverud,	1963-70
A. T. Hu,	1965-70	T. E. Dergazarian,	1959-63
E. W. Phillips,	1963-66	A. C. Swanson,	1962-64
G. C. Karris,	1965-68	D. U. Webb,	1967-68
S. K. Wollert,	1963-65	L. A. DuPlessis,	1960-61
S. Levine,	1960-61	H. K. Unger,	1963-64
J. L. Curnutt,	1969-70	R. S. Orehotsky,	1963-64
J. A. Rizos,	1962-63	R. V. Petrella,	1961-62
B. H. Justice,	1964	S. T. Hadden,	1962
F. L. Oetting,	1961	G. C. Sinke,	1961, 65, 69, 70

at

The Thermal Research Laboratory
Dow Chemical Company
Midland, Michigan

Technically Assisted by
The Thermochemical Working Group
Interagency Chemical Rocket Propulsion Group

July 1970

Foreword

The National Standard Reference Data System provides effective access to the quantitative data of physical science, critically evaluated and compiled for convenience, and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, with responsibility to administer it assigned to the National Bureau of Standards.

The System now comprises a complex of data centers and other activities, carried on in academic institutions and other laboratories both in and out of government. The independent operational status of existing critical data projects is maintained and encouraged. Data centers that are components of the NSRDS produce compilations of critically evaluated data, critical reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. In addition, the centers and projects establish criteria for evaluation and compilation of data and make recommendations on needed improvements in experimental techniques. They are normally closely associated with active research in the relevant field.

The technical scope of the NSRDS is indicated by the principal categories of data compilation projects now active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

The NSDRS receives advice and planning assistance from the National Research Council of the National Academy of Sciences-National Academy of Engineering. An overall Review Committee considers the program as a whole and makes recommendations on policy, long-term planning, and international collaboration. Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The NSRDS-NBS series of publications is intended primarily to include evaluated reference data and critical reviews of long-term interest to the scientific and technical community.

The JANAF Thermochemical Tables Project, sponsored and monitored by agencies of the Defense Department, has been considered an important part of the National Standard Reference Data System. The tables have found wide utility in technical areas far removed from those for which the work was initiated. Consequently, when plans for a Second Edition of the JANAF Thermochemical Tables were under discussion, a suggestion was made that they be incorporated into the NSRDS-NBS publication series. This suggestion was accepted, and the present volume, NSRDS-NBS 37, is the outcome. It is hoped that this publication channel will lead to even wider distribution and greater use of these very valuable tables.

LEWIS M. BRANSCOMB, *Director*

PREFACE TO THE FIRST EDITION

Beginning in the mid-1950's, when elements other than the conventional carbon, hydrogen, oxygen, nitrogen, chlorine, and fluorine came into consideration as rocket propellant ingredients, formidable difficulties were encountered in conducting rigorous theoretical performance calculations for these new propellants. The first major problem was calculational techniques. The second was the lack of accurate thermodynamic data.

By the end of 1959, the calculational technique problem had been substantially resolved by applying the method of minimization of free energy to large, high-speed digital computers. At this point the calculations became as accurate as the thermodynamic data upon which they were based. However, serious gaps were present in the available data. For propellant ingredients, only the standard heat of formation is required to conduct a performance calculation. However, this must be known to a high degree of accuracy. For combustion products, the enthalpy and entropy must be known, as a function of temperature, in addition to the standard heat of formation.

In order to resolve the problem, a substantial experimental thermodynamic research program was initiated under the sponsorship and technical direction of Project PRINCIPIA of the Advanced Research Projects Agency. Simultaneously, a project was initiated to critically evaluate and compile consistent tables of thermodynamic properties of propellant combustion products for use by the aerospace industry. This project, known as the "JANAF Thermochemical Tables," was undertaken by the Dow Chemical Company. Since the objective of the project was to have one single source of "best available data" prepared for use by the entire industry, the JANAF Thermochemical Panel undertook the task of furnishing a critical review of the Tables prior to their publication and distribution. This approach was designed to insure that the Tables be of the highest possible quality.

Washington, D.C.
July 1964

G. V. Mock
Advanced Research Project Agency

PREFACE TO THE SECOND EDITION

It is appropriate to call attention to some of the reasons for the phenomenal success of the JANAF Thermochemical Tables in achieving, first, the initial limited objective of providing the standard data for the chemical rocket propulsion industry, and later, upon publication, world-wide recognition as thermodynamic reference data of the highest quality and timeliness.

First, and most obvious, there was the selection and continued support of a highly competent evaluation team, themselves engaged in a broad spectrum of thermodynamic research. The personnel of the Thermal Research Laboratory of the Dow Chemical Company, under the direction of Dr. D. R. Stull and Dr. H. Prophet, have filled this role to a degree of excellence not likely to be exceeded anywhere. Moreover, the group has heroically remained productive in spite of many battles to retain continuing support, and the actual sharp reduction of funding over the past two years to a less-than-viable level.

A second important factor is the unusual approach to format, evaluation, and distribution of the Tables, as it has been followed since their inception. The primary distribution is in frequently issued loose-leaf supplements. Each previously issued table may thus be revised as often as necessary to take account of improved data. Each loose-leaf table is accompanied on its reverse side by a complete explanation of the selection of the key data, together with all references.

The third vital distinction of these Tables has been the existence of a continuing cognizant working group composed of technological users of data, thermodynamicists, and government sponsors of both research and development. Independent prepublication review of the Tables has been an important contribution of some of the members of this group; but its annual technical meetings have resulted in even more far-reaching benefits. Together, the users and generators of data have been able to establish realistic priorities for the species to be included in the Tables; at the same time the course of experimental research has been guided by the demonstration of absence or inadequacy of needed data. Although the working group no longer enjoys official recognition, the members and participants have enthusiastically volunteered to continue meeting in this important work.

Special words of appreciation are due to Dr. Charles W. Beckett, who has lined up all the technical presentations at the last six annual meetings of the working group; and to Mr. Curtis C. Selph who has served with wisdom and insight as the Air Force project monitor for the JANAF Thermochemical Tables contracts.

JOSEPH F. MASI
Air Force Office of Scientific Research

Arlington, Virginia
October, 1970

Members of the JANAF Thermochemical Panel (1959-1961) and the JANAF Thermochemical Working Group (1961-1964) were:

T. O. Dobbins, Advanced Research Projects Agency (Past Chairman)
W. H. Jones, Institute for Defense Analysis; Aerospace Corporation (Past Chairman)
W. G. May, Institute for Defense Analyses; Esso Research and Engineering Company
(Past Chairman)
C. W. Beckett, National Bureau of Standards (Vice Chairman)
G. W. Avery, Chemical Propulsion Information Agency (Past Secretary)
B. K. Farris, Chemical Propulsion Information Agency (Past Secretary)
T. L. Reedy, Chemical Propulsion Information Agency (Secretary)
B. J. Alley, Army Materiel Command
P. W. Bender, University of Wisconsin
W. A. Bennett, Bureau of Naval Weapons
B. Brown, Hercules Powder Company
C. L. Funk, Jet Propulsion Laboratory
J. S. Gordon, Thiokol Chemical Corporation
L. J. Gordon, Aerojet-General Corporation
S. A. Greene, North American Aviation, Incorporated
C. B. Henderson, Atlantic Research Corporation
D. L. Hildenbrand, Philco Corporation
J. L. Margrave, University of Wisconsin
J. P. McCullough, U.S. Bureau of Mines
P. L. Nichols, Jr., Jet Propulsion Laboratory
C. C. Selph, Air Force Systems Command
D. R. Stull, Dow Chemical Company

The Thermochemical Working Group of the Interagency Chemical Rocket Propulsion Group (ICRPG) has consisted of the following at various times during its existence (1964-1969).

Members

J. F. Masi, Air Force Office of Scientific Research (Chairman)
C. W. Beckett, National Bureau of Standards (Vice Chairman)
T. O. Dobbins, Advanced Research Projects Agency
S. Gordon, National Aeronautics and Space Administration
R. Jackel, Office of Naval Research
J. Murrin, Naval Ordnance Systems Command
R. Odom, Army Materiel Command
C. E. Selph, Air Force Rocket Propulsion Laboratory
D. Squire, Army Research Office

Participants

G. S. Bahn, Marquardt Corporation
B. Brown, Hercules, Incorporated
H. F. Calcote, AeroChem Research Laboratories
J. P. Coughlin, Aerojet-General Corporation
J. S. Gordon, Atlantic Research Corporation
D. R. Douslin, U.S. Bureau of Mines
M. Farber, Space Sciences, Incorporated
R. M. Fristrom, Applied Physics Laboratory
C. B. Henderson, Atlantic Research Corporation
D. L. Hildenbrand, Douglas Aircraft Company
J. L. Margrave, Rice University

W. G. May, Esso Research and Engineering Company
W. Mitchell, Thiokol Chemical Corporation
C. F. Robillard, Jet Propulsion Laboratory
L. Schieler, Aerospace Corporation
C. H. Shomate, Naval Weapons Center
D. R. Stull, Dow Chemical Company
M. Zimmer, Naval Ordnance Station

Secretariat (Chemical Propulsion Information Agency)

T. Gilliland
M. McCormack
T. L. Reedy

Project Personnel

The Tables began under the direction of Daniel R. Stull in 1959. Major contributions in the first two years were made by Thomas E. Dergazarian, Samuel Levine and Louis A. DuPlessis. In the years from 1961 to 1969 the major contributors were Jing Chao, Harold Prophet, Alan N. Syverud and Andrew T. Hu. In 1969 Harold Prophet succeeded Daniel R. Stull as project director. At present Alan N. Syverud, Andrew T. Hu and Jerry L. Curnutt are the principal contributors.

Special mention must be made of Alan N. Syverud for his help in the technical editing of the Tables. Also G. C. Sinke has aided the project on numerous occasions with criticism, advice and tables.

We also wish to acknowledge the valuable assistance of Norma Dumont 1959-64, Viola E. Harrington 1964-66, Carol S. Scheffler 1966-67, Wildene B. Harris 1967-68 and Mary J. Walter since 1968 in the typing of these Tables. Isabel Carr has provided valuable services to the group in abstracting, searching and ordering documents, and proof reading the Tables.

We also wish to thank the staff of the Computation Research Laboratory for their assistance in the many facets of the production of these Tables.

DANIEL R. STULL
HAROLD PROPHET

Contents

	Page
Foreword	iii
Preface to the First Edition	iv
Preface to the Second Edition	v
Members of the JANAF Thermochemical Panel	vi
Project Personnel	vii
Constants Used	1
Symbols and Terminology	2
Evaluation of Thermodynamic Data	4
Calculation Methods	9
Notes	11
Index to Tables	13
Tables	Tables (Arranged by Chemical Symbols)

C O N S T A N T S U S E D

The fundamental constants are those recommended by the International Union of Pure and Applied Chemistry as reported by F. D. Rossini, Pure and Applied Chemistry, 9, 453 (1964). The physical scale based on the atomic mass of $^{12}\text{C} = 12$ reported by A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962) is employed. The temperature scale is nominally the 1948 International Practical Temperature Scale for measured quantities and nominally the thermodynamic temperature scale for calculated gaseous quantities. The probable errors between these scales and the 1968 International Practical Temperature Scale are given by T. B. Douglas, J. Research Natl. Bur. Std. 73A, 451 (1969).

Fundamental Constants

<u>Name</u>	<u>Symbol</u>	<u>Value</u>	<u>Units</u>
Velocity of Light	c	2.997925×10^{10}	cm s ⁻¹
Planck Constant	h	6.6256×10^{-27}	erg s
Avogadro Constant	N	6.02252×10^{23}	mol ⁻¹
Faraday Constant	$\mathcal{F}$	96,487.0	C mol ⁻¹
Absolute temperature of the "ice point", 0°C	T ₀ °C	273.1500	K
Molar volume of ideal gas (1 atm)	V ₀ °C	22,413.6	cm ³ mol ⁻¹
Pressure-Volume product for a mole of gas at 0°C and zero pressure	$\begin{matrix} P=0 \\ (PV) \\ T_0^\circ\text{C} \end{matrix}$	2271.06	J mol ⁻¹
Electronic Charge	e	1.60210×10^{-19}	C
Gas constant	R	8.3143	J deg ⁻¹ mol ⁻¹
		1.987165	cal deg ⁻¹ mol ⁻¹
Boltzmann Constant	k	1.38054×10^{-16}	erg deg ⁻¹ molecule ⁻¹
Second radiation constant	c ₂	1.43879	cm deg
Constant relating wave number and energy per mole E, in the relation $(\Delta E) = Nhc(\Delta\nu) = Z(\Delta\nu)$	Z	11.96255	J cm mol ⁻¹

Defined Constants

<u>Name</u>	<u>Symbol</u>	<u>Value</u>	<u>Units</u>
Standard gravity	g	980.665	cm s ⁻²
Standard atmosphere	atm	101 325	N m ⁻²
Standard millimeter of mercury pressure	mmHg	1/760	atm
Thermochemical calorie	cal	4.1840	J

SYMBOLS AND TERMINOLOGY

Throughout these tables, the symbols used are defined as follows:

amorph.	Amorphous state	S	Entropy
B	The rotational constant for diatomic or linear molecules	T	Temperature in degrees Kelvin ($T^\circ = t^\circ + 273.15^\circ$)
C_p	Molar heat capacity at constant pressure	t	Temperature in degrees Celsius
c	Crystalline state	V	Volume
D	Centrifugal distortion constant	V_0	Potential barrier
D_0	Dissociation energy required to break a bond at 0°K	x	First order vibrational anharmonicity constant
E	Internal or intrinsic energy	y	Second order vibrational anharmonicity constant
G or F	Gibbs energy = $E + PV - TS = H - TS$	α	Vibrational-rotational interaction constant
g_i	Quantum weight of electronic states	ϵ	Electronic energy level
()	Parentheses following a vibrational frequency are used to indicate the degeneracy	μ	Reduced mass of the molecule
g	Gaseous state, or statistical weight	ρ	Density
GFW	Gram Formula Mass	σ	Symmetry number
gls	Glassy state	ω	Vibrational frequency
H	Enthalpy (or heat content) = $E + PV$	[]	Square brackets enclose estimated quantities
I_A, I_B, I_C	Principal moments of inertia of a molecule	<u>Subscripts</u>	
$I_A I_B I_C$	Product of the principal moments of inertia of a molecule	a	Atomization
K	Equilibrium constant	b	Boiling point at one atmosphere pressure
k	Hooke's Law force constant	c	Combustion, or critical state
liq. or l	Liquid state	d	Dissociation
ln	Logarithm to the base e ($e = 2.7182818$)	e	Equilibrium position
log	Logarithm to the base 10	f	Formation from elements in their standard states
n	Number of potential maxima in an internal rotation	i	The i th quantity
P	Pressure in atmospheres	m	Melting
r	Internuclear distance	p	Constant pressure
		r	Reaction
		s	Sublimation
		t	Transition
		v	Vaporization

In addition to the above symbols, the spectroscopic symbols and terminology employed by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., and "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., New York, are adopted.

Circular superscript, °, indicates the thermodynamic standard state.

Numerical subscript, as $_{298.15}$, denotes temperature in Kelvins.

Δ indicates the increment in a given property for a given process or reaction, taken as the value for the final state (or sum for the products) less that for the initial state (or sum for reactants).

ΔH , ΔG , ΔS , ΔC_p equal the increment in enthalpy, Gibbs energy, entropy and heat capacity, respectively, for a process or reaction.

ΔH_f° represents the standard enthalpy of formation, which is the increment in enthalpy associated with the reaction of forming the given compound from its elements, with each substance in its thermodynamic standard state at the given temperature.

$\Delta H_c^\circ_{298.15}$ symbolizes the enthalpy of combustion of a given substance, in gaseous oxygen to completely oxidized products at 25°C. and constant pressure, with all reactants and products in their appropriate standard states.

SYMBOLS AND TERMINOLOGY

$\Delta H_{298.15}^\circ$ represents the enthalpy change in a given reaction at 25°C and constant pressure with all the reactants and products in their appropriate standard states.

When the reaction or process evolves heat, the sign of the change in enthalpy is negative. Conversely, when the reaction or process absorbs heat, the sign of the change in enthalpy is positive.

ΔG_f° or ΔF_f° denotes the standard Gibbs energy of formation, which is the increment in Gibbs energy associated with the reaction of forming the given compound from its elements, with each substance in its thermodynamic standard state at the given temperature.

$\log_{10} K_p$ stands for the logarithm (to the base 10) of the thermodynamic equilibrium constant of formation for the reaction of forming the given compound from its elements at the indicated temperature.

$(H_T^\circ - H_{298.15}^\circ)$ indicates the enthalpy (or heat content) in the standard state at the temperature T less the enthalpy in the standard state at 298.15 K.

$(G_T^\circ - H_{298.15}^\circ)/T$ or $(F_T^\circ - H_{298.15}^\circ)/T$ denotes the Gibbs energy function in the standard state at temperature T, and is defined as $-S_T^\circ + (H_T^\circ - H_{298.15}^\circ)/T$.

S_T° represents the absolute entropy of the thermodynamic standard state at the absolute temperature T, omitting contributions from nuclear spins.

The Standard State is taken as the state at one atmosphere pressure and the temperature under consideration for the solid, liquid, and ideal gas. Only homogeneous substances are considered here.

The Reference State applies to elements in their stable standard state. Consequently the Reference State tables presented here are either single phase or polyphase tables.

CHANGES IN SYMBOLS ON TABLES DATED 6-30-66 OR LATER

The following symbols are used, without periods, to indicate units as follows:

<u>Symbol</u>	<u>Unit</u>	<u>Symbol</u>	<u>Unit</u>
Å	angstrom	eu	calories per degree-mole
atm	atmosphere	g	gram
cal	calorie	J	joule
deg	degree (temperature)	kcal	kilocalorie
°C	degree Celsius	mm	millimeter
°K	degree Kelvin	mol	mole
eV	electron volt	gibbs	calories per degree

Subscripts as defined earlier are used as symbol modifiers but are placed on the same line, thus, heat capacity is abbreviated as C_p° , enthalpy of formation as ΔH_f° , etc.

RELATIONSHIP TO SI UNITS

The symbols cal. mole⁻¹ deg⁻¹ and gibbs/mol are identical and refer to units of calories per degree-mole. These units can be converted to SI units of joules per degree-mole by multiplying the tabulated values by 4.184. Similarly values in kilocalories per mole can be converted to joules per mole by multiplying with the factor 4184. For further discussions of the SI system and for conversions from other units the reader should consult Pure and Applied Chemistry, 21, 1 (1970).

EVALUATION OF THERMODYNAMIC DATA

A. Interconsistency

The basic aim of these thermodynamic property tables is to provide a related and consistent set of enthalpies and Gibbs energies of formation. This allows the prediction of the enthalpy and Gibbs energy changes of any reaction among the constituents of the tables. Since the enthalpy and Gibbs energy of formation are related to each other by the entropy of formation we may choose to make consistent any two of these quantities. The entropy, which is an absolute quantity in thermochemical calculations, is ideal for this purpose. Since the enthalpy of reaction is the most common link between different materials, we adopt it as the other consistent quantity. Unfortunately enthalpies are not absolute quantities and in order to achieve consistency it is necessary to provide a consistent base. This is done by referring all enthalpies of formation to the elements in their reference states. By convention the enthalpy of formation of an element in its reference state is zero at all temperatures.

The reference state may be single phase or multiphase and examples of both kinds are found in this compilation. In these tables we have generally chosen the ideal diatomic gas for the reference state of permanent gases such as O_2 , N_2 , Cl_2 etc. For elements which are solid at room temperature we adopt the solid state up to the melting point, then the liquid up to the boiling point, and then the gas phase. These choices are arbitrary and vary in different compilations. Enthalpies or Gibbs energies of formation taken from different sources should be checked to ensure that the reference states are the same.

The choice of reference states is the first step in any scheme for interconsistency, and is the relation of all quantities to comparable bases. The next step in obtaining an interconsistent set of values, ideally, would be to take all the measured values of enthalpies, Gibbs energies and entropies of reaction and, after adjustment to the proper reference states, to solve the whole set simultaneously. This would provide values for enthalpies, Gibbs energies and entropies which when combined would yield the minimum overall deviations from the measured values. We have already taken this approach in a limited sense by treating groups of interrelated fluorides simultaneously. Hopefully with even larger memories in computers we shall be able to move towards the ultimate goal. As an interim solution it is necessary to fix, simultaneously when possible, certain key values for common reactants such as water, hydrochloric acid, etc., these can then be used to help fix smaller groups of interrelated compounds.

Because of the several revisions of these tables we do not claim to maintain perfect interconsistency. However, the consistency of the tables is a prime concern and a cause for revision if the effects are of the same order of magnitude as the stated uncertainties. As an example, over 100 fluoride tables have been revised since a new HF gas table was adopted in December 1968.

Another type of consistency is involved in systems where properties must be estimated. For example the estimation of certain properties of a series of halides must be done so that the proper graduation in properties occurs from fluoride to iodide and from polyhalide to monohalide. Similarly the evaluation of experimental data must be done in a consistent manner, and this is discussed in the next section.

B. General Evaluation Techniques

1. The Second-Law Method

Starting from the equation $\Delta G^\circ = -T\ln K$, by differentiation with respect to T and substitution of $d(\Delta G^\circ)/dT = -\Delta S^\circ$, we obtain $\Delta H^\circ = RT^2 d(\ln K)/dT$, the well known van't Hoff equation. By substituting $dT = -T^2 d(1/T)$ one obtains $\Delta H^\circ = -Rd(\ln K)/d(1/T)$, thus, the slope of a $\ln K$ versus $1/T$ plot is $-\Delta H^\circ/R$. If ΔH° is constant then the slope is constant and the plot is a straight line. Since the variation of ΔH° with temperature is often quite small it is customary to assume a straight line relationship. This method of obtaining heats of reaction from equilibrium measurements is known as a "second-law" calculation. However, it should be noted that for greatest accuracy the equilibrium measurements should extend over a wide range of temperature, and in this case ΔH° is probably not constant. Curvature corrections can be applied by assuming a specific form for the variation of ΔH° with temperature, however, the effects of such corrections are of significance only with very precise measurements. It should be noted that the second law cannot be applied to a single observation, but the third-law method, which is described below, can be used. The second-law method can be applied when only relative values of the equilibrium constant are available, for example, from mass-spectroscopic intensity measurements.

2. The Third-Law Method

The third-law method is based on a knowledge of the absolute entropy of the reactants and products. It allows the calculation of a reaction enthalpy from each data point when the change in the Gibbs-energy function for the reaction is known. The Gibbs-energy function is defined as $gef_T = (G_T^\circ - H_{ref}^\circ)/T$ and is easily calculated from the relation

$$S_T^\circ = -(G_T^\circ - H_{ref}^\circ)/T = (H_T^\circ - H_{ref}^\circ)/T - (G_T^\circ - H_{ref}^\circ)/T$$

thus,

$$gef_T = -S_T^\circ + (H_T^\circ - H_{ref}^\circ)/T.$$

From the definition we can write for the change in a reaction

$$\Delta G^\circ/T = \Delta gef_T + \Delta H_{ref}^\circ/T = -R\ln K_p$$

thus,

$$\Delta H_{ref}^\circ/T = -R\ln K_p - \Delta gef_T$$

where Δ signifies Σ products $-\Sigma$ reactants.

In the JANAF Thermochemical Tables, Gibbs-energy functions are based on 298 K and, thus, yield enthalpies at 298 K regardless of the temperature of the reaction. It should be noted that, since most of these tables are single phase tables, the Gibbs-energy functions of liquids are based on liquid at 298 K even though it may not exist at 298 K. This differs from the usual convention of combining all condensed phases into one table; in this case the enthalpy of reaction refers to the state stable at the base temperature. In these tables the functions always refer to the state of the table at 298 K regardless of its stability. For

example, if the vapor pressure over liquid copper is analysed using $\text{Cu}(l)$ Gibbs-energy functions the enthalpy of vaporization at 298 K will result. To calculate the enthalpy of sublimation of Cu it is necessary to add the heat of melting at 298 K, which is the difference in the heat of formation of $\text{Cu}(l)$ and $\text{Cu}(c)$ at 298 K. It should also be noted that Gibbs-energy functions are always negative, thus the function $-(G_T^\circ - H_T^\circ)/T$ is usually tabulated and the proper sign must be remembered when using these functions.

The analysis of data by the third law is generally considered superior to the second-law analysis. It is definitely superior if the Gibbs-energy functions are measured, because each data point is independent of the others. Thus, third-law analysis will often reveal trends in the equilibrium constants of a set of data that indicate nonequilibrium or erroneous values. We have found a combination of the two methods to be so valuable that a third-law calculation is always accompanied by a second-law treatment of the same data. The calculation is done in ascending temperature order to give ΔH_{298} and its deviation from the mean, δ , and the calculated $\log K_p$ and its deviation from the least-squares line. Third-law analyses enables bad points to be seen as deviations from the general trend of the differences; thus the method can be used even when the Gibbs-energy functions are estimated. If these bad points are located on the ends of the data set, the second-law line often fits quite well through them and by itself does not arouse suspicion. Moreover, the dropping of such points can bring widely discordant slopes into agreement with each other and often with the third-law values. The data sets given in Table 1 illustrate these comments. The first set of data contains all the reported points and is in disagreement with earlier values around 54 kcal/mole. The third-law analysis indicates the first two points are poor, and the effect of dropping these two is shown in the second set of data. This latter second-law slope has changed considerably; the heat is in good agreement with the earlier data and with the third law. The size of the third-law deviations in the second set indicates that the data are not very reproducible. A deviation of 0.5 kcal at 1000°K represents an uncertainty of 30% in the measured equilibrium constants.

If measured Gibbs-energy functions are available, third-law analysis is preferred; however, if the data are good, the second-law value should agree. When the Gibbs-energy functions are estimated, the third-law values derived from them must be handled carefully. Values that are constant and that agree with the second-law enthalpy indicate that the Gibbs-energy functions and equilibrium data are mutually consistent. A drift with temperature of the third-law values indicates errors in either the data or the functions. The magnitude of such drifts is often given in the table write-up and represents the entropy change required to bring the second- and third-law values into agreement. If the drift is within the experimental entropy uncertainty then the data are acceptable. Drifts which are much larger than reasonable entropy errors generally indicate failure to attain equilibrium.

Table 1. Analysis of Equilibrium Data
 $\text{PbF}_2(c) \rightarrow \text{PbF}_2(g)$, data of Nesmeyanov and Iofa, Russ. J. Inorg. Chem. 4, 219 (1959)

Analysis I						Analysis II					
Third Law			Second Law			Third Law			Second Law		
T°K	ΔH_{298}	δ	Observed Log K_p	Calculated Log K_p	Difference	T°K	ΔH_{298}	δ	Observed Log K_p	Calculated Log K_p	Difference
792.0*	54.276	-1.105	-5.959	-6.015	0.057	852.0	54.980	-0.592	-5.222	-5.344	0.122
805.0*	54.004	-1.377	-5.653	-5.816	0.163	884.0	55.552	-0.020	-4.925	-4.900	-0.025
852.0	54.980	-0.401	-5.222	-5.207	-0.015	884.0	55.700	0.128	-4.962	-4.900	-0.061
884.0	55.552	0.171	-4.925	-4.820	-0.105	900.0	55.720	0.148	-4.754	-4.691	-0.063
884.0	55.700	0.319	-4.962	-4.820	-0.142	907.0	55.561	-0.011	-4.621	-4.601	-0.020
900.0	55.720	0.339	-4.754	-4.637	-0.117	911.0	55.824	0.253	-4.630	-4.551	-0.080
907.0	55.561	0.180	-4.521	-4.559	-0.062	921.0	54.998	-0.574	-4.301	-4.426	0.125
911.0	55.824	0.444	-4.630	-4.515	-0.115	936.0	55.988	0.416	-4.339	-4.245	-0.094
921.0	54.998	-0.383	-4.301	-4.407	0.106	941.0	55.757	0.185	-4.221	-4.186	-0.035
936.0	55.988	0.607	-4.339	-4.248	-0.091	950.0	54.957	-0.614	-3.923	-4.081	0.158
941.0	55.757	0.376	-4.221	-4.197	-0.024	958.0	56.122	0.550	-4.090	-3.989	-0.101
950.0	54.957	-0.423	-3.923	-4.105	0.182	984.0	55.661	0.089	-3.671	-3.701	0.030
958.0	56.122	0.741	-4.090	-4.025	-0.065	988.0	55.611	0.039	-3.614	-3.658	0.045
984.0	55.661	0.280	-3.671	-3.774	0.103	Average = 55.572			Standard deviation = 0.025		
988.0	55.611	0.230	-3.614	-3.737	0.123	$\Delta H_{298} = 55.57$			$\Delta H_{298} = 53.79$		
Average = 55.381			Standard deviation = 0.029			* Deleted in Analysis II					
$\Delta H_{298} = 55.38$			$\Delta H_{298} = 47.29$								

3. Heat Capacities

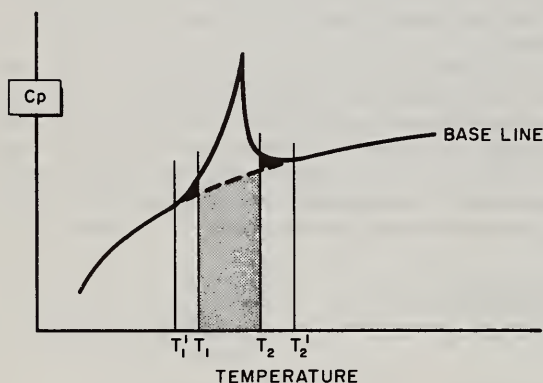
The evaluation of reported values is a relatively subjective procedure, but the analysis should be as objective as possible and therefore certain ground rules must be laid. The first step is the fitting by orthogonal polynomials and the computer-generated plotting of all information so that a general idea of the agreement can be visually obtained. If certain data sets differ from the majority, they are examined for possible causes of the difference. Calibration data, sample purity, and experimental scatter are checked. If the source of error can be located, the data are given appropriately less weight. Otherwise all data of equal reliability are considered equal, even if they disagree. Such data are then smoothed by a weighted orthogonal polynomial curvefit. Enthalpy data are smoothed similarly and heat capacities are derived directly from the differentiated polynomial. The smoothing of enthalpy data requires constraining the fit so that it passes through zero at the reference temperature. Additional constraints are often used to fix the heat capacity at 298 K, or to join enthalpy data smoothly with low-temperature heat capacities.

4. Transitions

The evaluation of solid state transitions involves first the recognition of the type of transition, which may not always be obvious. A first-order transition such as fusion involves a change of enthalpy and entropy at the transition point, whereas second-order transitions involve only discontinuities in heat capacity. Because of impurities and other factors, all first-order transitions do not occur at one temperature; rather, they spread a little on either side and are sometimes difficult to distinguish from λ -type second-order transitions. In order to evaluate the enthalpy of a first-order transition from heat-capacity data, an enthalpy change $(H_{T_2} - H_{T_1})$ from T_1 to T_2 °K must be reported on either side of the transition. The normal heat-capacity curve is extended forward and backward to the temperature of the transition-heat-capacity maximum to form a base line. If T_1' and T_2' are the temperatures at which the transitional heat capacity curve leaves and rejoins the base line, and ubl and obl designate under and over the base line, the heat of transition given by

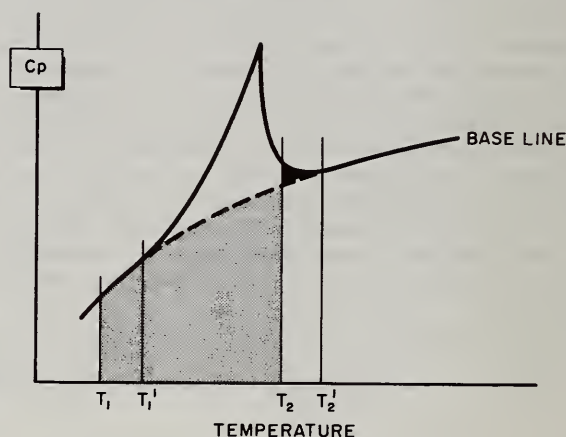
$$\Delta H_t = (H_{T_2} - H_{T_1}) - (H_{T_2} - H_{T_1})_{ubl} + (H_{T_1'} - H_{T_1})_{obl} + (H_{T_2'} - H_{T_2})_{obl}$$

Figures 1 and 2 show two possible cases. The shaded areas represent the enthalpy over the base line and cross-hatched areas the enthalpy under the base line.



EVALUATION OF TRANSITIONAL ENTHALPIES

FIGURE 1



EVALUATION OF TRANSITIONAL ENTHALPIES

FIGURE 2

Many enthalpies of fusion and enthalpies of solid-state transitions are obtained from enthalpy measurements and therefore require different treatment. Here the heats are given directly by the difference in enthalpy at the transition temperature. Normally, the enthalpy above and below can be smoothly extended to the temperature of transition, although the transition temperature may not be clearly obtainable from the enthalpy data.

The heats of the remaining transitions, vaporization and sublimation, are evaluated from equilibrium data by the second- and third-law methods just described except when calorimetric measurements are available.

5. Equilibrium

Perhaps the most significant factors to be established in evaluating equilibrium data are that equilibrium was attained and that the process was properly described. For example, in a sublimation process the most accurate measurements are valueless if the vapor phase is not uniquely defined. If polymerization or breakdown might have occurred, the first order of business is to establish the exact reaction. Because mass spectroscopy has shown that vapor phases are often extremely complex, it is almost a requirement that before equilibrium data can be accepted the vapor phases must be examined by a mass spectrometer to ensure their composition. Some methods of measurement are less accurate than others and should be given less weight. For example, equilibria determined in a mass spectrometer are usually quite rough because many approximations and uncertainties are involved in obtaining an absolute pressure measurement. On the other hand, measurements of the electromotive force of reversible cells can have great accuracy. Once the system is defined and equilibrium data are available, the data are analyzed by the second- and third-law methods.

CONSTRUCTION OF THE TABLES

1. Solid Phase

To produce a final table after all of the data have been evaluated or estimated, the enthalpy of formation, the entropy at 298 K, and the heat capacity at reasonable intervals through the temperature range of interest are needed. The enthalpy is obtained from the heat capacity by evaluating $\int_{298}^T C_p dT$. The entropy is similarly obtained from the heat capacity by evaluating $\int_{298}^T (C_p/T) dT$. The Gibbs energy function is then obtained from the relation $(G_T^\circ - H_{ref}^\circ)/T = -S_T^\circ + (H_T^\circ - H_{ref}^\circ)/T$. Enthalpies of

formation at temperatures other than 298 K require a knowledge of the enthalpies of the reference elements:

$$\Delta H_f^\circ = \Delta H_f^\circ_{298} + (H_T - H_{298})_{\text{compd}} - \sum (H_T - H_{298})_{\text{elements}}$$

The Gibbs energy of formation is readily calculated from the heat of formation when the entropies of the elements are known. Thus

$$\Delta G_f^\circ = \Delta H_f^\circ - T[S_T(\text{compd}) - \sum S_T(\text{elements})]$$

The logarithm of the equilibrium constant of formation is then found from the relation $\Delta G_f^\circ = -4.5756T \log K_p$.

Until now, we have only considered the calculation of values above 298 K; however, it is desirable to have data all the way to absolute zero. The temperature 0 K is a natural base for measurements involving gases in their lowest energy state, and values are needed in order to convert to the thermochemical reference temperature of 298 K. There is no basic difference in evaluating low-temperature data, but many more heat-capacity points are needed because of the large curvature. It is also necessary to evaluate the starting entropy at some temperature above 0 K because data rarely extend to below 5 K. In order to evaluate enthalpy it is necessary to start with a value above zero and integrate up to 298 K; then the value at 298 K is subtracted from the intermediate values, giving negative values below 298 K.

The tables extend to well above the normal melting point to facilitate the use of the tables by computers which can then interpolate values accurately right at the melting point. Dotted and solid lines indicate the end of the phase stability and solid-state transitions respectively.

2. Liquid Phase

The construction is identical with that used for the solid phase; however, the required data at 298 K are not usually readily available. The data are obtained by calculating a preliminary table using the chosen heat capacities with zero values for $\Delta H_f^\circ_{298}$ and S°_{298} . The correct starting values are then determined by comparing the values from the tables of crystal and liquid, using the following equations:

$$\Delta H_m^\circ = \Delta H_f^\circ(\ell) - \Delta H_f^\circ(c)$$

$$\Delta S_m^\circ = \frac{\Delta H_m^\circ}{T_m} = S^\circ_{T_m}(\ell) - S^\circ_{T_m}(c)$$

The correct values at 298 K may be obtained from the above relations. A typical liquid table is extrapolated both below the melting point and above the boiling point to facilitate interpolation near the phase boundaries.

3. Gas Phase

The data required for the various types of molecules are summarized below. The equations used are given in the section on Computational Methods. All molecules require the gram formula mass and enthalpy of formation at 298 K.

Additionally, monatomic species require: $\epsilon_0, \epsilon_1 \dots \epsilon_n$ and $g_0, g_1 \dots g_n$

Diatomic species require: $B_e, \sigma, x_e, \omega_e, \alpha_e, \epsilon_i, g_i$ ($i = 0, \dots, n$)

Linear polyatomic species require: B_e, σ, ω_i ($i = 1, \dots, 3N-5$), ϵ_i, g_i ($i = 0, \dots, n$)

Nonlinear polyatomic species require: $\sigma, \log I_A I_B I_C, \omega_i$ ($i = 1, \dots, 3N-6$), ϵ_i, g_i ($i = 0, \dots, n$)

ϵ_i is the energy of the i th electronic level

g_i is the statistical weight of the i th electronic level

B_e is the rotational constant

σ is the symmetry number

x_e is the anharmonicity correction = $\omega_e x_e / \omega_e$

ω_e is the fundamental frequency of a diatomic molecule

ω_i is a fundamental frequency of a polyatomic molecule

α_e is the rotational vibrational interaction constant

N is the number of atoms in the molecule

$I_A I_B I_C$ is the product of the moments of inertia

Monatomic species often have a large number of electronic levels; it is usual to average the higher levels taking account of the individual multiplicities. Diatomic and polyatomic species sometimes have several excited states which are low enough to make appreciable contributions. These states are treated by direct summation over the individual partition functions using anharmonic-oscillator approximations for each state. If vibrational and rotational constants for the higher states are not available the calculations are simplified by assuming the ground state values for each state.

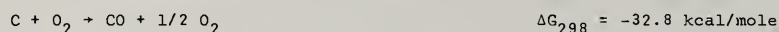
4. Multiphase Tables

Tables which show only values for the real phases at one atmosphere pressure are multiphase tables. In this compilation they are generally reference state tables, though some solid phase tables include more than one phase. Multiphase tables can always be recognized by the presence of solid lines, indicating phase transitions, on the table. They are prepared in a manner similar to tables for condensed phases. The functions are evaluated in the same manner as for a solid up to the first transition point; then the heat and entropy of transition are added and the integration is continued using the second-phase heat capacities. At each phase boundary the above process is repeated.

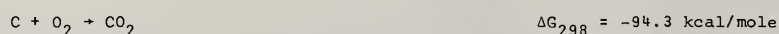
USE OF TABLES

The rapid proliferation of thermodynamic tabulations in recent years brings with it the possibility of serious abuse of the information in them. First, as we explained earlier, not all tabulations are based on the same reference states. To avoid this pitfall it is helpful to write down the reaction and check the value and state of each component. It is even better to utilize only a single compilation whenever possible, because values from different compilations may not be consistent or compatible. Second, the base temperatures of compilations differ between 0 and 298 K. Only enthalpies and Gibbs-energy functions are affected, but they can result in serious errors if used indiscriminately.

A different type of error is caused by misunderstanding the significance of negative Gibbs-energy changes. For example, many species in the JANAF Thermochemical Tables have large negative Gibbs energies of formation at 6000 K. This does not necessarily imply that the species are stable, but only that the Gibbs-energy change from the elemental reference state is negative. In fact, nearly all the elements are monatomic gases at 6000 K, and the reference states are generally unstable with respect to the atoms. Similarly, a negative Gibbs-energy change does not mean a reaction will occur, but means only that the reaction is favorable as written. For example, at 298 K



However, at normal pressures this reaction would generally be recognized as unlikely in view of



Similarly, in combining free energies of reaction, one should be careful not to combine impossible reactions with possible ones to obtain an over-all favorability:



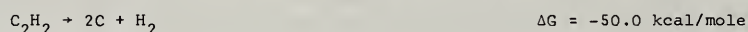
This equation is impossible because we cannot combine the reactions



and



by simple addition. Both reactions must be written so that they are possible. They then become



Then by simple addition



Although these tables have been continuously revised it is not possible to keep all the tables fully revised with the latest data. Thus, each table indicates the dates of each revision at the foot of the tabular values. The latest date is most important since information generated after that date has not been incorporated. The frequency of revisions often indicates the level of research activity on the compound and may indicate further changes in the future.

CALCULATIONAL METHODS

The presentation of Mayer and Mayer "Statistical Mechanics", John Wiley & Sons, Inc., New York, (1940) forms the basis for the expressions given below for the ideal gas state. The calculations have been carried out by a Burroughs B5500 electronic computer.

I. Ideal Monatomic gas

(a) Translation

$$\begin{aligned} (H^\circ - H_0^\circ)/T &= C_p^\circ = 4.967913 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ -(G^\circ - H_0^\circ)/T &= 6.863426 \log M + 11.439043 \log T - 7.282868 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ S^\circ &= 6.863426 \log M + 11.439043 \log T - 2.314954 \text{ cal deg}^{-1} \text{ mol}^{-1}. \end{aligned}$$

(b) Electronic

$$\begin{aligned} C_p^\circ &= \frac{4.113664}{T^2} \left[\frac{\sum \epsilon_i^2 g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} - \left(\frac{\sum \epsilon_i g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} \right)^2 \right] \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ (H^\circ - H_0^\circ)/T &= \frac{2.859114}{T} \frac{\sum \epsilon_i g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ -(G^\circ - H_0^\circ)/T &= 4.575617 \log \sum g_i e^{-\frac{1.438790 \epsilon_i}{T}} \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ S^\circ &= \frac{2.859114}{T} \frac{\sum \epsilon_i g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} + 4.575617 \log \sum g_i e^{-\frac{1.438790 \epsilon_i}{T}} \text{ cal deg}^{-1} \text{ mol}^{-1}. \end{aligned}$$

II. Ideal Diatomic Gas

(a) Translation and Rotation

$$\begin{aligned} C_p^\circ &= 6.955079 + 0.0914148 (B/T)^2 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ (H^\circ - H_0^\circ)/T &= 6.955079 - 0.953038 (B/T) - 0.0914148 (B/T)^2 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ -(G^\circ - H_0^\circ)/T &= 6.863426 \log M + 11.439043 \log T - 4.575617 \log (B\sigma/T) + 0.953038 (B/T) \\ &\quad + 0.0457074 (B/T)^2 - 8.005804 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ S^\circ &= 6.863426 \log M + 11.439043 \log T - 4.575617 \log (B\sigma/T) - 0.0457074 (B/T)^2 - 1.050725 \\ &\quad \text{cal deg}^{-1} \text{ mol}^{-1}. \end{aligned}$$

where $B = (B_e - \alpha_e/2)$ when spectroscopic constants are available.

$$B = \frac{2.799076 \times 10^{-39}}{I} \text{ when calculated from a molecular model, (I in g cm}^2\text{)}$$

(b) Vibration

$$\begin{aligned} C_p^\circ &= 1.987165 u^2 e^{-u}/(1-e^{-u})^2 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ (H^\circ - H_0^\circ)/T &= 1.987165 u e^{-u}/(1-e^{-u}) \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ -(G^\circ - H_0^\circ)/T &= -4.575617 \log (1-e^{-u}) \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ S^\circ &= 1.987165 u e^{-u}/(1-e^{-u}) - 4.575617 \log (1-e^{-u}) \text{ cal deg}^{-1} \text{ mol}^{-1}. \end{aligned}$$

where $u = (1.438790/T) \cdot (\omega_e - 2\omega_e x_e)$ when spectroscopic constants are available.

$u = (1.438790/T)\omega$ where ω is the fundamental wave number of a harmonic oscillator.

(c) Electronic

Same as I(b) when the i th-state vibrational partition function, Q_v^i and the i th-state rotational partition function, Q_r^i , are equal to the respective ground state partition functions. In this case the partition function $Q = Q_t Q_v Q_r \sum_i Q_e^i$, otherwise all the thermodynamic functions are derived from $Q = Q_t \sum_i Q_e^i Q_v^i Q_r^i$, where Q_t is the translational partition function and $Q_e^i = g_i \exp(\epsilon_i/kT)$.

(d) Anharmonicity Corrections

$$C_p^\circ = 1.987615 \left[\frac{16\gamma}{u} - \frac{\delta u^2 e^u}{(e^u - 1)^2} + \frac{u^2 e^u (2\delta e^u - 4Xu - 8X)}{(e^u - 1)^3} + \frac{12Xu^3 e^{2u}}{(e^u - 1)^4} \right] \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$(H^\circ - H_0^\circ)/T = 1.987165 \left[\frac{8\gamma}{u} + \frac{u(\delta e^u - 2X)}{(e^u - 1)^2} + \frac{4Xu^2 e^u}{(e^u - 1)^3} \right] \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$-(G^\circ - H_0^\circ)/T = 1.987165 \left[\frac{8\gamma}{u} + \frac{\delta}{(e^u - 1)} + \frac{2Xu}{(e^u - 1)^2} \right] \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$S^\circ = 1.987165 \left[\frac{16\gamma}{u} + \frac{\delta}{(e^u - 1)} + \frac{\delta u e^u}{(e^u - 1)^2} + \frac{4Xu^2 e^u}{(e^u - 1)^3} \right] \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

where u is $(\omega_e - 2\omega_e x_e) \cdot 1.438790/T$

$$X = (\omega_e x_e)/\omega_e; \quad \delta = \alpha_e/B_e; \quad \gamma = B_e/\omega_e.$$

III. Linear Polyatomic Molecule

- (a) Translation and rotation same as for II (a).
- (b) Vibration same as II (b) for 3N-5 vibrational degrees of freedom.
- (c) Electronic same as II (c) where levels and quantum weight are known.
- (d) Anharmonic corrections neglected.

IV. Nonlinear Polyatomic Molecule (Rigid Rotator, Harmonic Oscillator).

(a) Translation and Rotation

$$C_p^\circ = 7.948662 \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$(H^\circ - H_0^\circ)/T = 7.948662 \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$-(G^\circ - H_0^\circ)/T = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log I_A I_B I_C \times 10^{117} - 10.297926 \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$S^\circ = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log I_A I_B I_C \times 10^{117} - 2.349265 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

- (b) Vibration same as II (b) for 3N-6 vibrational degrees of freedom.
- (c) Electronic same as II (c) where levels and quantum weight are known.
- (d) Anharmonic corrections neglected.

V. Condensed States

Evaluation of thermodynamic data for condensed states rests upon either measured or estimated information. Heat-capacity data are plotted, smoothed, and data for calculations read back at regular temperature intervals. Integration of this smoothed heat capacity data is carried out with the relations

$$H_T^\circ - H_{298.15}^\circ = \int_{298.15}^T C_p^\circ dT \quad S_T^\circ = \int_0^T \frac{C_p^\circ}{T} dT$$

by machine, three points at a time. The computer calculates the constants for a parabolic equation through the three points, and employs the constants to integrate the first temperature interval. The lowest point is discarded; the next higher point is combined with the two retained points; and a new set of parabolic constants calculated and used for integrating the next higher temperature interval. This recurrent procedure is well suited to this type of calculation. At the appropriate temperatures, transition enthalpies are added to the enthalpy total, while the quotient of the transition enthalpy divided by the absolute temperature is added to the entropy total.

NOTES

1. Indexing

The modified Hill indexing system, J. Am. Chem. Soc. **22**, 478-94 (1900), for Chemical Compounds as used by Chemical Abstracts and the Classification Division of the U. S. Patent Office is used to index the chemical compounds in this data collection. The arrangement of atomic symbols in chemical formulas is alphabetical except for carbon compounds. Thus, the indexing of chemical compounds is as follows: Ac (actinium compounds), Ag (silver compounds), Al (aluminum compounds), Am (americium compounds), Ar (argon), As (arsenic compounds), Au (gold compounds), B (boron compounds), Ba (barium compounds), Be (beryllium compounds), and so on throughout the alphabet. Once the correct order of the elements in the formula is deduced, the location of a compound within the group is easily accomplished. This obviates the need for pagination, and the index page indicates the correct order.

Organic (carbon) compounds represent a gigantic group, so that for convenience this one class of compounds presents the exceptions to the alphabetical rule. In carbon compounds the C always comes first, followed immediately by H if hydrogen is present, and then followed by any other elements present in their normal alphabetical order. The number of atoms of the element indexed first also influences the order of indexing the compound; e.g., all formulas with C (one carbon atom only) come before those with C₂ (two carbon atoms), followed by C₃ compounds, and so on. Thus: CHBF₄O (formyl fluoride, compound with BF₃), CHCl₃ (chloroform), CH₂F₃P (trifluoromethylphosphine), CH₃NO₃ (methyl nitrate), CH₄Cl₂Si (dichloromethylsilane), CH₁₀N₄O₃ (hydrazine carbonate), CO (carbon monoxide), CO₂ (carbon dioxide), CO₃Zn (zinc carbonate), CZr (zirconium carbide), C₂Ba (barium acetylide), C₂BrClF₂ (bromochlorodifluoroethylene), C₂Ca (calcium carbide), and so on. See any formula index of Chemical Abstracts for further details and examples.

2. Selection of Enthalpy Reference Temperature

Since no enthalpy measurements can be made in the sense of an absolute quantity, and since all enthalpy measurements are made as a difference between an initial and a final state, it is necessary to select the thermodynamic state to which all other thermodynamic states will be referred. For these tables, the thermodynamic state selected is chosen as the state at one atmosphere total pressure tabulated at 298.15 K. Note that the temperature 298 K listed in the table actually refers to 298.15 K, but decimals have been omitted in the temperature column. Usage in theoretical work indicates the selection of the state existing at absolute zero, which is a hypothetical state that is even approached by relatively few measurements. Values of the difference in heat between 298.15 and 0 K will permit theoretical workers to use these tables, so it was decided to tabulate values at 0 K. Modern usage of thermodynamic data sometimes requires application to conditions below ambient, so the decision was made to tabulate values at 0, 100, and 200 K where the information is available.

3. Limitations of Calculated Quantities

Calculation of the contributions of rotation and translation involves the use of quantum statistics, but to obtain a numerical solution the quantum statistics are usually replaced by classical statistics at temperatures above about 100 K. Attempts to employ these methods below 100 K lead into a temperature range where the approximation afforded by classical statistics no longer holds. For this reason the equations presented under "Calculational Methods" fail in the vicinity of 0 K. In agreement with the third law concept, C_p^o and S^o are zero at 0 K. For a reference element, log K_p is zero at 0 K, while for compounds the absolute values of the free energy function and log K_p become infinite at 0 K.

4. Reference State of an Element

A related set of thermodynamic property tables requires that there be a reference table of the thermodynamic properties for each element to which all other forms of that element or any compound involving that element may be referred. If the temperature range of interest (6000 K here) can be represented by a single phase for that material (say hydrogen) the tabulated values in the reference table will be smooth and regular. If the temperature range of interest includes more than one phase (say magnesium) there will be a solid phase (from 0 to 922 K, the melting point), a liquid phase (922 to 1378 K, where the vapor pressure reaches one atmosphere), and a gas phase (1378 to 6000 K), the tabulated values in the reference table will be discontinuous at these phase boundaries. Practical usage dictates that in so far as possible the phase most stable at one atmosphere pressure (that is, the form most easily worked with) be selected. This practice is followed in these tables, and does lead to discontinuities in the thermodynamic functions. Attention is called to these discontinuities in the polyphase reference-state tables by insertion of a solid line at the temperature of a phase transition. The phase transitions considered are: first-order solid-state transformations from one crystal type to some other, solid to liquid, and solid or liquid to gas at one atmosphere.

5. Single-Phase Table

It is expected that these tables will be employed on various problems solved by automatic machine computation. Such calculations are carried out in numerous ways, and vary from one installation to another. Programs to perform these calculations are simplified if the thermodynamic functions are smooth and extend beyond the actual range of use permitting a wide latitude in iterative procedures. For this reason, most tables other than elemental reference states are tabulated as single-phase tables. Thus, tables for the solid state are extrapolated well past the melting point; those for the liquid state are extrapolated below the melting point (into the supercooled-liquid range to 298.15 K) and well above the atmospheric boiling point, while gas tables are tabulated from 0 K to 6000 K. Care has been taken to preserve the correct free energy relationships between the extrapolated-phase functions and the functions of the real phase. Attention is called to these extrapolations by insertion of a dotted line at the temperature where the indicated phase meets an adjacent more stable phase, but for reasons mentioned above the indicated phase is extrapolated into a temperature range where it is thermodynamically unstable.

N O T E S

6. Mole

With each table and text there is listed either the atomic, molecular, or gram formula mass. It is generally understood that this mass in grams refers to Avogadro's number of atoms or molecules, and will be referred to simply as a "mole".

7. Point Groups and Ground-State Configurations

Throughout these tables the nomenclature and definition of the ground-state configurations and point groups are those in use by C. E. Moore, U. S. National Bureau of Standards Circular 467, (1949), and G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, (1950), and "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra", D. Van Nostrand Co., New York, (1945).

8. Decimal Places

Three decimal places have been arbitrarily carried in the tables even though in numerous cases the data do not warrant this accuracy. This has been done to preserve the proper relationship of the thermodynamic functions, and to facilitate machine interpolation of these values.

9. Higher Electronic Terms

A single electronic term of $30,000\text{ cm}^{-1}$ and above contributes a negligible amount to the thermodynamic functions at temperatures of 8000 K and below. On the other hand, a number of such terms cannot be neglected. In these cases, the number of terms and their values have been summed and their contribution included.

10. Estimated Vibrational Frequencies

Some vibrational frequencies have been estimated by analogy with related molecules. Occasionally, more than one frequency has been averaged at the same value. This is not to be confused with a true degeneracy which is indicated by placing the degeneracy value in parentheses following the frequency. However, when the information has been taken from another compilation, the degeneracies indicated by the compiler have been retained.

11. Quantum Weight

The term quantum weight is also referred to as statistical weight by many authors. The quantity is the product of the spin multiplicity and state degeneracy of the electronic level under consideration.

12. Isotope Effects

The functions calculated for gases from molecular constants are, in general, obtained from constants which have been corrected to the natural isotopic abundance.

INDEX TO TABLES

Filing Order	Table Title	Filing Order	Table Title
Al	Aluminum (ref. st.)	AlI ₃	Aluminum Triiodide (l)
Al	Aluminum (c)	AlI ₃	Aluminum Triiodide (g)
Al	Aluminum (l)	AlLiO ₂	Lithium Aluminate (c)
Al	Aluminum, Monatomic (g)	AlLiO ₂	Lithium Aluminate (l)
Al ⁺	Aluminum Unipositive Ion (g)	AlN	Aluminum Nitride (c)
AlBO ₂	Aluminum Boron Dioxide (g)	AlN	Aluminum Nitride (g)
AlBr	Aluminum Monobromide (g)	AlNaO ₂	Sodium Aluminate (c)
AlBr ₃	Aluminum Tribromide (c)	AlO	Aluminum Monoxide (g)
AlBr ₃	Aluminum Tribromide (l)	AlO ⁺	Aluminum Monoxide Unipositive Ion (g)
AlBr ₃	Aluminum Tribromide (g)	AlO ₂	Aluminum Dioxide (g)
AlCl	Aluminum Monochloride (g)	AlO ₂ ⁻	Aluminum Dioxide Uninegative Ion (g)
AlCl ⁺	Aluminum Monochloride Unipositive Ion (g)	AlS	Aluminum Sulfide (g)
AlClF	Aluminum Chlorofluoride (g)	Al ₂ BeO ₄	Beryllium Aluminate (c)
AlClF ₂	Aluminum Chlorodifluoride (g)	Al ₂ Br ₆	Aluminum Tribromide, Dimeric (g)
AlClO	Aluminum Oxychloride (c)	Al ₂ Cl ₆	Aluminum Trichloride, Dimer (g)
AlClO	Aluminum Oxychloride (g)	Al ₂ Cl ₉ K ₃	Potassium Nonachloroaluminate (c)
AlCl ₂	Aluminum Dichloride (g)	Al ₂ F ₆	Aluminum Trifluoride, Dimer (g)
AlCl ₂ ⁺	Aluminum Dichloride Unipositive Ion (g)	Al ₂ I ₆	Aluminum Triiodide, Dimeric (g)
AlCl ₂ ⁻	Aluminum Dichloride Uninegative Ion (g)	Al ₂ MgO ₄	Magnesium Aluminate (c)
AlCl ₂ F	Aluminum Dichlorofluoride (g)	Al ₂ O	Aluminum Suboxide (g)
AlCl ₃	Aluminum Trichloride (c)	Al ₂ O ⁺	Dialuminum Monoxide Unipositive Ion (g)
AlCl ₃	Aluminum Trichloride (l)	Al ₂ O ₂ ⁺	Aluminum Monoxide, Dimeric (g)
AlCl ₃	Aluminum Trichloride (g)	Al ₂ O ₂	Dialuminum Dioxide Unipositive Ion (g)
AlCl ₄ K	Potassium Tetrachloroaluminate (c)	Al ₂ O ₃	Aluminum Oxide (c, alpha)
AlCl ₄ Na	Sodium Tetrachloroaluminate (c)	Al ₂ O ₃	Aluminum Oxide (c, gamma)
AlCl ₆ K ₃	Tripotassium Hexachloroaluminate (c)	Al ₂ O ₃	Aluminum Oxide (l)
AlCl ₆ Na ₃	Trisodium Hexachloroaluminate (c)	Al ₂ O ₅ Si	Sillimanite (c)
AlF	Aluminum Monofluoride (g)	Al ₂ O ₅ Si	Andalusite (c)
AlF ⁺	Aluminum Monofluoride Unipositive Ion (g)	Al ₂ O ₅ Si	Kyanite (c)
AlFO	Aluminum Oxyfluoride (g)	Al ₆ O ₁₃ Si ₂	Mullite (c)
AlF ₂	Aluminum Difluoride (g)	B	Boron (ref. st.)
AlF ₂ ⁺	Aluminum Difluoride Unipositive Ion (g)	B	Boron, Beta-Rhombohedral (c)
AlF ₂ ⁻	Aluminum Difluoride Uninegative Ion (g)	B	Boron (l)
AlF ₃	Aluminum Trifluoride (c)	B	Boron, Monatomic (g)
AlF ₃	Aluminum Trifluoride (g)	B ⁺	Boron Unipositive Ion (g)
AlF ₄ Li	Lithium Tetrafluoroaluminate (g)	BBeO ₂	Beryllium Boron Dioxide (g)
AlF ₄ Na	Sodium Tetrafluoroaluminate (g)	BBr	Boron Monobromide (g)
AlF ₆ K ₃	Tripotassium Hexafluoroaluminate (c)	BBrCl	Boron Bromide Chloride (g)
AlF ₆ Li ₃	Trilithium Hexafluoroaluminate (c)	BBrCl ₂	Boron Bromide Dichloride (g)
AlF ₆ Li ₃	Trilithium Hexafluoroaluminate (l)	BBrF	Boron Bromide Fluoride (g)
AlF ₆ Na ₃	Cryolite (c)	BBrF ₂	Boron Bromide Difluoride (g)
AlF ₆ Na ₃	Cryolite (l)	BBrO	Boron Oxide Bromide (g)
AlH	Aluminum Monohydride (g)	BBr ₂	Boron Dibromide (g)
AlHO	Aluminum Monoxyhydride (g)	BBr ₂ Cl	Boron Dibromide Chloride (g)
AlHO	Aluminum Monohydroxide (g)	BBr ₂ F	Boron Dibromide Fluoride (g)
AlHO ⁺	Aluminum Monohydroxide Unipositive Ion (g)	BBr ₂ H	Boron Dibromide Hydride (g)
AlHO ⁻	Aluminum Monohydroxide Uninegative Ion (g)	BBr ₃	Boron Tribromide (l)
AlHO ₂	Aluminum Dioxyhydride (g)	BBr ₃	Boron Tribromide (g)
AlH ₄ Li	Lithium Aluminum Hydride (c)	BCl	Boron Monochloride (g)
AlI	Aluminum Monoiodide (g)	BCl ⁺	Boron Monochloride Unipositive Ion (g)
AlI ₃	Aluminum Triiodide (c)		

Filing Order	Table Title	Filing Order	Table Title
BClF	Boron Chloride Fluoride (g)	B ₂	Boron, Diatomic (g)
BClF ₂	Boron Chloride Difluoride (g)	B ₂ BeO ₄	Beryllium Diborate (g)
BClO	Boron Oxide Chloride (g)	B ₂ Be ₃ O ₆	Triberyllium Diborate (c)
BCl ₂	Boron Dichloride (g)	B ₂ Cl ₄	Boron Dichloride, Dimeric (g)
BCl ₂ ⁺	Boron Dichloride Unipositive Ion (g)	B ₂ F ₄	Boron Difluoride, Dimeric (g)
BCl ₂ ⁻	Boron Dichloride Uninegative Ion (g)	B ₂ H ₄ O ₄	Boron Dihydroxide, Dimeric (c)
BCl ₂ F	Boron Dichloride Fluoride (g)	B ₂ H ₄ O ₄	Boron Dihydroxide, Dimeric (g)
BCl ₂ H	Boron Dichloride Hydride (g)	B ₂ H ₆	Diborane (g)
BCl ₃	Boron Trichloride (g)	B ₂ Mg	Magnesium Diboride (c)
BF	Boron Monofluoride (g)	B ₂ O	Diboron Monoxide (g)
BFO	Boron Oxide Fluoride (g)	B ₂ O ₂	Boron Monoxide, Dimeric (g)
BF ₂	Boron Difluoride (g)	B ₂ O ₃	Boron Oxide (c)
BF ₂ ⁺	Boron Difluoride Unipositive Ion (g)	B ₂ O ₃	Boron Oxide (l)
BF ₂ ⁻	Boron Difluoride Uninegative Ion (g)	B ₂ O ₃	Boron Oxide (g)
BF ₂ H	Difluoroborane (g)	B ₂ O ₄ Pb	Lead Diborate (c)
BF ₂ HO	Boron Hydroxide Difluoride (g)	B ₂ Ti	Titanium Diboride (c)
BF ₂ O	Boron Oxide Difluoride (g)	B ₂ Ti	Titanium Diboride (l)
BF ₃	Boron Trifluoride (g)	B ₂ Zr	Zirconium Diboride (c)
BF ₄ K	Potassium Tetrafluoroborate (c)	B ₂ Zr	Zirconium Diboride (l)
BF ₄ K	Potassium Tetrafluoroborate (l)		
BF ₄ K	Potassium Tetrafluoroborate (g)	B ₃ Cl ₃ O ₃	Boron Oxide Chloride, Trimeric (g)
BH	Boron Monohydride (g)	B ₃ FH ₂ O ₃	Monofluoroboroxin (g)
BHO	Boron Oxide Hydride (g)	B ₃ F ₂ HO ₃	Difluoroboroxin (g)
BHO ⁺	Boron Oxide Hydride Unipositive Ion (g)	B ₃ F ₃ O ₃	Boron Oxide Fluoride, Trimeric (c)
BHO ₂	Metaboric Acid (c)	B ₃ F ₃ O ₃	Boron Oxide Fluoride, Trimeric (g)
BHO ₂	Metaboric Acid (g)	B ₃ H ₃ O ₃	Boroxin (c)
BH ₂	Boron Dihydride (g)	B ₃ H ₃ O ₃	Boroxin (g)
BH ₂ O ₂	Boron Dihydroxide (g)	B ₃ H ₃ O ₆	Metaboric Acid, Trimeric (g)
BH ₃	Boron Trihydride (g)	B ₃ H ₆ N ₃	Borazine (g)
BH ₃ O ₃	Boric Acid (c)		
BH ₃ O ₃	Boric Acid (g)	B ₄ K ₂ O ₇	Dipotassium Tetraboron Heptaoxide (c)
BH ₄ K	Potassium Tetrahydroborate (c)	B ₄ K ₂ O ₇	Dipotassium Tetraboron Heptaoxide (l)
BH ₄ Li	Lithium Tetrahydroborate (c)	B ₄ Li ₂ O ₇	Dilithium Tetraborate (c)
BH ₄ Na	Sodium Tetrahydroborate (c)	B ₄ Li ₂ O ₇	Dilithium Tetraborate (l)
BI	Boron Iodide (g)	B ₄ Mg	Magnesium Tetraboride (c)
BI ₂	Boron Diiodide (g)	B ₄ Na ₂ O ₇	Disodium Tetraborate (c)
BI ₃	Boron Triiodide (g)	B ₄ Na ₂ O ₇	Disodium Tetraborate (l)
BLiO ₂	Lithium Metaborate (c)	B ₄ O ₇ Pb	Lead Tetraborate (c)
BLiO ₂	Lithium Metaborate (l)	B ₅ H ₉	Pentaborane (l)
BLiO ₂	Lithium Metaborate (g)	B ₅ H ₉	Pentaborane (g)
BN	Boron Nitride (c)	B ₆ K ₂ O ₁₀	Dipotassium Hexaborate (c)
BN	Boron Nitride (g)	B ₆ Li ₂ O ₁₀	Dilithium Hexaborate (c)
BNaO ₂	Sodium Metaborate (c)	B ₆ Na ₂ O ₁₀	Disodium Hexaborate (c)
BNaO ₂	Sodium Metaborate (l)	B ₆ O ₁₀ Pb	Lead Hexaborate (c)
BNaO ₂	Sodium Metaborate (g)	B ₈ K ₂ O ₁₃	Dipotassium Octaborate (c)
BO	Boron Monoxide (g)	B ₈ K ₂ O ₁₃	Dipotassium Octaborate (l)
BO ₂	Boron Dioxide (g)	B ₈ Li ₂ O ₁₃	Dilithium Octaborate (c)
BO ₂ ⁻	Boron Dioxide Uninegative Ion (g)	B ₁₀ H ₁₄	Decaborane (c)
BS	Boron Monosulfide (g)	B ₁₀ H ₁₄	Decaborane (l)
BTi	Titanium Monoboride (c)	B ₁₀ H ₁₄	Decaborane (g)

Filing Order	Table Title
B ₁₀ O ₁₇ Pb ₂	Dilead Decaborate (c)
Be	Beryllium (ref. st.)
Be	Beryllium (c)
Be	Beryllium (l)
Be	Beryllium (g)
Be ⁺	Beryllium Unipositive Ion (g)
BeBr	Beryllium Monobromide (g)
BeBr ₂	Beryllium Dibromide (c)
BeBr ₂	Beryllium Dibromide (l)
BeBr ₂	Beryllium Dibromide (g)
BeCl	Beryllium Monochloride (g)
BeCl ⁺	Beryllium Monochloride Unipositive Ion (g)
BeClF	Beryllium Chloride Fluoride (g)
BeCl ₂	Beryllium Dichloride (c,α)
BeCl ₂	Beryllium Dichloride (c,β)
BeCl ₂	Beryllium Dichloride (l)
BeCl ₂	Beryllium Dichloride (g)
BeF	Beryllium Monofluoride (g)
BeF ₂	Beryllium Difluoride (c)
BeF ₂	Beryllium Difluoride (l)
BeF ₂	Beryllium Difluoride (g)
BeF ₃ Li	Lithium Trifluoroberyllate (c)
BeF ₃ Li	Lithium Beryllium Fluoride (g)
BeF ₄ Li ₂	Dilithium Tetrafluoroberyllate (c)
BeF ₄ Li ₂	Dilithium Tetrafluoroberyllate (l)
BeH	Beryllium Monohydride (g)
BeH ⁺	Beryllium Monohydride Unipositive Ion (g)
BeHO	Beryllium Monohydroxide (g)
BeHO ⁺	Beryllium Monohydroxide Unipositive Ion (g)
BeH ₂	Beryllium Dihydride (g)
BeH ₂ O ₂	Beryllium Hydroxide (c,α)
BeH ₂ O ₂	Beryllium Hydroxide (c,β)
BeH ₂ O ₂	Beryllium Hydroxide (g)
BeI	Beryllium Monoiodide (g)
BeI ₂	Beryllium Diiodide (c)
BeI ₂	Beryllium Diiodide (l)
BeI ₂	Beryllium Diiodide (g)
BeN	Beryllium Nitride (g)
BeO	Beryllium Oxide (c)
BeO	Beryllium Oxide (l)
BeO	Beryllium Oxide (g)
BeO ₄ S	Beryllium Sulfate (c,α)
BeO ₄ S	Beryllium Sulfate (c,β)
BeO ₄ S	Beryllium Sulfate (c,γ)
BeO ₄ W	Beryllium Tungstate (c)
Be ₂ Cl ₄	Beryllium Dichloride, Dimeric (g)
Be ₂ F ₂ O	Dilithium Oxide Difluoride (g)
Be ₂ O	Diberyllium Oxide (g)
Be ₂ O ₂	Beryllium Oxide, Dimeric (g)
Be ₂ O ₄ Si	Beryllium Orthosilicate (c)

Filing Order	Table Title
Be ₃ N ₂	Beryllium Nitride (c,α)
Be ₃ N ₂	Beryllium Nitride (l)
Be ₃ O ₃	Beryllium Oxide, Trimeric (g)
Be ₄ O ₄	Beryllium Oxide, Tetrameric (g)
Be ₅ O ₅	Beryllium Oxide, Pentameric (g)
Be ₆ O ₆	Beryllium Oxide, Hexameric (g)
Br	Bromine, Monatomic (g)
BrCl	Bromine Monochloride (g)
BrF	Bromine Monofluoride (g)
BrF ₃	Bromine Trifluoride (g)
BrF ₅	Bromine Pentafluoride (g)
BrH	Hydrogen Bromide (g)
BrH ₄ N	Ammonium Bromide (c)
BrHg	Mercurous Bromide (g)
BrI	Iodine Monobromide (g)
BrK	Potassium Bromide (c)
BrK	Potassium Bromide (l)
BrK	Potassium Bromide (g)
BrLi	Lithium Bromide (c)
BrLi	Lithium Bromide (l)
BrLi	Lithium Bromide (g)
BrMg	Magnesium Monobromide (g)
BrN	Nitrogen Bromide (g)
BrNO	Nitrosyl Bromide (g)
BrNa	Sodium Bromide (c)
BrNa	Sodium Bromide (l)
BrNa	Sodium Bromide (g)
BrP	Phosphorus Monobromide (g)
BrPb	Lead Monobromide (g)
BrTi	Titanium Monobromide (g)
BrW	Tungsten Monobromide (g)
BrZr	Zirconium Monobromide (g)
Br ₂	Bromine (ref. st.)
Br ₂	Bromine (l)
Br ₂	Bromine, Diatomic (g)
Br ₂ Fe	Iron Dibromide (c)
Br ₂ Fe	Iron Dibromide (l)
Br ₂ Fe	Iron Dibromide (g)
Br ₂ Hg	Mercuric Bromide (c)
Br ₂ Hg	Mercuric Bromide (l)
Br ₂ Hg	Mercuric Bromide (g)
Br ₂ Hg ₂	Mercurous Bromide (c)
Br ₂ K ₂	Potassium Bromide, Dimeric (g)
Br ₂ Li ₂	Lithium Bromide, Dimeric (g)
Br ₂ Mg	Magnesium Dibromide (c)
Br ₂ Mg	Magnesium Dibromide (l)
Br ₂ Mg	Magnesium Dibromide (g)
Br ₂ Na ₂	Sodium Bromide, Dimeric (g)
Br ₂ Pb	Lead Dibromide (c)

Filing Order	Table Title
Br ₂ Pb	Lead Dibromide (ℓ)
Br ₂ Pb	Lead Dibromide (g)
Br ₂ Ti	Titanium Dibromide (c)
Br ₂ Ti	Titanium Dibromide (g)
Br ₂ Zr	Zirconium Dibromide (c)
Br ₂ Zr	Zirconium Dibromide (ℓ)
Br ₂ Zr	Zirconium Dibromide (g)
Br ₃ OP	Phosphoryl Bromide (g)
Br ₃ P	Phosphorus Tribromide (g)
Br ₃ PS	Thiophosphoryl Bromide (g)
Br ₃ Ti	Titanium Tribromide (c)
Br ₃ Ti	Titanium Tribromide (g)
Br ₃ Zr	Zirconium Tribromide (c)
Br ₃ Zr	Zirconium Tribromide (g)
Br ₄ Fe ₂	Iron Dibromide, Dimeric (g)
Br ₄ Pb	Lead Tetrabromide (g)
Br ₄ Ti	Titanium Tetrabromide (c)
Br ₄ Ti	Titanium Tetrabromide (ℓ)
Br ₄ Ti	Titanium Tetrabromide (g)
Br ₄ Zr	Zirconium Tetrabromide (c)
Br ₄ Zr	Zirconium Tetrabromide (g)
Br ₅ W	Tungsten Pentabromide (c)
Br ₅ W	Tungsten Pentabromide (ℓ)
Br ₅ W	Tungsten Pentabromide (g)
Br ₆ W	Tungsten Hexabromide (c)
Br ₆ W	Tungsten Hexabromide (g)
C	Carbon (ref. st., Graphite)
C	Carbon, Monatomic (g)
C ⁻	Carbon Uninegative Ion (g)
CAI	Aluminum Carbide (g)
CB	Boron Carbide (g)
CB ₄	Boron Carbide (c)
CB ₄	Boron Carbide (ℓ)
CBe ₂	Beryllium Carbide (c)
CBe ₂	Beryllium Carbide (ℓ)
CBr	Carbon Monobromide (g)
CBrF ₃	Bromotrifluoromethane (g)
CBrN	Cyanogen Bromide (g)
CBr ₄	Carbon Tetrabromide (g)
CCl	Carbon Monochloride (g)
CClFO	Carbonyl Chlorofluoride (g)
CClF ₃	Chlorotrifluoromethane (g)
CClN	Cyanogen Chloride (g)
CClO	Carbonyl Monochloride (g)
CCl ₂	Carbon Dichloride (g)
CCl ₂ F ₂	Dichlorodifluoromethane (g)
CCl ₂ O	Carbonyl Chloride (g)
CCl ₃	Trichloromethyl (g)
CCl ₃ F	Trichlorofluoromethane (g)
CCl ₄	Carbon Tetrachloride (g)

Filing Order	Table Title
CF	Carbon Monofluoride (g)
CFN	Cyanogen Fluoride (g)
CFO	Carbonyl Monofluoride (g)
CF ₂	Carbon Difluoride (g)
CF ₂ O	Carbonyl Fluoride (g)
CF ₃	Trifluoromethyl (g)
CF ₃ I	Trifluoroiodomethane (g)
CF ₄	Carbon Tetrafluoride (g)
CF ₄ O	Trifluoromethyl Hypofluorite (g)
CH	Methyldiyne (g)
CHCl	Monochloromethylene (g)
CHClF ₂	Chlorodifluoromethane (g)
CHCl ₂ F	Dichlorofluoromethane (g)
CHCl ₃	Chloroform (g)
CHF	Monofluoromethylene (g)
CHFO	Formyl Fluoride (g)
CHF ₃	Trifluoromethane (g)
CHN	Hydrogen Cyanide (g)
CHNO	Hydrogen Isocyanate (g)
CHO	Formyl (g)
CHO ⁺	Formyl Unipositive Ion (g)
CHP	Methinophosphide (g)
CH ₂	Methylene (g)
CH ₂ ClF	Chlorofluoromethane (g)
CH ₂ Cl ₂	Dichloromethane (g)
CH ₂ F ₂	Difluoromethane (g)
CH ₂ O	Formaldehyde (g)
CH ₃	Methyl (g)
CH ₃ Cl	Methyl Chloride (g)
CH ₃ Cl ₃ Si	Trichloromethylsilane (g)
CH ₃ F	Fluoromethane (g)
CH ₃ F ₃ Si	Trifluoromethylsilane (g)
CH ₄	Methane (g)
CIN	Cyanogen Iodide (g)
CKN	Potassium Cyanide (c)
CKN	Potassium Cyanide (ℓ)
CKN	Potassium Cyanide (g)
CK ₂ O ₃	Potassium Carbonate (c)
CK ₂ O ₃	Potassium Carbonate (ℓ)
CLi ₂ O ₃	Lithium Carbonate (c)
CLi ₂ O ₃	Lithium Carbonate (ℓ)
CMgO ₃	Magnesium Carbonate (c)
CN	Cyano (g)
CN ⁺	Cyano Unipositive Ion (g)
CN ⁻	Cyano Uninegative Ion (g)
CNNa	Sodium Cyanide (c)
CNNa	Sodium Cyanide (ℓ)
CNNa	Sodium Cyanide (g)
CN ₂	CNN Radical (g)
CN ₂	NCN Radical (g)

Filing Order	Table Title
CNa ₂ O ₃	Sodium Carbonate (c)
CNa ₂ O ₃	Sodium Carbonate (l)
CO	Carbon Monoxide (g)
COS	Carbon Oxsulfide (g)
CO ₂	Carbon Dioxide (g)
CO ₂ ⁻	Carbon Dioxide Uninegative Ion (g)
CP	Carbon Phosphide (g)
CS	Carbon Monosulfide (g)
CS ₂	Carbon Disulfide (g)
CSi	Silicon Carbide (c,α)
CSi	Silicon Carbide (c,β)

CSi	Silicon Carbide (g)
CSi ₂	Disilicon Carbide (g)
CTi	Titanium Carbide (c)
CTi	Titanium Carbide (l)
CZr	Zirconium Carbide (c)
CZr	Zirconium Carbide (l)
C ₂	Carbon, Diatomic (g)
C ₂ ⁻	Dimeric Carbon Uninegative Ion (g)
C ₂ Be	Beryllium Carbide (g)
C ₂ Cl ₂	Dichloroacetylene (g)
C ₂ Cl ₄	Tetrachloroethylene (g)
C ₂ Cl ₆	Hexachloroethane (g)
C ₂ F ₂	Difluoroacetylene (g)
C ₂ F ₃ N	Trifluoroacetoneitrile (g)
C ₂ F ₄	Tetrafluoroethylene (g)
C ₂ F ₆	Hexafluoroethane (g)
C ₂ H	CCH Radical (g)
C ₂ HCl	Chloroacetylene (g)
C ₂ HF	Monofluoroacetylene (g)
C ₂ H ₂	Acetylene (g)
C ₂ H ₄	Ethylene (g)
C ₂ H ₄ O	Ethylene Oxide (g)
C ₂ K ₂ N ₂	Potassium Cyanide, Dimeric (g)
C ₂ Li ₂	Lithium Carbide (c)
C ₂ Mg	Magnesium Carbide (c)
C ₂ N	CNC Radical (g)
C ₂ N ₂	Cyanogen (g)
C ₂ N ₂ Na ₂	Sodium Cyanide, Dimeric (g)
C ₂ O	CCO Radical (g)
C ₂ Si	Silicon Dicarbid (g)
C ₃	Carbon, Trimeric (g)
C ₃ Al ₄	Aluminum Carbide (c)
C ₃ Mg ₂	Magnesium Carbide (c)
C ₃ O ₂	Carbon Suboxide (g)
C ₄	Carbon, Tetraatomic (g)
C ₄ H ₁₂ Si	Tetramethylsilane (g)
C ₄ N ₂	Carbon Subnitride (g)
C ₅	Carbon, Pentatomic (g)

Filing Order	Table Title
Ca	Calcium (ref. st.)
Ca	Calcium (α)
Ca	Calcium (β)
Ca	Calcium (l)
Ca	Calcium (g)
CaCl	Calcium Monochloride (g)
CaCl ₂	Calcium Chloride (c)
CaCl ₂	Calcium Chloride (l)
CaCl ₂	Calcium Chloride (g)
CaF	Calcium Monofluoride (g)
CaF ₂	Calcium Difluoride (c)
CaF ₂	Calcium Difluoride (l)
CaF ₂	Calcium Difluoride (g)
CaHO	Calcium Monohydroxide (g)
CaHO ⁺	Calcium Monohydroxide Unipositive Ion (g)
Cl	Chlorine, Monatomic (g)
Cl ⁺	Chlorine Unipositive Ion (g)
Cl ⁻	Chlorine Uninegative Ion (g)
ClCs	Cesium Monochloride (c)
ClCs	Cesium Monochloride (l)
ClCs	Cesium Monochloride (g)
ClCu	Copper Monochloride (c)
ClCu	Copper Monochloride (l)
ClCu	Copper Monochloride (g)
ClF	Chlorine Monofluoride (g)
ClFLi ₂	Lithium Chlorofluoride (g)
ClFMg	Magnesium Chloride Fluoride (g)
ClFO ₃	Perchloryl Fluoride (g)
ClF ₂ OP	Phosphoryl Difluorochloride (g)
ClF ₃	Chlorine Trifluoride (g)
ClF ₃ Si	Chlorotrifluorosilane (g)
ClF ₅	Chlorine Pentafluoride (g)
ClFe	Iron Monochloride (g)
ClH	Hydrogen Chloride (g)
ClHO	Hydrogen Oxychloride (g)
ClH ₃ Si	Chlorosilane (g)
ClH ₄ N	Ammonium Chloride (c)
ClH ₄ NO ₄	Ammonium Perchlorate (c)
ClHg	Mercurous Chloride (g)
ClI	Iodine Monochloride (c)
ClI	Iodine Monochloride (l)
ClI	Iodine Monochloride (g)
ClK	Potassium Chloride (c)
ClK	Potassium Chloride (l)
ClK	Potassium Chloride (g)
ClKO ₄	Potassium Perchlorate (c)
CLLi	Lithium Chloride (c)
CLLi	Lithium Chloride (l)
CLLi	Lithium Chloride (g)
CLLiO	Lithium Oxychloride (g)

Filing Order	Table Title
ClLiO ₄	Lithium Perchlorate (c)
ClLiO ₄	Lithium Perchlorate (l)
ClMg	Magnesium Monochloride (g)
ClMg ⁺	Magnesium Monochloride Unipositive Ion (g)
ClNO	Nitrosyl Chloride (g)
ClNO ₂	Nitryl Chloride (g)
ClNa	Sodium Chloride (c)
ClNa	Sodium Chloride (l)
ClNa	Sodium Chloride (g)
ClNaO ₄	Sodium Perchlorate (c)
ClO	Chlorine Monoxide (g)
ClOTi	Titanium Oxychloride (g)
ClO ₂	Chlorine Dioxide (g)
ClP	Phosphorus Monochloride (g)
ClPb	Lead Monochloride (g)
ClSi	Silicon Monochloride (g)
ClTi	Titanium Monochloride (g)
ClW	Tungsten Monochloride (g)
ClZr	Zirconium Monochloride (g)

Cl ₂	Chlorine, Diatomic (ref. st.,g)
Cl ₂ CS ₂	Cesium Monochloride, Dimeric (g)
Cl ₂ Cu	Copper Dichloride (c)
Cl ₂ FOP	Phosphoryl Fluorodichloride (g)
Cl ₂ Fe	Iron Dichloride (c)
Cl ₂ Fe	Iron Dichloride (l)
Cl ₂ Fe	Iron Dichloride (g)
Cl ₂ H ₂ Si	Dichlorosilane (g)
Cl ₂ Hg	Mercuric Chloride (c)
Cl ₂ Hg	Mercuric Chloride (l)
Cl ₂ Hg	Mercuric Chloride (g)
Cl ₂ Hg ₂	Mercurous Chloride (c)
Cl ₂ K ₂	Potassium Chloride, Dimeric (g)
Cl ₂ Li ₂	Lithium Chloride, Dimeric (g)
Cl ₂ Mg	Magnesium Dichloride (c)
Cl ₂ Mg	Magnesium Dichloride (l)
Cl ₂ Mg	Magnesium Dichloride (g)
Cl ₂ MoO ₂	Molybdenum Dioxydichloride (g)
Cl ₂ Na ₂	Sodium Chloride, Dimeric (g)
Cl ₂ O	Chlorine Monoxide (g)
Cl ₂ OTi	Titanium Oxydichloride (g)
Cl ₂ O ₂ W	Tungsten Dioxydichloride (c)
Cl ₂ O ₂ W	Tungsten Dioxydichloride (g)
Cl ₂ Pb	Lead Dichloride (c)
Cl ₂ Pb	Lead Dichloride (l)
Cl ₂ Pb	Lead Dichloride (g)
Cl ₂ Si	Silicon Dichloride (g)
Cl ₂ Ti	Titanium Dichloride (c)
Cl ₂ Ti	Titanium Dichloride (g)
Cl ₂ W	Tungsten Dichloride (c)

Filing Order	Table Title
Cl ₂ W	Tungsten Dichloride (g)
Cl ₂ Zr	Zirconium Dichloride (c)
Cl ₂ Zr	Zirconium Dichloride (l)
Cl ₂ Zr	Zirconium Dichloride (g)
Cl ₃ Cu ₃	Copper Monochloride, Trimeric (g)
Cl ₃ FSi	Trichlorofluorosilane (g)
Cl ₃ Fe	Iron Trichloride (c)
Cl ₃ Fe	Iron Trichloride (l)
Cl ₃ Fe	Iron Trichloride (g)
Cl ₃ HSi	Trichlorosilane (g)
Cl ₃ Li ₃	Lithium Chloride, Trimeric (g)
Cl ₃ OP	Phosphoryl Chloride (g)
Cl ₃ P	Phosphorus Trichloride (g)
Cl ₃ PS	Thiophosphoryl Chloride (g)
Cl ₃ Si	Silicon Trichloride (g)
Cl ₃ Ti	Titanium Trichloride (c)
Cl ₃ Ti	Titanium Trichloride (g)
Cl ₃ Zr	Zirconium Trichloride (c)
Cl ₃ Zr	Zirconium Trichloride (g)

Cl ₄ Mg ₂	Magnesium Dichloride, Dimeric (g)
Cl ₄ Mo	Molybdenum Tetrachloride (c)
Cl ₄ Mo	Molybdenum Tetrachloride (l)
Cl ₄ Mo	Molybdenum Tetrachloride (g)
Cl ₄ OW	Tungsten Oxytetrachloride (c)
Cl ₄ OW	Tungsten Oxytetrachloride (l)
Cl ₄ OW	Tungsten Oxytetrachloride (g)
Cl ₄ Pb	Lead Tetrachloride (g)
Cl ₄ Si	Silicon Tetrachloride (g)
Cl ₄ Ti	Titanium Tetrachloride (c)
Cl ₄ Ti	Titanium Tetrachloride (l)
Cl ₄ Ti	Titanium Tetrachloride (g)
Cl ₄ W	Tungsten Tetrachloride (c)
Cl ₄ W	Tungsten Tetrachloride (g)
Cl ₄ Zr	Zirconium Tetrachloride (c)
Cl ₄ Zr	Zirconium Tetrachloride (g)
Cl ₅ Mo	Molybdenum Pentachloride (c)
Cl ₅ Mo	Molybdenum Pentachloride (l)
Cl ₅ Mo	Molybdenum Pentachloride (g)
Cl ₅ P	Phosphorus Pentachloride (g)
Cl ₅ W	Tungsten Pentachloride (c)
Cl ₅ W	Tungsten Pentachloride (l)
Cl ₅ W	Tungsten Pentachloride (g)
Cl ₆ Fe ₂	Iron Trichloride, Dimeric (g)
Cl ₆ Mo	Molybdenum Hexachloride (c)
Cl ₆ Mo	Molybdenum Hexachloride (g)
Cl ₆ W	Tungsten Hexachloride (c,α)
Cl ₆ W	Tungsten Hexachloride (c,β)
Cl ₆ W	Tungsten Hexachloride (l)
Cl ₆ W	Tungsten Hexachloride (g)

Filing Order	Table Title
Cl_{10}W_2	Tungsten Pentachloride, Dimeric (g)
Co	Cobalt (ref. st.)
Co	Cobalt (c)
Co	Cobalt (l)
Co	Cobalt (g)
Co^+	Cobalt Unipositive Ion (g)
CoF_2	Cobalt Difluoride (c)
CoF_2	Cobalt Difluoride (l)
CoF_2	Cobalt Difluoride (g)
Cs	Cesium (ref. st.)
Cs	Cesium (c)
Cs	Cesium (l)
Cs	Cesium (g)
Cs^+	Cesium Unipositive Ion (g)
CsF	Cesium Monofluoride (c)
CsF	Cesium Monofluoride (l)
CsF	Cesium Monofluoride (g)
CsO	Cesium Monoxide (g)
Cs_2	Cesium, Dimeric (g)
Cs_2F_2	Cesium Monofluoride, Dimeric (g)
Cs_2O	Dicesium Monoxide (g)
Cu	Copper (ref. st.)
Cu	Copper (c)
Cu	Copper (l)
Cu	Copper (g)
Cu^+	Copper Unipositive Ion (g)
CuF	Copper Monofluoride (c)
CuF	Copper Monofluoride (g)
CuF_2	Copper Difluoride (c)
CuF_2	Copper Difluoride (l)
CuF_2	Copper Difluoride (g)
CuH_2O_2	Copper Dihydroxide (c)
CuO	Copper Monoxide (c)
CuO	Copper Monoxide (g)
CuO_4S	Copper Sulfate (c)
Cu_2	Copper, Diatomic (g)
Cu_2O	Dicopper Monoxide (c)
Cu_2O	Dicopper Monoxide (l)
$\text{Cu}_2\text{O}_5\text{S}$	Copper Oxide Sulfate (c)
F	Fluorine, Monatomic (g)
F^-	Fluorine Uninegative Ion (g)
FFe	Iron Monofluoride (g)
FH	Hydrogen Fluoride (g)
FHO	Hydrogen Oxyfluoride (g)
FH_3Si	Fluorosilane (g)
FHg	Mercurous Fluoride (g)
FI	Iodine Monofluoride (g)

Filing Order	Table Title
FK	Potassium Fluoride (c)
FK	Potassium Fluoride (l)
FK	Potassium Fluoride (g)
FLi	Lithium Fluoride (c)
FLi	Lithium Fluoride (l)
FLi	Lithium Fluoride (g)
FLiO	Lithium Oxyfluoride (g)
FMg	Magnesium Monofluoride (g)
FN	Nitrogen Monofluoride (g)
FNO	Nitrosyl Fluoride (g)
FNO_2	Nitryl Fluoride (g)
FNO_3	Fluorine Nitrate (g)
FNa	Sodium Fluoride (c)
FNa	Sodium Fluoride (l)
FNa	Sodium Fluoride (g)
FO	Fluorine Monoxide (g)
FOTi	Titanium Oxyfluoride (g)
FO_2	Monofluorine Dioxide (g)
FP	Phosphorus Monofluoride (g)
FPS	Phosphorus Thiofluoride (g)
FPb	Lead Monofluoride (g)
FSi	Silicon Monofluoride (g)
FTi	Titanium Monofluoride (g)
FW	Tungsten Monofluoride (g)
FZr	Zirconium Monofluoride (g)
F_2	Fluorine, Diatomic (ref.st.,g)
F_2Fe	Iron Difluoride (c)
F_2Fe	Iron Difluoride (l)
F_2Fe	Iron Difluoride (g)
F_2HK	Potassium Bifluoride (c)
F_2HK	Potassium Bifluoride (l)
$\text{F}_2\text{H}_2\text{Si}$	Difluorosilane (g)
F_2Hg	Mercuric Fluoride (c)
F_2Hg	Mercuric Fluoride (l)
F_2Hg	Mercuric Fluoride (g)
F_2Hg_2	Mercurous Fluoride (c)
F_2K^-	Potassium Difluoride Uninegative Ion (g)
F_2K_2	Potassium Fluoride, Dimeric (g)
F_2Li^-	Lithium Difluoride Uninegative Ion (g)
F_2Li_2	Lithium Fluoride, Dimeric (g)
F_2Mg	Magnesium Fluoride (c)
F_2Mg	Magnesium Fluoride (l)
F_2Mg	Magnesium Fluoride (g)
F_2N	Nitrogen Difluoride (g)
F_2N_2	Difluorodiazine, cis- (g)
F_2N_2	Difluorodiazine, trans- (g)
F_2Na^-	Sodium Difluoride Uninegative Ion (g)
F_2Na_2	Sodium Fluoride, Dimeric (g)
F_2O	Oxygen Difluoride (g)
F_2OS	Thionyl Fluoride (g)

Filing Order	Table Title	Filing Order	Table Title
F ₂ OSi	Silicon Oxydifluoride (g)	Fe	Iron (l)
F ₂ OTi	Titanium Oxydifluoride (g)	Fe	Iron (g)
F ₂ O ₂ S	Sulfuryl Fluoride (g)	FeH ₂ O ₂	Iron Dihydroxide (c)
F ₂ P	Phosphorus Difluoride (g)	FeH ₂ O ₂	Iron Dihydroxide (g)
F ₂ Pb	Lead Difluoride (c)	FeH ₃ O ₃	Iron Trihydroxide (c)
F ₂ Pb	Lead Difluoride (l)	FeI ₂	Iron Diiodide (c)
F ₂ Pb	Lead Difluoride (g)	FeI ₂	Iron Diiodide (l)
F ₂ Si	Silicon Difluoride (g)	FeI ₂	Iron Diiodide (g)
F ₂ Ti	Titanium Difluoride (g)	Fe _{0.947} O	Wüstite (c)
F ₂ Zr	Zirconium Difluoride (c)	FeO	Iron Oxide (c)
F ₂ Zr	Zirconium Difluoride (l)	FeO	Iron Oxide (l)
F ₂ Zr	Zirconium Difluoride (g)	FeO	Iron Oxide (g)
F ₃ Fe	Iron Trifluoride (c)	FeO ₄ S	Iron Sulfate (c)
F ₃ Fe	Iron Trifluoride (g)	Fe ₂ I ₄	Iron Diiodide, Dimeric (g)
F ₃ HSi	Trifluorosilane (g)	Fe ₂ O ₃	Hematite (c)
F ₃ Li ₃	Lithium Fluoride, Trimeric (g)	Fe ₂ O ₁₂ S ₃	Diiron Trisulfate (c)
F ₃ N	Nitrogen Trifluoride (g)	Fe ₃ O ₄	Magnetite (c)
F ₃ NO	Trifluoramine Oxide (g)	H	Hydrogen, Monatomic (g)
F ₃ OP	Phosphoryl Fluoride (g)	H ⁺	Proton (g)
F ₃ P	Phosphorus Trifluoride (g)	H ⁻	Hydrogen Uninegative Ion (g)
F ₃ PS	Thiophosphoryl Fluoride (g)	HHg	Mercury Monohydride (g)
F ₃ Si	Silicon Trifluoride (g)	HI	Hydrogen Iodide (g)
F ₃ Ti	Titanium Trifluoride (c)	HK	Potassium Hydride (c)
F ₃ Ti	Titanium Trifluoride (g)	HK	Potassium Hydride (g)
F ₃ Zr	Zirconium Trifluoride (c)	HKO	Potassium Hydroxide (c)
F ₃ Zr	Zirconium Trifluoride (g)	HKO	Potassium Hydroxide (l)
		HKO	Potassium Hydroxide (g)
F ₄ Mg ₂	Magnesium Difluoride, Dimeric (g)	HLi	Lithium Hydride (c)
F ₄ MoO	Molybdenum Oxytetrafluoride (g)	HLi	Lithium Hydride (l)
F ₄ N ₂	Tetrafluorohydrazine (g)	HLi	Lithium Hydride (g)
F ₄ OW	Tungsten Oxytetrafluoride (c)	HLiO	Lithium Hydroxide (c)
F ₄ OW	Tungsten Oxytetrafluoride (l)	HLiO	Lithium Hydroxide (l)
F ₄ OW	Tungsten Oxytetrafluoride (g)	HLiO	Lithium Hydroxide (g)
F ₄ Pb	Lead Tetrafluoride (g)	HMg	Magnesium Monohydride (g)
F ₄ S	Sulfur Tetrafluoride (g)	HMgO	Magnesium Monohydroxide (g)
F ₄ Si	Silicon Tetrafluoride (g)	HMgO ⁺	Magnesium Monohydroxide Unipositive Ion (g)
F ₄ Ti	Titanium Tetrafluoride (c)	HN	Imidogen (g)
F ₄ Ti	Titanium Tetrafluoride (g)	HNO	Nitroxyl (g)
F ₄ Zr	Zirconium Tetrafluoride (c)	HNO ₂	Nitrous Acid, cis- (g)
F ₄ Zr	Zirconium Tetrafluoride (g)	HNO ₂	Nitrous Acid, trans- (g)
F ₅ I	Iodine Pentafluoride (g)	HNO ₃	Nitric Acid (g)
F ₅ P	Phosphorus Pentafluoride (g)	HNa	Sodium Hydride (c)
F ₆ Mo	Molybdenum Hexafluoride (l)	HNa	Sodium Hydride (g)
F ₆ Mo	Molybdenum Hexafluoride (g)	HNaO	Sodium Hydroxide (c)
F ₆ S	Sulfur Hexafluoride (g)	HNaO	Sodium Hydroxide (l)
F ₆ W	Tungsten Hexafluoride (l)	HNaO	Sodium Hydroxide (g)
F ₆ W	Tungsten Hexafluoride (g)	HO	Hydroxyl (g)
F ₇ I	Iodine Heptafluoride (g)	HO ⁺	Hydroxyl Unipositive Ion (g)
		HO ⁻	Hydroxyl Uninegative Ion (g)
Fe	Iron (ref. st.)	HO ₂	Hydroperoxyl (g)
Fe	Iron (c)		

Filing Order	Table Title
HP	Phosphorus Monohydride (g)
HPb	Lead Monohydride (g)
HS	Sulfur Monohydride (g)
HSi	Silicon Monohydride (g)
HZr	Zirconium Hydride (g)
H ₂	Hydrogen, Diatomic (ref. st., g)
H ₂ K ₂ O ₂	Potassium Hydroxide, Dimeric (g)
H ₂ Li ₂ O ₂	Lithium Hydroxide, Dimeric (g)
H ₂ Mg	Magnesium Hydride (c)
H ₂ MgO ₂	Magnesium Dihydroxide (c)
H ₂ MgO ₂	Magnesium Dihydroxide (g)
H ₂ MoO ₄	Molybdic Acid (g)
H ₂ N	Amidogen (g)
H ₂ N ₂	Diimide (g)
H ₂ Na ₂ O ₂	Sodium Hydroxide, Dimeric (g)
H ₂ O	Water (g)
H ₂ O ₂	Hydrogen Peroxide (g)
H ₂ O ₄ S	Sulfuric Acid (l)
H ₂ O ₄ S	Sulfuric Acid (g)
H ₂ O ₄ W	Tungstic Acid (c)
H ₂ O ₄ W	Tungstic Acid (g)
H ₂ P	Phosphorus Hydride (g)
H ₂ S	Hydrogen Sulfide (g)
H ₂ Ti	Titanium Hydride (c)
H ₃ N	Ammonia (g)
H ₃ O ⁺	Hydronium Unipositive Ion (g)
H ₃ O ₄ P	Orthophosphoric Acid (c)
H ₃ O ₄ P	Orthophosphoric Acid (l)
H ₃ P	Phosphine (g)
H ₄ IN	Ammonium Iodide (c)
H ₄ N ₂	Hydrazine (l)
H ₄ N ₂	Hydrazine (g)
H ₄ Si	Silane (g)
Hg	Mercury (ref. st.)
Hg	Mercury (l)
Hg	Mercury, Monatomic (g)
HgI	Mercurous Iodide (g)
HgI ₂	Mercuric Iodide (c)
HgI ₂	Mercuric Iodide (l)
HgI ₂	Mercuric Iodide (g)
HgO	Mercuric Oxide (c)
HgO	Mercury Monoxide (g)
Hg ₂ I ₂	Mercurous Iodide (c)
Hg ₂ I ₂	Mercurous Iodide (l)
I	Iodine, Monatomic (g)
IK	Potassium Iodide (c)
IK	Potassium Iodide (l)
IK	Potassium Iodide (g)

Filing Order	Table Title
ILi	Lithium Iodide (c)
ILi	Lithium Iodide (l)
ILi	Lithium Iodide (g)
INO	Nitrosyl Iodide (g)
INa	Sodium Iodide (c)
INa	Sodium Iodide (l)
IPb	Lead Monoiodide (g)
ITi	Titanium Monoiodide (g)
IZr	Zirconium Monoiodide (g)
I ₂	Iodine (ref. st.)
I ₂	Iodine (l)
I ₂	Iodine, Diatomic (g)
I ₂ K ₂	Potassium Iodide, Dimeric (g)
I ₂ Li ₂	Lithium Iodide, Dimeric (g)
I ₂ Pb	Lead Diiodide (c)
I ₂ Pb	Lead Diiodide (l)
I ₂ Pb	Lead Diiodide (g)
I ₂ Ti	Titanium Diiodide (c)
I ₂ Ti	Titanium Diiodide (g)
I ₂ Zr	Zirconium Diiodide (c)
I ₂ Zr	Zirconium Diiodide (l)
I ₂ Zr	Zirconium Diiodide (g)
I ₃ Ti	Titanium Triiodide (c)
I ₃ Ti	Titanium Triiodide (g)
I ₃ Zr	Zirconium Triiodide (c)
I ₃ Zr	Zirconium Triiodide (g)
I ₄ Pb	Lead Tetraiodide (g)
I ₄ Ti	Titanium Tetraiodide (c)
I ₄ Ti	Titanium Tetraiodide (l)
I ₄ Ti	Titanium Tetraiodide (g)
I ₄ Zr	Zirconium Tetraiodide (c)
I ₄ Zr	Zirconium Tetraiodide (g)
K	Potassium (ref. st.)
K	Potassium (l)
K	Potassium, Monatomic (g)
K ⁺	Potassium Unipositive Ion (g)
KO	Potassium Monoxide (g)
KO ⁻	Potassium Monoxide Uninegative Ion (g)
K ₂	Potassium, Diatomic (g)
K ₂ O	Potassium Oxide (c)
K ₂ O ₂	Potassium Peroxide (c)
Li	Lithium (ref. st.)
Li	Lithium (c)
Li	Lithium (l)
Li	Lithium, Monatomic (g)
Li ⁺	Lithium Unipositive Ion (g)
LiN	Lithium Nitride (g)

Filing Order	Table Title	Filing Order	Table Title
LiNO	Lithium Nitroxide (g)	Mo	Molybdenum (c)
LiNaO	Lithium Sodium Oxide (g)	Mo	Molybdenum (l)
LiO	Lithium Monoxide (g)	Mo	Molybdenum, Monatomic (g)
LiO ⁻	Lithium Monoxide Uninegative Ion (g)	Mo ⁺	Molybdenum Unipositive Ion (g)
Li ₂	Lithium, Diatomic (g)	MoO	Molybdenum Monoxide (g)
Li ₂ O	Lithium Oxide (c)	MoO ₂	Molybdenum Dioxide (c)
Li ₂ O	Lithium Oxide (l)	MoO ₂	Molybdenum Dioxide (g)
Li ₂ O	Lithium Oxide (g)	MoO ₃	Molybdenum Trioxide (c)
Li ₂ O ₂	Lithium Peroxide (c)	MoO ₃	Molybdenum Trioxide (l)
Li ₂ O ₂	Lithium Monoxide, Dimeric (g)	MoO ₃	Molybdenum Trioxide (g)
Li ₂ O ₃ Si	Lithium Metasilicate (c)	N	Nitrogen, Monatomic (g)
Li ₂ O ₃ Si	Lithium Metasilicate (l)	NO	Nitric Oxide (g)
Li ₂ O ₃ Ti	Lithium Metatitanate (c)	NO ⁺	Nitric Oxide Unipositive Ion (g)
Li ₂ O ₃ Ti	Lithium Metatitanate (l)	NO ₂	Nitrogen Dioxide (g)
Li ₂ O ₅ Si ₂	Lithium Disilicate (c)	NO ₂ ⁻	Nitrogen Dioxide Negative Ion (g)
Li ₂ O ₅ Si ₂	Lithium Disilicate (l)	NO ₃	Nitrogen Trioxide (g)
Li ₃ N	Lithium Nitride (c)	NP	Phosphorus Nitride (g)
Mg	Magnesium (ref. st.)	NS	Sulfur Nitride (g)
Mg	Magnesium (c)	NSi	Silicon Nitride (g)
Mg	Magnesium (l)	NSi ₂	Disilicon Nitride (g)
Mg	Magnesium, Monatomic (g)	NTi	Titanium Nitride (c)
Mg ⁺	Magnesium Unipositive Ion (g)	NTi	Titanium Nitride (l)
MgN	Magnesium Nitride (g)	NZr	Zirconium Nitride (c)
MgO	Magnesium Oxide (c)	NZr	Zirconium Nitride (l)
MgO	Magnesium Oxide (l)	NZr	Zirconium Nitride (g)
MgO	Magnesium Oxide (g)	N ₂	Nitrogen (ref. st., g)
MgO ₃ Si	Magnesium Metasilicate (c)	N ₂ O	Dinitrogen Monoxide (g)
MgO ₃ Si	Magnesium Metasilicate (l)	N ₂ O ₃	Dinitrogen Trioxide (g)
MgO ₃ Ti	Magnesium Metatitanate (c)	N ₂ O ₄	Nitrogen Tetroxide (c)
MgO ₃ Ti	Magnesium Metatitanate (l)	N ₂ O ₄	Dinitrogen Tetroxide (l)
MgO ₄ S	Magnesium Sulfate (c)	N ₂ O ₄	Nitrogen Tetroxide (g)
MgO ₄ S	Magnesium Sulfate (l)	N ₂ O ₅	Dinitrogen Pentoxide (g)
MgO ₄ W	Magnesium Tungstate (c)	N ₄ Si ₃	Silicon Nitride (c,a)
MgO ₅ Ti ₂	Magnesium Dtitanate (c)	N ₅ P ₃	Triphosphorus Pentanitride (c)
MgO ₅ Ti ₂	Magnesium Dtitanate (l)	Na	Sodium (ref. st.)
MgS	Magnesium Sulfide (c)	Na	Sodium (c)
MgS	Magnesium Sulfide (g)	Na	Sodium (l)
Mg ₂ O ₄ Si	Magnesium Orthosilicate (c)	Na	Sodium Monatomic (g)
Mg ₂ O ₄ Si	Magnesium Orthosilicate (l)	Na ⁺	Sodium Unipositive Ion (g)
Mg ₂ O ₄ Ti	Magnesium Orthotitanate (c)	NaO	Sodium Monoxide (g)
Mg ₂ O ₄ Ti	Magnesium Orthotitanate (l)	NaO ⁻	Sodium Monoxide Uninegative Ion (g)
Mg ₂ Si	Magnesium Silicide (c)	NaO ₂	Sodium Superoxide (c)
Mg ₂ Si	Magnesium Silicide (l)	Na ₂	Sodium Diatomic (g)
Mg ₃ N ₂	Magnesium Nitride (c)	Na ₂ O	Disodium Monoxide (c)
Mg ₃ O ₈ P ₂	Magnesium Orthophosphate (c)	Na ₂ O	Disodium Monoxide (l)
Mg ₃ O ₈ P ₂	Magnesium Orthophosphate (l)	Na ₂ O ₂	Disodium Dioxide (c)
Mo	Molybdenum (ref. st.)	Na ₂ O ₃ Si	Sodium Metasilicate (c)
		Na ₂ O ₃ Si	Sodium Metasilicate (l)

Filing Order	Table Title
Na ₂ O ₄ S	Sodium Sulfate (c,V)
Na ₂ O ₄ S	Sodium Sulfate (c,III)
Na ₂ O ₄ S	Sodium Sulfate (c,I)
Na ₂ O ₄ S	Sodium Sulfate (c,δ)
Na ₂ O ₄ S	Sodium Sulfate (ℓ)
Na ₂ O ₄ W	Sodium Tungstate (c)
Na ₂ O ₅ Si ₂	Sodium Disilicate (c)
Na ₂ O ₅ Si ₂	Sodium Disilicate (ℓ)
Na ₂ S	Sodium Sulfide (c)
Na ₂ S	Sodium Sulfide (ℓ)
O	Oxygen, Monatomic (g)
O ⁻	Oxygen Uninegative Ion (g)
OP	Phosphorus Monoxide (g)
OPb	Lead Monoxide (c, Red)
OPb	Lead Monoxide (c, Yellow)
OPb	Lead Monoxide (ℓ)
OPb	Lead Monoxide (g)
OS	Sulfur Monoxide (g)
OS ₂	Disulfur Monoxide (g)
OSi	Silicon Monoxide (g)
OTi	Titanium Monoxide (c,α)
OTi	Titanium Monoxide (c,β)
OTi	Titanium Monoxide (ℓ)
OTi	Titanium Monoxide (g)
OW	Tungsten Monoxide (g)
OZr	Zirconium Monoxide (g)
O ₂	Oxygen, Diatomic (ref. st., g)
O ₂ ⁻	Diatomic Oxygen Uninegative Ion (g)
O ₂ P	Phosphorus Dioxide (g)
O ₂ Pb	Lead Dioxide (c)
O ₂ S	Sulfur Dioxide (g)
O ₂ Si	Quartz (c)
O ₂ Si	Cristobalite (c,low)
O ₂ Si	Cristobalite (c,high)
O ₂ Si	Silicon Dioxide (ℓ)
O ₂ Si	Silicon Dioxide (g)
O ₂ Ti	Anatase (c)
O ₂ Ti	Rutile (c)
O ₂ Ti	Titanium Dioxide (ℓ)
O ₂ Ti	Titanium Dioxide (g)
O ₂ W	Tungsten Dioxide (c)
O ₂ W	Tungsten Dioxide (g)
O _{2.72} W	Tungsten Oxide (c)
O _{2.90} W	Tungsten Oxide (c)
O _{2.96} W	Tungsten Oxide (c)
O ₂ Zr	Zirconium Dioxide (c)
O ₂ Zr	Zirconium Dioxide (ℓ)
O ₂ Zr	Zirconium Dioxide (g)

Filing Order	Table Title
O ₃	Ozone (g)
O ₃ PbSi	Lead Metasilicate (c)
O ₃ S	Sulfur Trioxide (g)
O ₃ Ti ₂	Dititanium Trioxide (c)
O ₃ Ti ₂	Dititanium Trioxide (ℓ)
O ₃ W	Tungsten Trioxide (c)
O ₃ W	Tungsten Trioxide (ℓ)
O ₃ W	Tungsten Trioxide (g)
O ₄ Pb ₂ Si	Lead Orthosilicate (c)
O ₄ Pb ₃	Lead Orthoplumbate (c)
O ₄ SiZr	Zirconium Orthosilicate (c)
O ₅ Ti ₃	Trititanium Pentoxide (c,α)
O ₅ Ti ₃	Trititanium Pentoxide (c,β)
O ₅ Ti ₃	Trititanium Pentoxide (ℓ)
O ₆ P ₄	Phosphorus Trioxide, Dimeric (g)
O ₆ W ₂	Tungsten Trioxide, Dimeric (g)
O ₈ W ₃	Tritungsten Octaoxide (g)
O ₉ W ₃	Tungsten Trioxide, Trimeric (g)
O ₁₀ P ₄	Phosphorus Pentoxide, Dimeric (c)
O ₁₀ P ₄	Phosphorus Pentoxide, Dimeric (g)
O ₁₂ W ₄	Tungsten Trioxide, Tetrameric (g)
P	Phosphorus (ref. st.)
P	Phosphorus (c, Red, V)
P	Phosphorus (c, White)
P	Phosphorus (ℓ)
P	Phosphorus (g)
PS	Phosphorus Sulfide (g)
P ₂	Phosphorus, Diatomic (g)
P ₄	Phosphorus, Tetratomic (g)
P ₄ S ₃	Phosphorus Sulfide (c)
P ₄ S ₃	Phosphorus Sulfide (ℓ)
P ₄ S ₃	Phosphorus Sulfide (g)
Pb	Lead (ref. st.)
Pb	Lead (c)
Pb	Lead (ℓ)
Pb	Lead (g)
Pb ₂	Lead, Diatomic (g)
S	Sulfur (ref. st.)
S	Sulfur (c)
S	Sulfur (ℓ)
S	Sulfur, Monatomic (g)
SSi	Silicon Monosulfide (g)
S ₂	Sulfur, Diatomic (g)
S ₂ Si	Silicon Disulfide (c)
S ₂ Si	Silicon Disulfide (ℓ)
S ₈	Sulfur Octatomic (g)

Filing Order	Table Title
Si	Silicon (ref. st.)
Si	Silicon (c)
Si	Silicon (l)
Si	Silicon, Monatomic (g)
Si ₂	Silicon, Diatomic (g)
Si ₃	Silicon, Triatomic (g)
Ti	Titanium (ref. st.)
Ti	Titanium (c,α)
Ti	Titanium (c,β)
Ti	Titanium (l)
Ti	Titanium, Monatomic (g)
Ti ⁺	Titanium Unipositive Ion (g)

Filing Order	Table Title
W	Tungsten (ref. st.)
W	Tungsten (c)
W	Tungsten (l)
W	Tungsten, Monatomic (g)
W ⁺	Tungsten Unipositive Ion
Zr	Zirconium (ref. st.)
Zr	Zirconium (c,α)
Zr	Zirconium (c,β)
Zr	Zirconium (l)
Zr	Zirconium (g)
Zr ⁺	Zirconium Unipositive Ion (g)
e ⁻	Electron Gas (ref. st.)

At. Wt. = 26.9815

(REFERENCE STATE)

ALUMINUM (Al)

0 to 933°K. Crystal
933 to 2786.8°K. Liquid
2786.8 to 8000°K. Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	keal. mole ⁻¹	ΔF°	Log K _f
0	.000	.000	INFINITE	- 1.094	.000	.000	.000
100	3.116	1.650	11.530	- .988	.000	.000	.000
200	5.156	4.572	7.302	- .568	.000	.000	.000
298	5.686	6.769	6.769	.000	.000	.000	.000
400	6.814	8.805	6.769	.011	.000	.000	.000
500	6.163	8.528	7.002	.010	.000	.000	.000
600	6.717	11.134	7.968	.000	.000	.000	.000
700	6.999	12.190	8.497	2.585	.000	.000	.000
800	7.370	13.147	9.019	3.302	.000	.000	.000
900	7.501	14.048	9.528	4.064	.000	.000	.000
1000	7.588	17.003	10.705	7.397	.000	.000	.000
1100	7.588	18.324	10.911	8.150	.000	.000	.000
1200	7.588	18.968	11.557	8.915	.000	.000	.000
1300	7.588	19.593	12.152	9.673	.000	.000	.000
1400	7.588	20.156	12.704	10.432	.000	.000	.000
1500	7.588	20.679	13.216	11.191	.000	.000	.000
1600	7.588	21.169	13.700	11.950	.000	.000	.000
1700	7.588	21.629	14.153	12.709	.000	.000	.000
1800	7.588	22.063	14.581	13.467	.000	.000	.000
1900	7.588	22.473	14.985	14.226	.000	.000	.000
2000	7.588	22.867	15.370	14.985	.000	.000	.000
2100	7.588	23.242	15.735	15.744	.000	.000	.000
2200	7.588	23.585	16.084	16.503	.000	.000	.000
2300	7.588	23.923	16.418	17.261	.000	.000	.000
2400	7.588	24.246	16.737	18.020	.000	.000	.000
2500	7.588	24.555	17.044	18.779	.000	.000	.000
2600	7.588	24.853	17.338	19.538	.000	.000	.000
2700	7.588	25.139	17.622	20.297	.000	.000	.000
2800	4.971	50.501	18.192	90.466	.000	.000	.000
2900	4.971	50.675	19.309	90.963	.000	.000	.000
3000	4.971	50.844	20.357	91.460	.000	.000	.000
3100	4.971	51.007	21.343	91.957	.000	.000	.000
3200	4.972	51.165	22.273	92.454	.000	.000	.000
3300	4.973	51.318	23.151	92.951	.000	.000	.000
3400	4.975	51.466	23.981	93.449	.000	.000	.000
3500	4.977	51.610	24.769	93.946	.000	.000	.000
3600	4.979	51.751	25.516	94.444	.000	.000	.000
3700	4.982	51.887	26.227	94.942	.000	.000	.000
3800	4.986	52.020	26.904	95.441	.000	.000	.000
3900	4.991	52.150	27.550	95.939	.000	.000	.000
4000	4.996	52.276	28.166	96.439	.000	.000	.000
4100	5.002	52.399	28.756	96.939	.000	.000	.000
4200	5.010	52.520	29.320	97.439	.000	.000	.000
4300	5.019	52.638	29.861	97.941	.000	.000	.000
4400	5.029	52.754	30.380	98.443	.000	.000	.000
4500	5.041	52.867	30.879	98.947	.000	.000	.000
4600	5.055	52.978	31.358	99.451	.000	.000	.000
4700	5.071	53.086	31.819	99.958	.000	.000	.000
4800	5.088	53.193	32.263	100.466	.000	.000	.000
4900	5.108	53.299	32.691	100.975	.000	.000	.000
5000	5.130	53.402	33.105	101.487	.000	.000	.000
5100	5.154	53.504	33.503	102.001	.000	.000	.000
5200	5.181	53.604	33.889	102.518	.000	.000	.000
5300	5.211	53.703	34.262	103.038	.000	.000	.000
5400	5.244	53.801	34.623	103.560	.000	.000	.000
5500	5.280	53.897	34.972	104.087	.000	.000	.000
5600	5.319	53.993	35.311	104.617	.000	.000	.000
5700	5.361	54.087	35.640	105.150	.000	.000	.000
5800	5.406	54.181	35.959	105.689	.000	.000	.000
5900	5.456	54.274	36.268	106.232	.000	.000	.000
6000	5.508	54.366	36.569	106.780	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1955

Aluminum (Al)

(Crystal) At. Wt. = 26.9815

T, °K.	C _p	$\frac{\text{cal. mole}^{-1}\text{deg.}^{-1}}{S^\circ}$	$\frac{-(F^\circ - H^\circ_{298})}{T}$	$\frac{\text{kcal. mole}^{-1}}{H^\circ - H^\circ_{298}}$	ΔH°_f	ΔF°_f	Log K _p
0	0.000	0.000	INFINITE	1.094	0.000	0.000	INFINITE
100	3.116	1.850	11.530	1.988	0.000	0.000	0.000
200	5.458	4.722	7.782	2.586	0.000	0.000	0.000
298	5.486	6.762	7.762	0.000	0.000	0.000	0.000
300	5.814	6.605	6.769	0.11	0.000	0.000	0.000
400	6.163	8.528	7.002	0.610	0.000	0.000	0.000
500	6.450	9.934	7.452	1.241	0.000	0.000	0.000
600	6.717	11.134	7.969	1.900	0.000	0.000	0.000
700	6.999	12.190	8.497	2.585	0.000	0.000	0.000
800	7.370	13.147	9.019	3.302	0.000	0.000	0.000
900	7.901	14.044	9.526	4.044	0.000	0.000	0.000
1000	8.430	14.907	10.023	4.883	0.000	0.000	0.000
1100	8.800	15.728	10.505	5.746	2.410	0.687	0.089
1200	9.080	16.506	10.973	6.640	2.275	0.701	0.128
1300	9.350	17.243	11.427	7.561	2.112	0.943	0.159
1400	9.600	17.945	11.866	8.509	1.923	1.172	0.183
1500	9.850	18.616	12.295	9.481	1.710	1.385	0.202

ALUMINUM (Al)

(CRYSTAL)

AT. WT. = 26.9815

$$\Delta H^\circ_f 0 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H^\circ_f 298.15 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H^\circ_m = 2.56 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\Delta H^\circ_m 298.15 = 78.0 \text{ kcal. mole}^{-1}$$

$$S^\circ_{298.15} = 6.769 \pm 0.02 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T^\circ_m = 933^\circ\text{K.}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The low temperature heat capacity curve is based on the work of N. E. Phillips, *Phys. Rev.* **114**, 676 (1959) in the range 0.1 to 4°K; J. A. Cox and M. H. Reesom, *Physica* **4**, 835 (1937) from 1-20°K. and M. G. Glaue and P. F. Meads, *J. Am. Chem. Soc.* **63**, 1897 (1941). The high temperature enthalpy adopted here is that of R. A. McDonald, private communication, Dow Thermal Research Laboratory, Oct. 1965. This data is in general agreement with the measurements of J. H. Averbury and E. Griffiths, *Proc. Phys. Soc. (London)* **38**, 378 (1926); E. D. Eastman, A. M. Williams and T. F. Young, *J. Am. Chem. Soc.* **45**, 1178 (1924); M. B. Kandel and R. Hultgren, private communication to D. R. Stull from R. L. Orr Mar. 29, 1960; S. Satoh, *Sci. Papers, Inst. Phys. Chem. Res. (Tokyo)* **29**, 19 (1936); P. Wust, A. Mauthen and R. Durrer, *Forsch. Arb. Ver. deut. Ing. No. 204 (1918). Other investigations have been discussed by R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley "Selected Value of Thermodynamic Properties of Metals and Alloys", John Wiley and Sons, Inc., New York, (1963). These other determinations generally lay below the adopted values.*

Melting Data.

The heat of melting was reported by McDonald, loc. cit.. It is in good agreement with the selected value of Hultgren et al, loc. cit. The chosen value also has eliminated uncertainty due to reaction of the liquid aluminum and its vessel by use of BN and TiB₂ containers. The melting point of 933°K. was chosen at the limit of the "well established" 932 ± 1°K., as more likely representing pure aluminum. This choice was based mainly on the work of M. F. Roess and H. T. Wensei, *J. Res. Natl. Bur. Std.* **44**, 247 (1935).

Sublimation Data.

See Al(g) for details.

$$\Delta H_f^{298.15} = 8.42 \text{ gibbs/mol}$$

$$\Delta H_m^\circ = 2.56 \pm 0.05 \text{ kcal/mol}$$

$$\Delta H_v^\circ = 69.497 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 8.42 \text{ gibbs/mol}$$

$$T_m^\circ = 933^\circ \text{K}$$

$$T_b^\circ = 2766.8^\circ \text{K}$$

Heat of Formation

The heat of formation is calculated from that of the crystal by adding the heat of melting and the difference between $H_{298}^\circ - H_{298}^\circ$ for (c) and (l).

Heat Capacity and Entropy

The heat capacity is adopted from the enthalpy measurements of R. A. McDonald, private communication, Thermal Research Laboratory, The Dow Chemical Company, Midland, Michigan, Oct. 1965. The liquid enthalpies were determined in crucibles of BN and Ti_2 sealed in a platinum-rhodium capsule. The liquid enthalpies are in agreement with the determination of J. W. Auberry and E. Griffiths, Proc. Phys. Soc. (London) 38, 378 (1976) and higher, by as much as 12 percent, than those of F. Wust, A. Meuthen and R. Dorrer, Forsch. Arb. Deut. Ing. No 204 (1918) and S. Umino, Sci. Repts. Tohoku. Imp. Univ. Ser 1, 15, 597 (1926). The enthalpy data is adequately represented by a constant heat capacity. The entropy is calculated from that of the crystal in a manner analogous to the heat of formation.

Melting Data

See Al(c) for details.

Vaporization Data

The temperature of boiling and the heat of vaporization are derived from the adopted functions and the heat of sublimation in order to maintain thermodynamic consistency.

T, °K	C_p°	$S^\circ - (C_p^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°	$\log K_p$
100	7.588	8.420	8.420	.000	2.072	1.589
200	7.588	8.467	8.420	.014	2.075	1.576
300	7.588	8.467	8.420	.014	2.075	1.576
400	7.588	8.467	8.420	.014	2.075	1.576
500	7.588	8.467	8.420	.014	2.075	1.576
600	7.588	8.467	8.420	.014	2.075	1.576
700	7.588	8.467	8.420	.014	2.075	1.576
800	7.588	8.467	8.420	.014	2.075	1.576
900	7.588	8.467	8.420	.014	2.075	1.576
1000	7.588	8.467	8.420	.014	2.075	1.576
1100	7.588	8.467	8.420	.014	2.075	1.576
1200	7.588	8.467	8.420	.014	2.075	1.576
1300	7.588	8.467	8.420	.014	2.075	1.576
1400	7.588	8.467	8.420	.014	2.075	1.576
1500	7.588	8.467	8.420	.014	2.075	1.576
1600	7.588	8.467	8.420	.014	2.075	1.576
1700	7.588	8.467	8.420	.014	2.075	1.576
1800	7.588	8.467	8.420	.014	2.075	1.576
1900	7.588	8.467	8.420	.014	2.075	1.576
2000	7.588	8.467	8.420	.014	2.075	1.576
2100	7.588	8.467	8.420	.014	2.075	1.576
2200	7.588	8.467	8.420	.014	2.075	1.576
2300	7.588	8.467	8.420	.014	2.075	1.576
2400	7.588	8.467	8.420	.014	2.075	1.576
2500	7.588	8.467	8.420	.014	2.075	1.576
2600	7.588	8.467	8.420	.014	2.075	1.576
2700	7.588	8.467	8.420	.014	2.075	1.576
2800	7.588	8.467	8.420	.014	2.075	1.576
2900	7.588	8.467	8.420	.014	2.075	1.576
3000	7.588	8.467	8.420	.014	2.075	1.576
3100	7.588	8.467	8.420	.014	2.075	1.576
3200	7.588	8.467	8.420	.014	2.075	1.576
3300	7.588	8.467	8.420	.014	2.075	1.576
3400	7.588	8.467	8.420	.014	2.075	1.576
3500	7.588	8.467	8.420	.014	2.075	1.576
3600	7.588	8.467	8.420	.014	2.075	1.576
3700	7.588	8.467	8.420	.014	2.075	1.576
3800	7.588	8.467	8.420	.014	2.075	1.576
3900	7.588	8.467	8.420	.014	2.075	1.576
4000	7.588	8.467	8.420	.014	2.075	1.576

Aluminum (Al)

At. Wt. = 26.9815

T, °K.	C _p	S° - (F° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f ⁰	Log K _p
0	0.000	INFINITE	1.054	77.440	INFINITE
100	6.020	33.345	1.065	74.753	-163.365
200	5.290	37.231	1.065	71.505	-76.134
298	5.112	39.304	1.065	68.300	-50.063
300	5.111	39.335	1.069	66.239	-49.710
400	5.047	40.795	1.071	65.000	-35.513
500	5.016	41.416	1.070	61.787	-27.006
600	5.002	42.039	1.071	58.402	-21.345
700	4.997	42.666	1.071	55.231	-16.293
800	4.993	43.291	1.071	52.321	-11.293
900	4.983	43.916	1.071	49.224	-6.753
1000	4.966	44.540	1.071	46.342	-1.126
1100	4.974	45.165	1.071	43.576	4.657
1200	4.974	45.790	1.071	40.835	10.408
1300	4.974	46.415	1.071	38.116	16.159
1400	4.974	47.040	1.071	35.416	21.910
1500	4.973	47.665	1.071	32.735	27.661
1600	4.974	48.290	1.071	30.073	33.412
1700	4.972	48.915	1.071	27.429	39.163
1800	4.972	49.540	1.071	24.794	44.914
1900	4.971	50.165	1.071	22.177	50.665
2000	4.971	50.790	1.071	19.573	56.416
2100	4.971	51.415	1.071	16.982	62.167
2200	4.971	52.040	1.071	14.404	67.918
2300	4.970	52.665	1.071	11.841	73.669
2400	4.970	53.290	1.071	9.294	79.420
2500	4.970	53.915	1.071	6.759	85.171
2600	4.970	54.540	1.071	4.239	90.922
2700	4.970	55.165	1.071	1.729	96.673
2800	4.970	55.790	1.071	-0.784	102.424
2900	4.971	56.415	1.071	-3.294	108.175
3000	4.971	57.040	1.071	-5.804	113.926
3100	4.971	57.665	1.071	-8.314	119.677
3200	4.972	58.290	1.071	-10.824	125.428
3300	4.973	58.915	1.071	-13.334	131.179
3400	4.975	59.540	1.071	-15.844	136.930
3500	4.977	60.165	1.071	-18.354	142.681
3600	4.979	60.790	1.071	-20.864	148.432
3700	4.982	61.415	1.071	-23.374	154.183
3800	4.986	62.040	1.071	-25.884	159.934
3900	4.991	62.665	1.071	-28.394	165.685
4000	4.996	63.290	1.071	-30.904	171.436
4100	5.002	63.915	1.071	-33.414	177.187
4200	5.010	64.540	1.071	-35.924	182.938
4300	5.019	65.165	1.071	-38.434	188.689
4400	5.029	65.790	1.071	-40.944	194.440
4500	5.041	66.415	1.071	-43.454	200.191
4600	5.055	67.040	1.071	-45.964	205.942
4700	5.071	67.665	1.071	-48.474	211.693
4800	5.086	68.290	1.071	-50.984	217.444
4900	5.106	68.915	1.071	-53.494	223.195
5000	5.130	69.540	1.071	-56.004	228.946
5100	5.154	70.165	1.071	-58.514	234.697
5200	5.161	70.790	1.071	-61.024	240.448
5300	5.211	71.415	1.071	-63.534	246.199
5400	5.244	72.040	1.071	-66.044	251.950
5500	5.260	72.665	1.071	-68.554	257.701
5600	5.319	73.290	1.071	-71.064	263.452
5700	5.361	73.915	1.071	-73.574	269.203
5800	5.406	74.540	1.071	-76.084	274.954
5900	5.456	75.165	1.071	-78.594	280.705
6000	5.506	75.790	1.071	-81.104	286.456

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965

ALUMINUM (Al)

(IDEAL GAS)

AT. WT. = 26.9815

Ground State Configuration $2p^1/2$
 $S^{\circ}_{298.15} = 39.304 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^{\circ}_f 0 = 77.44 \pm 0.9 \text{ kcal. mole}^{-1}$
 $\Delta H^{\circ}_f 298.15 = 76.0 \pm 0.9 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

ϵ_1 , cm. ⁻¹	g_1	ϵ_1 , cm. ⁻¹	g_1	ϵ_1 , cm. ⁻¹	g_1
0	2	32700	18	42200	12
112	4	37689	2	43600	20
25348	2	39930	10	44430	18
29100	12	40275	6	46130	84
		41319	14		

Heat of Formation.

The heat of sublimation of aluminum has been derived from a second and third law analysis of the vapor pressure data of several investigators; the results are tabulated below.

Ref.	Range °K.	Method	Points	ΔH°_{298} subli. kcal. mole ⁻¹	Drift cal. deg. ⁻¹ mole ⁻¹
1	1273-1473	Knudsen	10*	76.3 ± 2.3	75.32 ± 0.7
2	1734-2237	Boiling	4	83.1 ± 0.3	74.58 ± 1.8
3	1393-1468	Knudsen	10	89.8 ± 32.9	77.29 ± 3.7
4	1410-1468	Knudsen	6	71.9 ± 19.2	78.4 ± 1.3
5	1511-1723	Mass Spec	11	77.2 ± 2	70.5
6	2473	Boiling	1		77.35
7	1476	Knudsen	1		
8	1400-1611	Torsion	104	80.3 ± 1.2	79.5 ± 0.3

*1 point rejected due to failure of statistical test.

References:

- Yu. A. Prigal'kov, Yu. A. Spozhnikov and A. V. Tsyplyayeva, Izv. Akad. Nauk. SSR, Otd. Tech. Nauk. No. 1, 106 (1959).
- E. Baur and R. Brunner, Helv. Chim. Acta, **37**, 958 (1954).
- L. Brewer and A. W. Searcy, J. Am. Chem. Soc. **73**, 5308 (1951).
- Ref. 3 omitting data from TaC cells.
- R. P. Porter, P. Schissel and M. O. Inghram, J. Chem. Phys. **23**, 339 (1955).
- H. von Wartenberg, Z. Elektrochem. **19**, 482 (1913).
- L. Parkas, Z. Physik, **7**, 735 (1931).
- N. D. Potter, Philco Corporation, Newport Beach, California. Private communication Jan. 11, 1966.

It is apparent that there is little real agreement in the data; in Ref. 3 some of this is due to diffusion of liquid Al through the TaC crucibles, while Ref. 8 reports surface oxidation of the sample. The data for Ref. 5 have been reworked since they corrected their data using ΔC_p between (1) and (g) of -2 cal. deg.⁻¹ mole⁻¹, where our tables give a value of -2.62 cal. deg.⁻¹ mole⁻¹. Ref. 8 has obtained by far the largest number of data points all of which are in good agreement, show no trend and little scatter. Ref. 1 has gone to a great deal of trouble to ensure uniform heating, total collection of effluents and good Knudsen conditions and also has no trend. It is difficult to imagine why these two series differ by a factor of 3 in the pressure. An intermediate value of the heat of sublimation has been adopted at 78 ± 2 kcal. mole⁻¹. This choice is also indicated by the decomposition of AlN(c) to Al(g) and 1/2 N₂(g), which has been well established as 163.7 ± 0.8 kcal. mole⁻¹, combined with the heat of formation of AlN(c) = -78 ± 0.3 kcal. mole⁻¹, to yield $\Delta H^{\circ}_{sub} \text{ Al} = 77.7 \pm 0.9 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The electronic ground state configuration and the higher electronic levels are taken from C. E. Moore, Natl. Bur. Stds. Circular 467, "Atomic Energy Levels" Washington 1949.

Aluminum Unipositive Ion (Al⁺)
(Ideal Gas) Mol. Wt. = 26.98095

ALUMINUM UNIPOSITIVE ION (Al⁺) (IDEAL GAS) MOL. WT. = 26.98095

Ground State Configuration 1s² 2s² 2p⁶ 3s¹
ΔH_f⁰ = 215.4 ± .5 kcal/mole
ΔH_f^{298.15} = 217.3 ± .5 kcal/mole
S_{298.15}⁰ = 35.813 cal. deg.⁻¹ mole⁻¹

Electronic Levels and Quantum Weight

E _i , cm. ⁻¹	g _i	E _i , cm. ⁻¹	g _i
0.0	1	94084.5	1
37392.0	1	94146.8	3
37453.8	3	94267.7	5
37579.3	5	95348.2	1
59849.7	3	95546.8	7
85479.0	5	95547.9	5
91271.2	3	95548.8	3

Heat of Formation.
The heat of formation was calculated from the equation: Al(g) - e⁻ → Al⁺(g) with the JANAP auxiliary value for Al(g) using an I.P. = 4.627916 X 10⁴ cm.⁻¹ (136.047 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.
The electronic levels and quantum weights were obtained from C. E. Moore loc. cit. The electronic levels above 1 X 10⁵ cm.⁻¹ were omitted because their contribution is negligible below 6000°K. The H⁺-H₂₉₈²⁹⁸ value at 0°K. is -1.481 kcal/mole.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S ⁰ - (F ⁰ - H ₂₉₈ ⁰)/T cal. mole ⁻¹	H ⁰ - H ₂₉₈ ⁰ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0						
100	4.968	35.813	0.000	217.300	207.153	-151.840
200	4.968	35.813	0.000	217.307	207.090	-150.858
300	4.968	35.813	0.009	217.307	207.090	-150.858
400	4.968	35.813	0.036	217.307	207.090	-150.858
500	4.968	35.813	0.081	217.307	207.090	-150.858
600	4.968	35.813	0.136	217.307	207.090	-150.858
700	4.968	35.813	0.201	217.307	207.090	-150.858
800	4.968	35.813	0.276	217.307	207.090	-150.858
900	4.968	35.813	0.361	217.307	207.090	-150.858
1000	4.968	35.813	0.456	217.307	207.090	-150.858
1100	4.968	35.813	0.561	217.307	207.090	-150.858
1200	4.968	35.813	0.676	217.307	207.090	-150.858
1300	4.968	35.813	0.801	217.307	207.090	-150.858
1400	4.968	35.813	0.936	217.307	207.090	-150.858
1500	4.968	35.813	1.081	217.307	207.090	-150.858
1600	4.968	35.813	1.236	217.307	207.090	-150.858
1700	4.968	35.813	1.401	217.307	207.090	-150.858
1800	4.968	35.813	1.576	217.307	207.090	-150.858
1900	4.968	35.813	1.761	217.307	207.090	-150.858
2000	4.968	35.813	1.956	217.307	207.090	-150.858
2100	4.968	35.813	2.161	217.307	207.090	-150.858
2200	4.968	35.813	2.376	217.307	207.090	-150.858
2300	4.968	35.813	2.601	217.307	207.090	-150.858
2400	4.968	35.813	2.836	217.307	207.090	-150.858
2500	4.968	35.813	3.081	217.307	207.090	-150.858
2600	4.968	35.813	3.336	217.307	207.090	-150.858
2700	4.968	35.813	3.601	217.307	207.090	-150.858
2800	4.968	35.813	3.876	217.307	207.090	-150.858
2900	4.968	35.813	4.161	217.307	207.090	-150.858
3000	4.968	35.813	4.456	217.307	207.090	-150.858
3100	4.968	35.813	4.761	217.307	207.090	-150.858
3200	4.968	35.813	5.076	217.307	207.090	-150.858
3300	4.968	35.813	5.401	217.307	207.090	-150.858
3400	4.968	35.813	5.736	217.307	207.090	-150.858
3500	4.968	35.813	6.081	217.307	207.090	-150.858
3600	4.968	35.813	6.436	217.307	207.090	-150.858
3700	4.968	35.813	6.801	217.307	207.090	-150.858
3800	4.968	35.813	7.176	217.307	207.090	-150.858
3900	4.968	35.813	7.561	217.307	207.090	-150.858
4000	4.968	35.813	7.956	217.307	207.090	-150.858
4100	4.968	35.813	8.361	217.307	207.090	-150.858
4200	4.968	35.813	8.776	217.307	207.090	-150.858
4300	4.968	35.813	9.201	217.307	207.090	-150.858
4400	4.968	35.813	9.636	217.307	207.090	-150.858
4500	4.968	35.813	10.081	217.307	207.090	-150.858
4600	4.968	35.813	10.536	217.307	207.090	-150.858
4700	4.968	35.813	11.001	217.307	207.090	-150.858
4800	4.968	35.813	11.476	217.307	207.090	-150.858
4900	4.968	35.813	11.961	217.307	207.090	-150.858
5000	4.968	35.813	12.456	217.307	207.090	-150.858
5100	4.968	35.813	12.961	217.307	207.090	-150.858
5200	4.968	35.813	13.476	217.307	207.090	-150.858
5300	4.968	35.813	14.001	217.307	207.090	-150.858
5400	4.968	35.813	14.536	217.307	207.090	-150.858
5500	4.968	35.813	15.081	217.307	207.090	-150.858
5600	4.968	35.813	15.636	217.307	207.090	-150.858
5700	4.968	35.813	16.201	217.307	207.090	-150.858
5800	4.968	35.813	16.776	217.307	207.090	-150.858
5900	4.968	35.813	17.361	217.307	207.090	-150.858
6000	4.968	35.813	17.956	217.307	207.090	-150.858

June 30, 1968

Aluminum Boron Dioxide (AlBO₂)

(Ideal Gas) GFW = 69.7913

T, °K	C _p ^a	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈ kcal/mol	ΔH ^b	ΔG ^c	Log Kp
0	0.000	INFINITE	2.870	-128.809	-128.809	INFINITE
100	8.336	53.455	2.068	-128.832	-128.832	283.792
200	10.473	59.555	1.157	-129.103	-129.103	142.020
298	12.627	64.420	0.000	-129.400	-131.566	96.436
300	12.653	64.498	-0.023	-129.406	-131.574	95.851
400	14.289	68.377	1.376	-129.685	-132.253	72.260
500	15.445	71.697	2.866	-129.970	-132.862	58.074
600	16.294	74.592	4.454	-130.271	-133.413	48.596
700	16.936	77.154	6.117	-130.587	-133.912	41.809
800	17.432	79.449	7.837	-130.927	-134.365	36.707
900	17.821	81.526	9.600	-131.306	-134.773	32.727
1000	18.129	83.420	11.398	-131.723	-135.151	29.493
1100	18.377	85.160	13.224	-132.176	-135.504	26.823
1200	18.578	86.768	15.072	-132.668	-135.831	24.591
1300	18.743	88.261	16.938	-133.190	-136.132	22.697
1400	18.879	89.655	18.820	-133.746	-136.401	21.068
1500	18.993	90.962	20.713	-134.333	-136.638	19.654
1600	19.089	92.191	22.618	-134.950	-136.842	18.412
1700	19.171	93.351	24.531	-135.600	-137.015	17.313
1800	19.240	94.448	26.451	-136.280	-137.152	16.333
1900	19.300	95.490	28.379	-137.000	-137.256	15.453
2000	19.353	96.482	30.311	-137.760	-137.333	14.659
2100	19.398	97.427	32.249	-138.571	-137.393	13.939
2200	19.438	98.330	34.191	-139.420	-137.436	13.281
2300	19.473	99.195	36.136	-140.306	-137.464	12.679
2400	19.504	100.025	38.085	-141.228	-137.478	12.125
2500	19.531	100.821	40.037	-142.184	-137.478	11.605
2600	19.556	101.588	42.000	-143.174	-137.464	11.113
2700	19.578	102.326	44.000	-144.199	-137.436	10.657
2800	19.598	103.039	46.043	-145.256	-137.393	10.233
2900	19.616	103.727	48.121	-146.344	-137.333	9.833
3000	19.632	104.392	50.240	-147.464	-137.256	9.453
3100	19.647	105.036	52.399	-148.614	-137.164	9.093
3200	19.660	105.660	54.599	-149.794	-137.051	8.757
3300	19.673	106.265	56.839	-151.004	-136.913	8.443
3400	19.684	106.853	59.119	-152.244	-136.758	8.149
3500	19.694	107.423	61.449	-153.514	-136.590	7.875
3600	19.704	107.978	63.828	-154.814	-136.409	7.621
3700	19.713	108.518	66.257	-156.144	-136.213	7.377
3800	19.721	109.044	68.727	-157.504	-136.000	7.143
3900	19.728	109.557	71.239	-158.894	-135.773	6.919
4000	19.735	110.056	73.794	-160.314	-135.533	6.705
4100	19.742	110.544	76.394	-161.764	-135.280	6.491
4200	19.748	111.019	79.039	-163.244	-135.015	6.287
4300	19.753	111.484	81.729	-164.754	-134.736	6.093
4400	19.759	111.938	84.464	-166.294	-134.443	5.909
4500	19.765	112.382	87.244	-167.864	-134.136	5.731
4600	19.768	112.817	90.069	-169.464	-133.815	5.564
4700	19.772	113.242	92.939	-171.094	-133.480	5.409
4800	19.776	113.658	95.854	-172.754	-133.131	5.264
4900	19.780	114.066	98.814	-174.444	-132.768	5.129
5000	19.784	114.466	101.819	-176.164	-132.393	5.004
5100	19.787	114.858	104.869	-177.914	-132.006	4.889
5200	19.790	115.242	107.964	-179.694	-131.606	4.784
5300	19.793	115.619	111.104	-181.504	-131.193	4.689
5400	19.796	115.989	114.289	-183.344	-130.768	4.604
5500	19.799	116.352	117.519	-185.214	-130.331	4.529
5600	19.801	116.709	120.794	-187.114	-129.880	4.464
5700	19.804	117.059	124.119	-189.044	-129.415	4.409
5800	19.806	117.404	127.494	-191.004	-128.936	4.364
5900	19.808	117.742	130.919	-193.004	-128.443	4.329
6000	19.810	118.075	134.394	-195.034	-127.936	4.304

June 30, 1966

ALUMINUM BORON DIOXIDE (AlBO₂)

(IDEAL GAS)

Point Group [C_{2v}]
 $\Delta H_f^\circ = -128.8 \pm 4$ kcal/mol
 $S_{298.15}^\circ = [64.4]$ gibbs/mol
 $\Delta H_f^\circ = -129.4 \pm 4$ kcal/mol
 $\Delta H_{298.15}^\circ = -129.4 \pm 4$ kcal/mol
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
[2000](1)	[600](1)
[1000](1)	[350](1)
[600](1)	[800](1)

Bond Distances: Al-O = [1.66] Å O-B = [1.36] Å B-O = [1.20] Å
 Bond Angle: Al-O-B = [145]° O-B-O = [180]°
 Product of the Moments of Inertia: $I_A I_B I_C = [6.65357] \times 10^{-115}$ g³ cm⁶

$\sigma = 1$

Heat of Formation

The heat of formation, ΔH_f° (AlBO₂, g) = -129.4 ± 4 kcal/mol, was calculated from the heat of reaction, $\Delta H_{1500}^\circ = -14.7 \pm 3.2$ kcal/mol for $1/2 \text{ Al}_2\text{O}_3(\text{g}) + 1/2 \text{ B}_2\text{O}_3(\text{g}) = \text{AlBO}_2(\text{g})$ with all JANAF auxiliary data. The value of ΔH_{1500}° was obtained from the mass spectrometric determination of ion intensity ratios by A. Buchler, P. E. Blackburn and J. L. Stauffer, "Thermodynamics of Vaporization in the Aluminum Oxide-Boron Oxide System," ARPA Order No 315-62, Arthur D. Little, Inc., Cambridge, Mass.

Heat Capacity and Entropy

The bent molecular structure, the bond distances O-B and B-O, and the bond angle O-B-O were assumed to be the same as those in LiBO₂(g). The bond distance Al-O and the bond angle Al-O-B were estimated to be the same as those in Al₂O(g). The three principal moments of inertia are $I_A = 0.7255 \times 10^{-39}$, $I_B = 29.9238 \times 10^{-39}$, and $I_C = 30.6495 \times 10^{-39}$ g cm². The vibrational frequencies were estimated by comparison with those in LiBO₂(g), Al₂O(g), B₂O₃(g), and AlCl(g).

AlBO₂

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	INFINITE	2.287	5.337	INFINITE
100	7.225	64.631	64.496	5.597	3.371
200	8.092	53.926	58.013	5.339	2.442
298	8.509	57.246	57.246	3.600	4.417
300	8.514	57.299	57.246	3.588	4.433
400	8.710	50.778	57.583	4.266	4.059
500	8.816	61.734	58.224	4.458	4.621
600	8.881	63.347	58.948	4.673	4.580
700	8.920	65.673	60.120	4.850	4.459
800	8.959	67.671	61.058	5.322	4.459
900	8.986	69.671	61.058	5.322	4.459
1000	9.009	71.588	64.423	10.748	4.026
1100	9.028	72.176	64.889	10.748	4.026
1200	9.042	72.258	64.933	10.748	4.026
1300	9.052	72.282	64.933	10.748	4.026
1400	9.058	72.288	64.933	10.748	4.026
1500	9.062	72.290	64.933	10.748	4.026
1600	9.106	72.176	64.889	10.748	4.026
1700	9.150	72.258	64.933	10.748	4.026
1800	9.194	72.282	64.933	10.748	4.026
1900	9.146	73.744	66.157	13.396	3.842
2000	9.158	74.213	66.558	15.311	3.804
2100	9.171	74.660	66.933	15.228	3.768
2200	9.186	75.096	67.282	18.065	3.731
2300	9.196	75.496	67.622	18.065	3.703
2400	9.208	75.887	67.977	18.065	3.672
2500	9.220	76.264	68.301	19.006	3.644
2600	9.232	76.625	68.615	20.928	3.617
2700	9.244	76.974	68.919	21.752	3.591
2800	9.256	77.314	69.214	22.576	3.564
2900	9.267	77.635	69.466	23.403	3.537
3000	9.279	77.950	69.773	24.231	3.524
3100	9.291	78.254	70.042	25.059	3.503
3200	9.303	78.549	70.303	25.889	3.484
3300	9.316	78.834	70.558	26.714	3.465
3400	9.326	79.114	70.805	27.542	3.446
3500	9.338	79.385	71.046	28.370	3.427
3600	9.349	79.648	71.281	29.198	3.408
3700	9.351	79.904	71.511	30.026	3.389
3800	9.353	80.160	71.736	30.854	3.370
3900	9.354	80.416	71.956	31.682	3.351
4000	9.356	80.635	72.168	32.510	3.332
4100	9.407	80.867	72.378	34.308	3.283
4200	9.450	81.094	72.582	36.106	3.234
4300	9.493	81.314	72.782	37.904	3.185
4400	9.442	81.533	72.979	39.702	3.136
4500	9.453	81.745	73.172	41.500	3.087
4600	9.455	81.953	73.360	43.298	3.038
4700	9.457	82.158	73.546	45.096	2.989
4800	9.458	82.354	73.729	46.894	2.940
4900	9.459	82.552	73.905	48.692	2.891
5000	9.511	82.744	74.080	50.490	2.842
5100	9.522	82.933	74.252	52.288	2.793
5200	9.534	83.118	74.420	54.086	2.744
5300	9.545	83.303	74.588	55.884	2.695
5400	9.557	83.478	74.756	57.682	2.646
5500	9.568	83.653	74.910	59.480	2.597
5600	9.579	83.826	75.067	61.278	2.548
5700	9.591	83.996	75.222	63.076	2.499
5800	9.602	84.165	75.376	64.874	2.450
5900	9.614	84.337	75.525	66.672	2.401
6000	9.625	84.488	75.673	68.470	2.352

Dec. 31, 1961; Sept. 30, 1964

Electronic Levels and Quantum Weight

$$\frac{G_i}{\sigma_i}, \text{ cm.}^{-1} \frac{g_i}{1}$$

$$\omega_e x_e = 1.276 \text{ cm.}^{-1} \quad \sigma = 1$$

$$\omega_e = 0.1586 \text{ cm.}^{-1} \quad r_e = 2.295 \text{ \AA}$$

$$\omega_e = 377.40 \text{ cm.}^{-1}$$

$$B_e = 0.1586 \text{ cm.}^{-1}$$

Heat of Formation.

S. A. Semakovich, Zh. Fizik, Khim. 50, 933 (1957) measured the vapor pressure of the reaction $\text{Al(l)} + \text{NaBr(l)} \rightarrow \text{Na(g)} + \text{AlBr(g)}$ at 1175°K. By the third law method the heat of reaction (ΔH_f° , 298.15) was evaluated to be 108.31 kcal. mole⁻¹. The value of ΔH_f° 298.15 for AlBr(g) was calculated as 3.6 ± 5.0 kcal. mole⁻¹. Based on this value the dissociation energy (D_0°) was derived to be 4.3 ± 0.2 e.v. which is in excellent agreement with the value, $D_0^\circ = 4.3 \pm 0.2$ e.v., reported by A. G. Daydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The dissociation energy (D_0°) of AlBr(g) was reported to be 2.4 e.v. and 105 kcal. mole⁻¹ (4.55 e.v.) by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950 and R. P. Barrow, Trans. Faraday Soc. 56, 952 (1960), respectively. However, using these D_0° values, the corresponding values of ΔH_f° 298.15 for AlBr(g) were found to be 48.55 and -1.11 kcal. mole⁻¹. The adopted value was calculated from the vapor pressure data reported by S. A. Semakovich, loc. cit.

Heat Capacity and Entropy.

The spectroscopic constants were taken from G. Herzberg, loc. cit. and corrected to the average isotopic species.

Aluminum Boron Dioxide (AlBO₂)
(Ideal Gas) GFW = 69.7913

T, °K	Cp°	S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	-0.000	INFINITE	-2.870	-128.809	-128.809	INFINITE
100	8.336	53.455	-2.068	-128.832	-128.832	283.792
200	10.453	59.825	-1.137	-129.103	-130.789	142.920
298	12.627	64.420	-0.000	-129.400	-131.560	96.436
300	12.663	64.498	-0.023	-129.406	-131.574	95.951
400	14.448	65.926	1.866	-129.970	-132.662	58.074
500	15.445	71.697	6.596	-129.970	-132.662	58.074
600	16.294	74.592	6.454	-130.271	-133.413	48.596
700	16.936	77.154	6.117	-130.587	-133.912	41.809
800	17.432	79.459	5.653	-130.927	-134.365	36.707
900	17.822	81.482	5.082	-131.293	-134.682	32.058
1000	18.119	83.240	4.420	-131.686	-134.951	28.493
1100	18.377	85.160	3.738	-132.108	-135.176	25.482
1200	18.578	86.768	3.027	-132.557	-135.362	22.951
1300	18.749	88.053	2.290	-133.030	-135.507	20.858
1400	18.879	89.055	1.533	-133.525	-135.612	19.165
1500	18.993	90.092	77.153	-134.039	-135.682	17.812
1600	19.089	92.191	78.055	-134.570	-135.721	16.781
1700	19.171	93.351	78.921	-135.117	-135.736	15.909
1800	19.240	94.570	79.750	-135.678	-135.736	15.081
1900	19.300	95.749	80.544	-136.253	-135.716	14.295
2000	19.353	96.882	81.296	-136.840	-135.671	13.559
2100	19.398	97.977	82.070	-137.437	-135.609	12.869
2200	19.438	98.930	82.789	-138.043	-135.536	12.225
2300	19.473	99.750	83.461	-138.658	-135.456	11.625
2400	19.504	100.455	84.156	-139.282	-135.366	11.065
2500	19.531	101.051	84.807	-139.914	-135.266	10.545
2600	19.556	101.588	85.437	-140.553	-135.156	10.065
2700	19.578	102.056	86.049	-141.200	-135.036	9.625
2800	19.598	102.456	86.637	-141.854	-134.906	9.225
2900	19.616	102.797	87.221	-142.514	-134.766	8.865
3000	19.632	103.092	87.782	-143.179	-134.616	8.535
3100	19.647	103.336	88.328	-143.848	-134.456	8.235
3200	19.663	103.536	88.869	-144.520	-134.286	7.965
3300	19.679	103.695	89.406	-145.194	-134.106	7.715
3400	19.694	103.816	89.939	-145.870	-133.916	7.485
3500	19.709	103.901	90.477	-146.548	-133.716	7.265
3600	19.724	103.978	90.958	-147.228	-133.506	7.065
3700	19.739	104.028	91.438	-147.909	-133.286	6.885
3800	19.753	104.056	91.918	-148.591	-133.056	6.725
3900	19.778	104.056	92.397	-149.274	-132.816	6.585
4000	19.793	104.056	92.876	-149.958	-132.566	6.465
4100	19.742	110.544	93.106	-150.642	-132.306	6.365
4200	19.733	111.033	93.527	-151.326	-132.036	6.285
4300	19.725	111.522	93.948	-152.010	-131.756	6.215
4400	19.759	111.038	94.343	-152.694	-131.466	6.155
4500	19.763	112.382	94.739	-153.378	-131.166	6.105
4600	19.768	112.817	95.127	-154.062	-130.856	6.065
4700	19.776	113.252	95.512	-154.746	-130.536	6.035
4800	19.780	113.656	95.892	-155.430	-130.206	6.015
4900	19.780	114.066	96.269	-156.114	-129.866	6.005
5000	19.784	114.466	96.609	-156.800	-129.516	6.005
5100	19.787	114.858	96.903	-157.486	-129.156	6.015
5200	19.793	115.252	97.153	-158.172	-128.786	6.035
5300	19.793	115.656	97.310	-158.858	-128.406	6.065
5400	19.796	115.989	97.489	-159.544	-128.016	6.105
5500	19.799	116.352	97.679	-160.230	-127.616	6.155
5600	19.801	116.709	97.865	-160.916	-127.206	6.215
5700	19.804	117.066	98.056	-161.602	-126.786	6.285
5800	19.808	117.442	98.250	-162.288	-126.356	6.365
5900	19.810	117.820	98.448	-162.974	-125.916	6.465
6000	19.810	118.075	98.655	-163.660	-125.466	6.585

June 30, 1966

ALUMINUM BORON DIOXIDE (AlBO₂) (IDEAL GAS) OPW = 69.7913

Point Group [C_{2v}]
S°_{298.15} = [64.4] gibbs/mol
Ground State Quantum Weight = [1]
ΔHf°₀ = -128.8 ± 4 kcal/mol
ΔHf°_{298.15} = -129.4 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω _i , cm ⁻¹	ω _i , cm ⁻¹
[2000](1)	[600](1)
[1000](1)	[350](1)
[600](1)	[800](1)

Bond Distances: Al-O = [1.66] Å O-B = [1.36] Å B-O = [1.20] Å
Bond Angle: Al-O-B = [145]° O-B-O = [180]°
Product of the Moments of Inertia: I_AI_BI_C = [6.65357] X 10⁻¹¹⁵ g³ cm⁶

G = 1

Heat of Formation.

The heat of formation, ΔHf°₂₉₈ (AlBO₂, g) = -129.4 ± 4 kcal/mol, was calculated from the heat of reaction, ΔHf°₁₅₀₀ = -14.7 ± 3.2 kcal/mol for 1/2 Al₂O₃(g) + 1/2 B₂O₃(g) = AlBO₂(g) with all JANAP auxiliary data. The value of ΔHf°₁₅₀₀ was obtained from the mass spectrometric determination of ion intensity ratios by A. Büchler, P. E. Blackburn and J. L. Stauffer, "Thermodynamics of Vaporization in the Aluminum Oxide-Boron Oxide System," ARPA Order No 315-62, Arthur D. Little, Inc., Cambridge, Mass.

Heat Capacity and Entropy.

The bent molecular structure, the bond distances O-B and B-O, and the bond angle O-B-O were assumed to be the same as those in LiBO₂(g). The bond distance Al-O and the bond angle Al-O-(BO) were estimated to be the same as those in Al₂O(g). The three principal moments of inertia are I_A = 0.7255 X 10⁻³⁵, I_B = 29.9238 X 10⁻³⁵, and I_C = 30.6493 X 10⁻³⁵ g cm².

The vibrational frequencies were estimated by comparison with those in LiBO₂(g), Al₂O(g), B₂O₃(g), and AlCl(g).

AlBO₂

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	-0.000	INFINITE	-2.287	5.337	5.337	INFINITE
100	7.223	48.631	64.406	5.597	3.371	-
200	8.026	53.026	58.013	5.330	2.442	2.669
298	8.506	57.246	57.246	3.600	6.026	4.417
300	8.514	57.299	57.246	3.588	6.086	4.433
400	8.716	61.716	58.478	3.439	6.241	4.450
500	8.816	61.734	58.474	3.558	10.573	4.621
600	8.881	63.347	58.048	3.673	12.576	4.580
700	8.926	64.720	59.677	3.530	14.541	4.540
800	8.959	65.914	60.383	3.425	16.469	4.499
900	8.983	66.951	61.041	3.349	18.361	4.459
1000	9.009	67.819	61.697	3.297	20.235	4.378
1100	9.028	68.578	62.302	3.264	22.156	4.290
1200	9.046	69.265	62.875	3.246	24.134	4.213
1300	9.062	70.259	63.418	3.231	26.151	4.148
1400	9.077	71.502	63.922	3.220	28.201	4.092
1500	9.092	71.586	64.423	3.211	30.281	4.036
1600	9.106	72.176	64.889	3.203	32.391	3.979
1700	9.120	72.728	65.334	3.196	34.531	3.922
1800	9.133	73.250	65.767	3.190	36.701	3.865
1900	9.146	73.743	66.188	3.184	38.901	3.808
2000	9.158	74.213	66.598	3.178	41.131	3.751
2100	9.171	74.660	66.993	3.172	43.391	3.694
2200	9.183	75.087	67.374	3.166	45.681	3.637
2300	9.196	75.496	67.743	3.160	47.991	3.579
2400	9.208	75.887	68.100	3.154	50.321	3.522
2500	9.220	76.264	68.439	3.148	52.671	3.464
2600	9.232	76.625	68.765	3.142	55.041	3.407
2700	9.244	76.974	69.078	3.136	57.431	3.350
2800	9.256	77.310	69.377	3.130	59.841	3.292
2900	9.267	77.633	69.663	3.124	62.271	3.235
3000	9.279	77.945	69.935	3.118	64.721	3.178
3100	9.291	78.254	70.202	3.112	67.191	3.120
3200	9.303	78.549	70.453	3.106	69.681	3.063
3300	9.314	78.836	70.697	3.100	72.191	3.005
3400	9.326	79.114	70.934	3.094	74.721	2.948
3500	9.338	79.385	71.166	3.088	77.271	2.890
3600	9.349	79.648	71.281	3.082	79.841	2.833
3700	9.361	79.904	71.511	3.076	82.431	2.775
3800	9.372	80.154	71.735	3.070	85.041	2.718
3900	9.383	80.400	71.954	3.064	87.671	2.660
4000	9.396	80.635	72.168	3.058	90.321	2.603
4100	9.407	80.867	72.378	3.052	92.991	2.545
4200	9.419	81.094	72.582	3.046	95.681	2.488
4300	9.430	81.315	72.783	3.040	98.391	2.430
4400	9.442	81.533	72.980	3.034	101.121	2.373
4500	9.453	81.745	73.172	3.028	103.871	2.315
4600	9.465	81.953	73.360	3.022	106.641	2.258
4700	9.476	82.157	73.545	3.016	109.431	2.199
4800	9.488	82.356	73.727	3.010	112.241	2.142
4900	9.499	82.551	73.905	3.004	115.071	2.084
5000	9.511	82.744	74.080	3.000	117.921	2.026
5100	9.522	82.933	74.252	2.994	120.791	1.968
5200	9.534	83.118	74.420	2.988	123.681	1.910
5300	9.547	83.298	74.586	2.982	126.591	1.852
5400	9.559	83.474	74.748	2.976	129.521	1.794
5500	9.568	83.653	74.910	2.970	132.471	1.736
5600	9.579	83.826	75.067	2.964	135.441	1.678
5700	9.591	83.996	75.222	2.958	138.431	1.620
5800	9.602	84.162	75.375	2.952	141.441	1.562
5900	9.613	84.325	75.525	2.946	144.471	1.504
6000	9.625	84.488	75.673	2.940	147.521	1.446

Dec. 31, 1961J Sept. 30, 1964

Ground State Configuration 1Σ⁺
ΔH_f⁰ = 5.3 ± 5.0 kcal. mole⁻¹
ΔH_f⁰ 298.15 = 57.246 cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ 298.15 = 3.6 ± 5.0 kcal. mole⁻¹

Electronic Levels and Quantum Weight

ϵ_i , cm. ⁻¹	$\frac{g_i}{g_1}$
0	1

$\omega_e = 377.40$ cm.⁻¹
 $\omega_e x_e = 1.276$ cm.⁻¹
 $\sigma = 1$
 $\omega_e = 0.1586$ cm.⁻¹
 $\omega_e = 0.00849$ cm.⁻¹
 $r_e = 2.295$ Å

Heat of Formation.

S. A. Semenkovich, Zh. Prikl. Khim. 50, 933 (1957) measured the vapor pressure of the reaction $Al(1) + HgBr(1) \rightarrow Na(g) + AlBr(g)$ at 1175°K. By the third law method the heat of reaction (ΔH_f^0 298.15) was evaluated to be 108.31 kcal. mole⁻¹. The value of ΔH_f^0 298.15 for AlBr(g) was calculated as 3.6 ± 5.0 kcal. mole⁻¹. Based on this value the dissociation energy (D_0^0) was derived to be 4.3 ± 0.2 e.v. which is in excellent agreement with the value, $D_0 = 4.3 \pm 0.2$ e.v., reported by A. O. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The dissociation energy (D_0^0) of AlBr(g) was reported to be 2.4 e.v. and 105 kcal. mole⁻¹ (4.55 e.v.) by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950 and R. F. Barrow, Trans. Faraday Soc. 56, 952 (1960), respectively. However, using these D_0^0 values, the corresponding values of ΔH_f^0 298.15 for AlBr(g) were found to be 48.55 and -1.11 kcal. mole⁻¹. The adopted value was calculated from the vapor pressure data reported by S. A. Semenkovich, loc. cit.

Heat Capacity and Entropy.

The spectroscopic constants were taken from O. Herzberg, loc. cit. and corrected to the average isotopic species.

Aluminum Tribromide (AlBr₃)
(Crystal) GFW = 266.7085

AlBr₃

GFW = 266.7085

(CRYSTAL)

ALUMINUM TRIBROMIDE (AlBr₃)

$\Delta H_f^\circ = -121.4 \pm 3 \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = -126.0 \pm 3 \text{ kcal/mol}$
 $\Delta H_m^\circ = 2.69 \text{ kcal/mol}$

$S_{298.15}^\circ = 43.08 \pm 0.25 \text{ gibbs/mol}$

$T_m = 370.6^\circ\text{K}$

Heat of Formation

The value of ΔH_f° for AlBr₃(c) is that selected by the National Bureau of Standards (1). The methods and auxiliary data used to obtain their value are not given. Their result is apparently based on the heats of reaction of aqueous solutions of AlBr₃ measured by Berthelot (2).

Heat Capacity and Entropy

The heat capacity of AlBr₃(c) has been measured from 11.6° to 308.1°K by Justice (3) and the enthalpy from 337° to 367°K by Fischer (4). The heat capacities used are derived from curve fits of these data. The Cp values above 370.6°K are obtained by graphical extrapolation. Justice (3) reported the value of $S_{298}^\circ = 0.951 \text{ eu}$.

Melting Data

Fischer (4) determined the melting temperature (T_m) of AlBr₃(c). The heat of melting (ΔH_m°) is calculated from the enthalpies of AlBr₃(c) and AlBr₃(l) at the melting temperature. The enthalpy of the crystal at the melting point was determined from the curve used for the heat capacity calculations. The enthalpy of the liquid at the melting point was determined from a linear least squares fit to the enthalpy data for AlBr₃(l) reported by Fischer (4).

References

1. U. S. Natl. Bur. Std. Tech. Note 270-2, 1966.
2. M. P. E. Berthelot, Ann. Chim. Phys. (5) 13, 185 (1879).
3. B. H. Justice, The Dow Chemical Co., Midland, Michigan, Quarterly Progress Report AFRL-TR-66, 175, October, 1966, Contract AF04611-11201.
4. W. Fischer, Z. Anorg. Chem. 200, 332 (1931).

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	16.927	0.00	INFINITE	5.234	-121.355	-121.355	INFINITE
100	21.499	20.655	62.555	4.190	-121.416	-121.386	265.288
200	24.040	33.990	45.185	2.239	-121.663	-121.277	132.526
298	24.040	43.075	0.000	-0.000	-126.000	-120.553	86.368
300	24.097	43.324	43.075	-0.045	-126.016	-120.519	87.798
370.6	28.150	50.702	43.067	2.833	-126.325	-116.513	61.460
500	29.400	57.190	46.061	5.565	-135.410	-111.659	48.806
600	29.700	62.597	48.380	8.530	-134.436	-107.002	38.875
700	29.720	67.167	50.657	14.521	-133.577	-98.155	26.913
800	29.740	71.467	52.654	18.469	-132.821	-89.302	22.799
900	29.760	74.451	55.263	17.449	-131.711	-83.889	22.799
1000	29.780	77.787	57.361	20.426	-133.417	-89.546	19.570
1100	29.800	80.627	59.349	23.405	-132.550	-85.203	16.928
1200	29.820	83.220	61.232	29.386	-131.663	-80.732	15.401
1300	29.840	85.780	62.942	32.358	-129.948	-72.615	14.336
1400	29.860	87.820	64.710	32.358	-129.948	-72.615	14.336
1500	29.880	89.851	66.320	35.341	-129.082	-66.552	9.988

AlBr₃

Aluminum Tribromide (AlBr₃)

(Liquid) GFW = 266.7085

AlBr₃

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	Kcal/mol	ΔHf°	ΔGf°	Log Kp
0								
100	20.869	49.352	49.352	.000	-123.633	-120.057		88.004
200	20.869	49.352	49.352	.000	-123.633	-120.057		87.815
300	20.869	49.352	49.352	.000	-123.633	-120.057		87.626
400	20.869	49.352	49.352	.000	-123.633	-120.057		87.437
500	20.869	49.352	49.352	.000	-123.633	-120.057		87.248
600	20.869	49.352	49.352	.000	-123.633	-120.057		87.059
700	20.869	49.352	49.352	.000	-123.633	-120.057		86.870
800	20.869	49.352	49.352	.000	-123.633	-120.057		86.681
900	20.869	49.352	49.352	.000	-123.633	-120.057		86.492
1000	20.869	49.352	49.352	.000	-123.633	-120.057		86.303
1100	20.869	49.352	49.352	.000	-123.633	-120.057		86.114
1200	20.869	49.352	49.352	.000	-123.633	-120.057		85.925
1300	20.869	49.352	49.352	.000	-123.633	-120.057		85.736
1400	20.869	49.352	49.352	.000	-123.633	-120.057		85.547
1500	20.869	49.352	49.352	.000	-123.633	-120.057		85.358

ALUMINUM TRIBROMIDE (AlBr₃)

(LIQUID)

GFW = 266.7085

$$S_{298.16}^{\circ} = 49.352 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = -123.633 \pm 3 \text{ kcal/mol}$$

$$T_m = 370.6^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 2.69 \text{ kcal/mol}$$

$$T_b = 529^{\circ}\text{K (to dimer gas)}$$

$$\Delta H_v^{\circ} = 5.92 \text{ kcal/mol (to dimer gas)}$$

Heat of Formation

The heat of formation (ΔH_{298}°) of $\text{AlBr}_3(\ell)$ is calculated from ΔH_{298}° of $\text{AlBr}_3(\text{c})$ plus the heat of melting (ΔH_m°) and the enthalpy differences ($H_{370.6}^{\circ} - H_{298}^{\circ}$) of the crystal and liquid.

Heat Capacity and Entropy

Fischer (1) has measured the enthalpy of $\text{AlBr}_3(\ell)$ from 371° to 406°K. The heat capacity used is derived from a linear least squares fit to his data. The resulting constant value for the heat capacity is adopted for temperatures above 406°K. The entropy (S_{298}°) of $\text{AlBr}_3(\ell)$ was determined in a manner analogous to that for the heat of formation.

Melting Data

See $\text{AlBr}_3(\text{c})$ table for details.

Vaporization Data

The heat of vaporization (ΔH_v°) of $\text{AlBr}_3(\ell)$ is determined from the work of Fischer et al. (2). The boiling temperature (T_b) was calculated from their vapor pressure data. See $\text{Al}_2\text{Br}_6(\text{g})$ table for details.

References

1. W. Fischer, Z. Anorg. Chem., 200, 332 (1931).
2. W. Fischer, O. Rahlfs and R. B. Benze, Z. Anorg. Chem., 205, 1, (1932).

AlBr₃

Aluminum Tribromide (AlBr₃)
(Ideal Gas) GFW = 266.7085

AlBr₃

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^c	Log Kp
0	0.000	INFINITE	-	0.000	-	95.664	INFINITE
100	16.228	66.428	90.992	3.354	-95.662	-100.229	216.051
200	17.245	77.365	86.171	1.761	-94.285	-104.574	114.273
298	18.469	84.513	81.513	0.000	-101.100	-108.008	79.172
300	18.594	84.627	81.514	0.034	-101.126	-108.050	78.714
400	19.320	90.030	76.266	1.914	-101.206	-108.085	59.055
500	19.320	94.312	68.668	3.833	-112.243	-107.052	46.792
600	19.481	97.850	68.227	5.773	-112.293	-105.010	38.614
700	19.582	100.861	69.522	7.727	-112.364	-104.958	32.769
800	19.648	103.490	71.369	9.669	-112.405	-103.874	28.332
900	19.687	105.846	73.427	11.627	-112.429	-102.752	24.210
1000	19.727	107.874	75.247	13.427	-112.443	-101.532	22.190
1100	19.752	109.755	76.873	15.001	-112.454	-100.248	19.888
1200	19.771	111.475	78.287	16.377	-112.459	-98.912	17.985
1300	19.786	113.058	79.506	17.555	-112.460	-97.491	16.384
1400	19.798	114.513	80.585	18.564	-112.460	-96.004	15.004
1500	19.807	115.891	81.563	19.435	-112.460	-94.494	13.748
1600	19.815	117.170	82.435	20.194	-112.460	-92.954	12.711
1700	19.821	118.371	83.208	20.867	-112.460	-91.405	11.777
1800	19.827	119.504	83.897	21.460	-112.460	-89.849	10.926
1900	19.832	120.581	84.501	21.994	-112.460	-88.285	10.146
2000	19.835	121.613	85.026	22.478	-112.460	-86.713	9.530
2100	19.839	122.561	85.470	22.914	-112.460	-85.135	8.923
2200	19.841	123.434	85.837	23.304	-112.460	-83.550	8.369
2300	19.844	124.246	86.127	23.650	-112.460	-81.958	7.863
2400	19.846	124.999	86.341	23.964	-112.460	-80.360	7.406
2500	19.848	125.621	86.482	24.241	-112.460	-78.758	6.972
2600	19.850	126.120	86.544	24.484	-112.460	-77.152	6.576
2700	19.852	126.599	86.534	24.694	-112.460	-75.542	6.210
2800	19.853	127.051	86.451	24.869	-112.460	-73.928	5.885
2900	19.854	127.481	86.294	25.019	-112.460	-72.311	5.595
3000	19.855	127.891	86.061	25.144	-112.460	-70.691	5.330
3100	19.856	128.282	85.756	25.245	-112.460	-69.066	5.090
3200	19.857	128.657	85.381	25.324	-112.460	-67.438	4.878
3300	19.858	129.018	84.937	25.384	-112.460	-65.807	4.692
3400	19.859	129.367	84.414	25.429	-112.460	-64.173	4.530
3500	19.860	129.702	83.814	25.459	-112.460	-62.537	4.380
3600	19.860	130.021	83.133	25.474	-112.460	-60.900	4.240
3700	19.861	130.326	82.374	25.474	-112.460	-59.261	4.110
3800	19.862	130.618	81.539	25.460	-112.460	-57.619	3.990
3900	19.862	130.899	80.629	25.434	-112.460	-55.975	3.880
4000	19.863	131.169	79.644	25.400	-112.460	-54.329	3.780
4100	19.863	131.428	78.584	25.358	-112.460	-52.681	3.690
4200	19.863	131.676	77.459	25.309	-112.460	-51.032	3.610
4300	19.864	131.914	76.270	25.255	-112.460	-49.382	3.540
4400	19.864	132.142	75.026	25.197	-112.460	-47.732	3.480
4500	19.864	132.361	73.729	25.135	-112.460	-46.082	3.430
4600	19.865	132.570	72.374	25.069	-112.460	-44.432	3.390
4700	19.865	132.769	70.971	24.999	-112.460	-42.782	3.360
4800	19.865	132.958	69.519	24.925	-112.460	-41.132	3.340
4900	19.865	133.138	67.999	24.847	-112.460	-39.482	3.330
5000	19.866	133.309	66.424	24.765	-112.460	-37.832	3.330
5100	19.866	133.472	64.794	24.679	-112.460	-36.182	3.340
5200	19.866	133.627	63.114	24.589	-112.460	-34.532	3.360
5300	19.867	133.774	61.379	24.495	-112.460	-32.882	3.390
5400	19.867	133.913	59.589	24.397	-112.460	-31.232	3.430
5500	19.867	134.044	57.754	24.295	-112.460	-29.582	3.480
5600	19.867	134.168	55.874	24.189	-112.460	-27.932	3.540
5700	19.867	134.285	53.949	24.079	-112.460	-26.282	3.610
5800	19.867	134.395	51.979	23.965	-112.460	-24.632	3.690
5900	19.867	134.500	49.964	23.847	-112.460	-22.982	3.780
6000	19.868	134.600	47.914	23.725	-112.460	-21.332	3.880

Dec. 31, 1961; June 30, 1964; June 30, 1967

ALUMINUM TRIBROMIDE (AlBr₃) (IDEAL GAS)

GFW = 266.7085

ΔH₀⁰ = -95.7 ± 4 kcal/mol

ΔH_{298.15}⁰ = -101.1 ± 4 kcal/mol

Point Group {D_{3h}}

S_{298.15}⁰ = 84.5 gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[215] (1)	[100] (2)
[109] (1)	[418] (2)

σ = {6}

Bond Distance: Al-Br = [2.27] Å

Bond Angle: Br-Al-Br = [120]°

Product of the Moments of Inertia: I_{AlBr₃}⁰ = 2.16 × 10⁻¹¹¹ g² cm⁶

Heat of Formation

Fischer et al. (1) have determined the equilibrium constants for the reaction 2AlBr₃(g) = Al₂Br₆(g) from vapor density measurements. The heats of reaction are calculated from these data using both second law and third law methods. The adopted value of ΔH₂₉₈⁰ is -101.1 ± 4 kcal/mol. The results of the calculations are as follows:

Range	No. Pts.	ΔH ₂₉₈ ⁰ kcal/mol	ΔH ₂₉₈ ⁰ kcal/mol	Drift, Δu	H ₂₉₈ ⁰ kcal/mol
605-854	4	Second Law	Third Law	0.16 ± 1.33	-98.4
	7			-0.20 ± 0.67	-98.5

*Calculation based on the third law value of ΔH₂₉₈⁰

Heat Capacity and Entropy

The molecular structure of AlBr₃(g) is assumed to be the same as that of AlF₃(g). The bond distance was estimated by Heise and Wieland (2). The vibrational frequencies are estimated from the force constants of BBr₃(g) (3) and then adjusted so that the values of ΔH₂₉₈⁰ obtained by the second and third law methods are in good agreement. The principal moments of inertia are: I_A = I_B = 1.03 × 10⁻³⁷, and I_C = 2.05 × 10⁻³⁷ g cm².

References

1. W. Fischer, O. Rahlfs and B. Benze, Z. Anorg. Chem. **205**, 1 (1932).
2. M. Heise and K. Weiland, Helv. Chim. Acta **34**, 2182 (1951).
3. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945.

AlBr₃

$$\Delta H_f^\circ = -12.34 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -12.30 \pm 1.0 \text{ kcal/mol}$$

Electronic Levels and Quantum Weight				
ϵ_i , cm ⁻¹	0	24541	24615	24680
g_i	1	2	2	2
ω_e	480.0 cm ⁻¹			
$\omega_e x_e$	1.94 cm ⁻¹			
ρ_e	0.24262 cm ⁻¹			
α_e	0.00159 cm ⁻¹			
r_e	2.1298 Å			

Heat of Formation

Equilibrium constants as a function of temperature for the reaction $2\text{Al}(t) + \text{AlCl}_3(g) \rightarrow 3\text{AlCl}(g)$ have been reported by many investigators. The data were subjected to second and third law analyses with results as follows (Alr at 298.15°K refers to $2\text{Al}(c) + \text{AlCl}_3(g) \rightarrow 3\text{AlCl}(g)$):

Investigator(s)	Temp. Range °K	Number of Data Points	ΔH_f° , kcal/mol AlCl ₃	Drift eu
Rao and Dadage (1)	1125-1475	11	102.3±1.6	102.8±0.8
Frisch et al. (2)	931-1034	9	99.7±1.1	106.7±0.5
Gross et al. (3)	1225-1278	7	a	109.7±2.8
Ginsberg et al. (4)	1423-1500	8	91.4±1.8	104.7±0.8
Semenkovich (5)	1223-1473	6	89.2±0.4	98.5±1.3
Heimgartner (6)	978-1383	13	58.8±2.5	100.0±9.5
Weiss (7)	1273-1473	3	93.1±3.4	86.3±1.2
Pinchuk et al. (8)	1173-1373	3	86.0±7.5	95.0±1.9
Mitani et al. (9)	1273-1473	b	88.9	99.1±2.1
Kikuchi et al. (10)	1273-1523	b	78.7	98.7±5.0
Tanabe et al. (11)	1173-1573	b	93.3	94.6±0.5
Russell et al. (12)	1388	1	103.8	0.9

a. Temperature range too small for significant second law calculation.

b. These data available only as equations as given in Chemical Abstracts.

Unfortunately, most of the data are very discordant and of no help in defining $\Delta H_f^\circ(\text{AlCl}, g)$. The results of Rao and Dadage (1) cover a temperature range of 300°K, show good compatibility with the thermodynamic functions, are near an average of all the data, and are judged most acceptable. The third-law heat of reaction derived from their data is adopted and combined with the heat of formation of $\text{AlCl}_3(g)$ to give $\Delta H_f^\circ(298.15)(\text{AlCl}, g) = -12.30 \pm 1.0 \text{ kcal/mol}$.

Gross et al. (3) reported equilibrium constants for the reaction of aluminum with sodium chloride and potassium chloride and Pinchuk et al. (8) determined equilibrium constants for reaction of aluminum with sodium chloride and magnesium chloride. The results of Pinchuk et al. (8) are suspect in that the partial pressures of sodium and magnesium chlorides they calculate from their data exceed the saturation pressures calculated from JANAF data. The data of Gross et al. (3) were recalculated to allow for effects of dimer in sodium chloride and potassium chloride vapors (JANAF data):

Reaction	T, °K	Kp(atm) ²	$\Delta H_f^\circ(298.15)(\text{AlCl}, g)$, kcal/mol
$\text{NaCl}(g) + \text{Al}(t) \rightarrow \text{AlCl}(g) + \text{Na}(g)$	1043	4.178x10 ⁻¹⁰	109.24
$\text{NaCl}(g) + \text{Al}(t) \rightarrow \text{AlCl}(g) + \text{Na}(g)$	1243	1.138x10 ⁻⁶	102.31
$\text{KCl}(g) + \text{Al}(t) \rightarrow \text{AlCl}(g) + \text{K}(g)$	1023	5.14x10 ⁻¹¹	110.47

The result for $\text{NaCl}(s)$ is the average of 12 experiments whereas the $\text{NaCl}(t)$ and $\text{KCl}(s)$ are based on 5 and 3 experiments, respectively, and the $\text{NaCl}(s)$ value is considered the most reliable. The derived heat of formation is in good agreement with the value selected on the basis of the Rao and Dadage data.

Barrow (13) has compared thermochemical and spectroscopic dissociation energies for monohalides of B, Al, Ga, In, and Tl. A short extrapolation of vibrational levels gives $D_0 = 124.1 \text{ kcal/mol}$ for AlCl while predissociation indicates $D_0 \leq 120.1 \text{ kcal/mol}$. The maximum predissociation value gives $\Delta H_f^\circ(298.15)(\text{AlCl}, g) = -14.1 \text{ kcal/mol}$, in reasonable agreement with the selected value. Barrow (13) speculates that a potential maximum occurs in the A'' state of Alr and AlCl which causes extrapolation of vibrational levels to give erroneous heats of dissociation.

Heat Capacity and Entropy

The vibrational frequency and anharmonicity constants were taken from Herzberg (14) and the structural constants are based on microwave spectroscopy by Lide (15). The electronic levels were reported by Sharma (16).

References

1. D. Rao and V. V. Dadage, J. Phys. Chem., **70**, 1394 (1966).
2. M. A. Frisch, M. A. Greenbaum, and M. J. Plesch, J. Phys. Chem., **69**, 3001 (1965).
3. P. Gross, C. S. Campbell, P. J. C. Kent, and D. L. Levi, Discus. Faraday Soc., **4**, 206 (1948).
4. H. Ginsberg and V. Sparwald, Aluminium **41**, 219 (1965).
5. S. A. Semenkovich, Zh. Fiz. Khim., **33**, 1781 (1960).
6. P. Heimgartner, Schweiz. Arch. Angew. Wiss. Tech., **18**, 241 (1952).
7. Y. M. Pinchuk and A. B. Bakhmetev, Zh. Fiz. Khim., **34**, 214 (1960).
8. H. Mitani and H. Nagai, Nippon Kinzoku Gakkaishi, **24**, 1295 (1960).
9. T. Kikuchi, T. Kurosawa, and T. Yagihashi, Trans. Japan Inst. Metals, **2**, 71 (1964).
10. I. Tanabe, H. Konno, Y. Sawada, and T. Takahashi, Doki Inst. Metals, **122-7** (1964); CA **62**, 4957h.
11. A. P. Russell, R. E. Martin, and C. N. Cochran, J. Amer. Chem. Soc., **73**, 1466 (1951).
12. G. Herzberg, Spectra of Diatomic Molecules, 2nd ed., Van Nostrand, New York, 1950.
13. D. R. Lide, Jr., J. Chem. Phys., **42**, 1013 (1965).
14. D. Sharma, Astrophys. J., **133**, 210 (1951).

June 30, 1961; Sept. 30, 1964; June 30, 1970

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	Log Kp
0	0.000	INFINITE	INFINITE	2.228	12.337	INFINITE
100	7.057	46.141	61.455	1.531	12.094	31.222
200	7.778	51.245	58.199	1.000	12.150	16.006
298	8.263	54.435	54.435	0.000	12.300	10.574
300	8.290	54.507	54.455	-0.015	12.303	13.959
400	8.559	56.932	54.784	1.859	12.473	11.305
500	8.709	58.860	55.413	1.723	12.667	9.932
600	8.802	60.456	56.124	2.599	12.884	9.002
700	8.865	61.818	56.483	3.483	13.125	8.326
800	8.910	63.005	57.341	4.371	13.396	7.809
900	8.945	64.057	58.207	5.264	13.710	7.397
1000	8.974	65.001	58.840	6.160	14.059	7.021
1100	8.998	65.857	59.480	7.059	14.403	6.688
1200	9.016	66.641	60.008	7.940	14.721	6.406
1300	9.037	67.363	60.546	8.862	15.018	6.162
1400	9.054	68.034	61.057	9.767	15.284	5.950
1500	9.070	68.659	61.543	10.673	15.530	5.763
1600	9.085	69.245	62.007	11.581	15.765	5.597
1700	9.099	69.796	62.449	12.480	15.985	5.447
1800	9.113	70.317	62.872	13.401	16.192	5.312
1900	9.126	70.810	63.277	14.313	16.385	5.190
2000	9.139	71.278	63.665	15.226	16.568	5.078
2100	9.152	71.724	64.038	16.181	16.730	4.975
2200	9.165	72.150	64.397	17.037	16.872	4.880
2300	9.177	72.558	64.743	17.974	17.003	4.791
2400	9.190	72.949	65.077	18.892	17.126	4.709
2500	9.202	73.324	65.400	19.812	17.245	4.633
2600	9.215	73.685	65.711	20.733	17.365	4.561
2700	9.228	74.033	66.013	21.655	17.477	4.494
2800	9.242	74.369	66.306	22.578	17.586	4.430
2900	9.256	74.694	66.589	23.503	17.693	4.366
3000	9.271	75.008	66.865	24.429	17.798	4.302
3100	9.287	75.312	67.132	25.387	17.898	4.240
3200	9.304	75.607	67.393	26.327	17.992	4.178
3300	9.323	75.894	67.646	27.216	18.080	4.116
3400	9.343	76.173	67.893	28.151	18.169	4.054
3500	9.364	76.444	68.133	29.087	18.256	3.992
3600	9.386	76.708	68.368	30.024	18.342	3.930
3700	9.410	76.965	68.597	30.964	18.426	3.868
3800	9.441	77.217	68.820	31.907	18.508	3.806
3900	9.472	77.462	69.039	32.853	18.589	3.744
4000	9.504	77.703	69.252	33.802	18.670	3.682
4100	9.539	77.938	69.461	34.784	18.748	3.620
4200	9.577	78.168	69.664	35.770	18.826	3.558
4300	9.618	78.394	69.866	36.669	18.902	3.496
4400	9.661	78.615	70.062	37.633	18.978	3.434
4500	9.707	78.833	70.255	38.602	19.054	3.372
4600	9.754	79.047	70.448	39.575	19.129	3.310
4700	9.807	79.257	70.639	40.553	19.204	3.248
4800	9.862	79.464	70.811	41.536	19.278	3.186
4900	9.919	79.668	70.990	42.523	19.352	3.124
5000	9.978	79.869	71.165	43.520	19.426	3.062
5100	10.040	80.067	71.338	44.521	19.499	3.000
5200	10.105	80.261	71.512	45.526	19.572	2.938
5300	10.171	80.456	71.675	46.526	19.645	2.876
5400	10.240	80.647	71.839	47.532	19.718	2.814
5500	10.311	80.835	72.001	48.539	19.791	2.752
5600	10.384	81.022	72.160	49.545	19.864	2.690
5700	10.458	81.207	72.317	50.552	19.937	2.628
5800	10.534	81.389	72.472	51.577	19.999	2.566
5900	10.611	81.570	72.625	52.774	19.998	2.504
6000	10.689	81.749	72.775	53.839	19.971	2.442

Aluminum Monochloride Unipositive Ion (AlCl⁺)

(Ideal Gas) GFW = 62.4339

ALUMINUM MONOCHLORIDE UNIPOSITIVE ION (AlCl⁺) (IDEAL GAS) GFW = 62.4339

AlCl⁺

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal/mol	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	8.317	56.604	56.604	.000	205.000	196.777	-144.242
300	8.324	56.656	56.604	.015	205.006	196.726	-143.315
400	8.582	56.489	56.336	.862	205.336	193.917	-105.951
500	8.726	60.421	56.965	1.728	205.641	191.026	-83.497
600	8.815	62.021	57.678	2.605	205.922	188.076	-66.507
700	8.874	63.384	58.398	3.490	206.179	185.080	-57.785
800	8.918	64.572	59.097	4.380	206.405	182.050	-49.734
900	8.952	65.625	59.765	5.273	206.589	178.995	-43.466
1000	8.979	66.569	60.399	6.170	204.202	176.104	-38.487
1100	9.002	67.426	61.000	7.069	204.391	173.285	-34.429
1200	9.023	68.210	61.568	7.970	204.580	170.449	-31.043
1300	9.041	68.933	62.107	8.873	204.770	167.596	-28.175
1400	9.058	69.604	62.619	9.778	204.961	164.731	-25.716
1500	9.074	70.229	63.106	10.685	205.151	161.849	-23.581
1600	9.088	70.815	63.570	11.593	205.345	158.956	-21.712
1700	9.103	71.367	64.012	12.503	205.538	156.052	-20.062
1800	9.116	71.887	64.435	13.414	205.732	153.135	-18.593
1900	9.129	72.381	64.841	14.326	205.926	150.209	-17.278
2000	9.142	72.849	65.230	15.239	206.120	147.270	-16.093
2100	9.155	73.296	65.603	16.154	206.315	144.321	-15.020
2200	9.167	73.722	65.963	17.070	206.510	141.364	-14.043
2300	9.180	74.130	66.309	17.988	206.706	138.401	-13.151
2400	9.192	74.521	66.648	18.906	206.902	135.428	-12.332
2500	9.204	74.896	66.968	19.826	207.098	132.443	-11.578
2600	9.216	75.257	67.278	20.747	207.295	129.454	-10.882
2700	9.228	75.605	67.580	21.669	207.491	126.456	-10.236
2800	9.240	75.941	67.872	22.593	207.687	123.458	-9.638
2900	9.252	76.266	68.156	23.517	207.883	120.460	-9.080
3000	9.264	76.579	68.432	24.443	208.079	117.462	-8.569
3100	9.277	76.883	68.699	25.370	208.275	114.464	-8.051
3200	9.289	77.178	68.960	26.298	208.471	111.466	-7.533
3300	9.302	77.464	69.213	27.228	208.667	108.468	-7.040
3400	9.315	77.742	69.460	28.159	208.863	105.470	-6.568
3500	9.329	78.012	69.701	29.091	209.059	102.472	-6.108
3600	9.343	78.275	69.935	30.025	209.255	99.474	-5.656
3700	9.358	78.531	70.164	30.960	209.451	96.476	-5.214
3800	9.373	78.781	70.387	31.896	209.647	93.478	-4.782
3900	9.388	79.025	70.606	32.834	209.843	90.480	-4.358
4000	9.405	79.263	70.819	33.774	210.039	87.482	-3.944
4100	9.422	79.495	71.028	34.715	210.235	84.484	-3.532
4200	9.440	79.722	71.234	35.658	210.431	81.486	-3.120
4300	9.458	79.945	71.432	36.603	210.627	78.488	-2.708
4400	9.477	80.162	71.628	37.550	210.823	75.490	-2.296
4500	9.497	80.376	71.820	38.499	211.019	72.492	-1.884
4600	9.518	80.585	72.009	39.449	211.215	69.494	-1.472
4700	9.540	80.790	72.193	40.402	211.411	66.496	-1.060
4800	9.563	80.991	72.374	41.357	211.607	63.498	-0.648
4900	9.586	81.186	72.552	42.315	211.803	60.500	-0.236
5000	9.611	81.382	72.727	43.275	212.000	57.502	0.176
5100	9.636	81.573	72.899	44.237	212.196	54.504	0.588
5200	9.662	81.760	73.067	45.202	212.392	51.506	0.996
5300	9.688	81.944	73.233	46.169	212.588	48.508	1.404
5400	9.716	82.126	73.396	47.140	212.784	45.510	1.812
5500	9.744	82.304	73.556	48.113	212.980	42.512	2.220
5600	9.773	82.480	73.714	49.088	213.176	39.514	2.628
5700	9.803	82.653	73.869	50.067	213.372	36.516	3.036
5800	9.833	82.824	74.022	51.049	213.568	33.518	3.444
5900	9.864	82.992	74.173	52.034	213.764	30.520	3.852
6000	9.896	83.156	74.321	53.022	213.960	27.522	4.260

June 30, 1966; June 30, 1970

Ground State Configuration [2s]
S^{298.15} = [56.0 ± 0.5] gibbs/mol
ΔHf^{298.15} = 205 ± 10 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm⁻¹ g_i
[260000] 0 [2] [4]
 ω_e = [465] cm⁻¹ $\omega_e x_e$ = [2] cm⁻¹ $\sigma = 1$
 B_e = [0.2273] cm⁻¹ B_e = [0.0013] cm⁻¹ r_e = [2.2] Å

Heat of Formation

D. L. Hildenbrand, E. Murad, L. P. Theard and F. Ju, Aeronutronic Report No. U-3197, July 30, 1965, under contract AF 04(611)-10743, reported an appearance potential of 9.4 ± 0.4eV for AlCl⁺. They suggested that the magnitude of the value indicated formation by direct ionization of AlCl(g).

R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858 (1960), obtained an appearance potential of 19.7 ± 0.5eV for AlCl⁺ which they attributed to formation from AlCl(g). Assuming the process to be AlCl₃(g) + e⁻ → AlCl⁺(g) + 2Cl(g) + 2e⁻ ΔH = 454 kcal, one obtains ΔHf²⁹⁸(AlCl⁺) = 257 kcal/mol, or an ionization potential of 11.6eV. This would almost certainly represent an upper limit, since the fragments could easily contain excess kinetic energy.

We adopt the ionization potential of 9.4 ± 0.4eV obtained by Hildenbrand et al., which yields ΔHf²⁹⁸(AlCl⁺, g) = 205 ± 10 kcal/mol.

Heat Capacity and Entropy

AlCl⁺ is isoelectronic with MgCl, and the electronic configuration of the ground state and first excited state are estimated to be those for MgCl. The vibrational frequency, anharmonicity constant and bond length are estimated by comparison with those for MgCl and AlCl. The rotational constant is calculated from the bond length and atomic masses, and ω_e is calculated from the other constants assuming a Morse potential function. The enthalpy at 0°K is -2.236 kcal/mol.

AlCl⁺

Point Group C_{2v} $\Delta H_f^\circ = [-120 \pm 20] \text{ kcal. mole}^{-1}$ $\Delta H_f^\circ = [87.388] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^\circ = [-120 \pm 20] \text{ kcal. mole}^{-1}$

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

 $\omega, \text{ cm}^{-1}$

[590] (1)

[730] (1)

Bond Distances: Al-F = [1.63] Å

Bond Angle: Cl-Al-F = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.48427 \times 10^{-114}] \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The value of ΔH_f° 298.15 for AlClF(g) was calculated based on an assumption that $\Delta H_f^\circ = 0$ for the reaction $\text{AlF}_2(\text{g}) + \text{AlCl}_2(\text{g}) = 2\text{AlClF}(\text{g})$. The ΔH_f° 298.15 values for $\text{AlF}_2(\text{g})$ and $\text{AlCl}_2(\text{g})$ used for calculation are -185.0 and -75.0 kcal. mole⁻¹, respectively.

Heat Capacity and Entropy.

The vibrational frequencies were estimated to be consistent with those for $\text{AlF}_2(\text{g})$ and $\text{AlCl}_2(\text{g})$. The bond distances of Al-F and Al-Cl were estimated to be the same as those in $\text{AlF}_3(\text{g})$ and $\text{AlCl}_3(\text{g})$, respectively. The bond angle and ground state quantum weight were estimated to be consistent with those for $\text{AlF}_2(\text{g})$ molecule. The three principal moments of inertia are: $I_A = 2.41078 \times 10^{-39}$, $I_B = 2.3289 \times 10^{-39}$ and $I_C = 2.64387 \times 10^{-38} \text{ g. cm.}^2$.

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	Log K _p
0	0.000	INFINITE	INFINITE	2.870	-119.624	INFINITE
100	8.387	43.003	46.413	1.082	-119.793	131.209
200	11.566	67.388	67.388	0.000	-120.000	90.089
300	11.604	67.460	67.386	0.021	-120.004	89.347
400	12.372	70.913	67.534	1.223	-120.186	87.656
500	12.536	73.727	68.758	2.406	-120.394	84.532
600	13.126	76.095	69.787	3.785	-120.601	81.555
700	13.316	78.134	70.837	5.108	-120.830	78.774
800	13.446	79.921	71.863	6.486	-121.083	76.174
900	13.536	81.510	72.849	7.916	-121.364	73.725
1000	13.606	82.941	73.787	9.413	-121.668	71.404
1100	13.657	84.240	74.679	10.916	-121.991	69.191
1200	13.696	85.430	75.526	12.464	-122.332	67.074
1300	13.727	86.527	76.331	13.255	-122.661	65.046
1400	13.752	87.546	77.096	14.029	-122.969	63.095
1500	13.772	88.495	77.823	14.788	-123.253	61.222
1600	13.789	89.385	78.520	15.536	-123.558	59.418
1700	13.802	90.221	79.184	16.273	-123.792	57.674
1800	13.814	91.010	79.819	17.004	-124.058	56.079
1900	13.824	91.753	80.421	17.729	-124.346	54.618
2000	13.832	92.467	81.012	18.450	-124.552	53.279
2100	13.839	93.142	81.574	19.162	-124.741	52.049
2200	13.846	93.786	82.114	19.867	-124.962	50.918
2300	13.851	94.401	82.635	20.561	-125.225	49.878
2400	13.856	94.991	83.136	21.246	-125.518	48.920
2500	13.860	95.556	83.623	21.923	-125.775	48.044
2600	13.864	96.100	84.093	22.592	-126.041	47.244
2700	13.867	96.623	84.547	23.254	-126.313	46.514
2800	13.870	97.128	84.986	23.912	-126.592	45.844
2900	13.873	97.615	85.415	24.567	-126.877	45.229
3000	13.876	98.083	85.829	25.217	-127.165	44.664
3100	13.878	98.540	86.232	25.862	-127.459	44.144
3200	13.880	98.981	86.624	26.502	-127.764	43.664
3300	13.882	99.408	87.005	27.137	-128.079	43.224
3400	13.883	99.822	87.376	27.767	-128.399	42.824
3500	13.885	100.225	87.737	28.392	-128.724	42.464
3600	13.886	100.616	88.089	29.012	-129.054	42.144
3700	13.888	100.996	88.433	29.627	-129.389	41.864
3800	13.889	101.367	88.768	30.237	-129.729	41.624
3900	13.890	101.729	89.096	30.842	-130.074	41.424
4000	13.891	102.079	89.416	31.442	-130.424	41.264
4100	13.892	102.422	89.729	32.037	-130.779	41.144
4200	13.893	102.757	90.036	32.627	-131.139	41.064
4300	13.894	103.084	90.335	33.212	-131.504	41.024
4400	13.894	103.403	90.629	33.792	-131.874	41.014
4500	13.895	103.716	90.916	34.367	-132.249	41.034
4600	13.896	104.021	91.198	34.937	-132.629	41.084
4700	13.896	104.320	91.474	35.502	-133.014	41.164
4800	13.897	104.612	91.744	36.062	-133.404	41.264
4900	13.898	104.899	92.010	36.617	-133.799	41.384
5000	13.898	105.180	92.270	37.167	-134.199	41.524
5100	13.899	105.455	92.526	37.712	-134.604	41.684
5200	13.899	105.725	92.778	38.252	-135.014	41.864
5300	13.899	105.990	93.024	38.787	-135.429	42.064
5400	13.900	106.249	93.267	39.317	-135.849	42.284
5500	13.900	106.504	93.503	39.842	-136.274	42.524
5600	13.901	106.755	93.740	40.362	-136.704	42.784
5700	13.901	107.001	93.970	40.877	-137.139	43.064
5800	13.901	107.243	94.197	41.387	-137.579	43.364
5900	13.902	107.480	94.420	41.892	-138.024	43.684
6000	13.902	107.714	94.640	42.392	-138.474	44.024

Aluminum Chloride Difluoride (AlClF₂)

(Ideal Gas) Mol Wt. = 100.437

AlClF₂

MOL. WT. = 100.437

ALUMINUM CHLORIDE DIFLUORIDE (AlClF₂) (IDEAL GAS)

Point Group C_{2v}
 $\Delta H_f^\circ = [-235.8 \pm 20] \text{ kcal. mole}^{-1}$
 $S^\circ_{298.15} = [71.242] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = [-237.6 \pm 20] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ_{298.15} = [-237.6 \pm 20] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
[500] (1)	[250] (1)	
[280] (1)	[800] (1)	
[200] (1)	[900] (1)	
Bond Distances: Al-P = [1.65]Å Al-Cl = [2.14]Å		
Bond Angle: Cl-Al-P = [120]° P-Al-P = [120]°		
Product of the Moments of Inertia: I _A I _B I _C = 1.47245 X 10 ⁻¹¹³ g. ³ cm. ⁶		
Heat of Formation: $\Delta H_f^\circ = 0$ for the reaction AlCl ₃ (g) + 2AlF ₃ (g) = 3AlClF ₂ (g). The values of ΔH_f° 298.15 for AlF ₃ (g) and AlCl ₃ (g) used for calculation are -286.5 and -139.7 kcal. mole ⁻¹ , respectively.		

$\sigma^\circ = 2$

Heat Capacity and Entropy

The vibrational frequencies were estimated by comparison with those for AlF₃(g) and AlCl₃(g). The bond distances of Al-P and Al-Cl atoms were assumed to be the same as those in AlF₃(g) and AlCl₃(g), respectively. The bond angles and ground state quantum weight were estimated by comparison with those for AlF₃(g). The three principal moments of inertia are 1.28827 X 10⁻³⁸, 2.79746 X 10⁻³⁸ and 4.08573 X 10⁻³⁸ g.² cm.²

T. °K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH_f°	Log K _p
0	0.000	0.000	INFINITE	-3.531	-236.830	INFINITE
100	10.409	57.062	83.720	2.666	-236.329	516.471
200	13.670	65.385	72.616	1.446	-237.399	257.262
298	15.663	71.242	61.000	0.000	-237.600	171.837
300	15.693	71.330	61.242	0.299	-237.603	170.763
400	16.993	76.046	51.875	1.568	-237.746	127.479
500	17.816	79.933	43.109	3.412	-237.863	101.494
600	18.349	83.232	35.529	5.222	-237.976	84.163
700	18.697	86.089	28.976	7.076	-238.099	71.777
800	18.957	88.546	23.246	8.984	-238.222	62.483
900	19.134	90.847	18.076	10.865	-238.403	55.249
1000	19.266	92.871	13.286	12.785	-241.087	49.418
1100	19.366	94.712	8.1333	14.717	-241.195	44.628
1200	19.444	96.400	3.1796	16.657	-241.302	40.693
1300	19.500	97.954	-1.8138	18.600	-241.410	37.468
1400	19.544	99.406	-6.7422	20.558	-241.514	34.815
1500	19.594	100.757	-11.6747	22.515	-241.621	31.839
1600	19.627	102.023	-16.6075	24.476	-241.729	29.638
1700	19.654	103.213	-21.5441	26.441	-241.837	27.695
1800	19.677	104.346	-26.4846	28.406	-241.945	25.948
1900	19.697	105.402	-31.4284	30.376	-242.053	24.422
2000	19.714	106.413	-36.3746	32.346	-242.177	23.029
2100	19.728	107.375	-41.3233	34.319	-242.288	21.769
2200	19.753	108.273	-46.2722	36.292	-242.407	20.625
2300	19.775	109.114	-51.2211	38.262	-242.526	19.596
2400	19.792	110.011	-56.1700	40.242	-242.650	18.615
2500	19.770	110.818	-61.1189	42.219	-242.776	17.731
2600	19.778	111.594	-66.0678	44.197	-242.904	16.915
2700	19.791	112.340	-71.0167	46.175	-243.035	16.156
2800	19.800	113.060	-75.9656	48.153	-243.172	15.440
2900	19.806	113.755	-80.9145	50.133	-243.313	14.766
3000	19.801	114.426	-85.8634	52.113	-243.459	14.132
3100	19.806	115.075	-90.8123	54.093	-243.595	13.539
3200	19.811	115.704	-95.7612	56.074	-243.735	12.987
3300	19.817	116.314	-100.7101	58.054	-243.879	12.476
3400	19.817	116.905	-105.6590	60.037	-244.027	11.998
3500	19.820	117.480	-110.6079	62.019	-244.177	11.552
3600	19.823	118.038	-115.5568	64.001	-244.330	11.136
3700	19.826	118.580	-120.5057	65.984	-244.486	10.748
3800	19.828	119.110	-125.4546	67.966	-244.645	10.389
3900	19.832	119.625	-130.4035	69.949	-244.806	10.058
4000	19.832	120.127	-135.3524	71.932	-244.969	9.757
4100	19.834	120.617	-140.3013	73.915	-245.134	9.485
4200	19.836	121.094	-145.2502	75.898	-245.302	9.242
4300	19.839	121.563	-150.1991	77.882	-245.472	9.017
4400	19.843	122.018	-155.1480	79.866	-245.645	8.811
4500	19.841	122.464	-160.0969	81.850	-245.821	8.623
4600	19.842	122.900	-165.0458	83.835	-246.000	8.456
4700	19.845	123.327	-170.0000	85.820	-246.181	8.309
4800	19.847	123.747	-174.9542	87.806	-246.364	8.181
4900	19.846	124.154	-179.9084	89.788	-246.550	8.062
5000	19.847	124.554	-184.8626	91.772	-246.739	7.957
5100	19.848	124.948	-189.8168	93.757	-246.930	7.866
5200	19.850	125.333	-194.7710	95.742	-247.123	7.787
5300	19.851	125.711	-199.7252	97.727	-247.318	7.719
5400	19.851	126.082	-204.6794	99.712	-247.515	7.662
5500	19.851	126.446	-209.6336	101.697	-247.714	7.615
5600	19.852	126.804	-214.5878	103.682	-247.915	7.577
5700	19.852	127.157	-219.5420	105.667	-248.118	7.544
5800	19.853	127.503	-224.4962	107.652	-248.323	7.516
5900	19.854	127.840	-229.4504	109.637	-248.530	7.492
6000	19.855	128.174	-234.4046	111.624	-248.739	7.468

AlClF₂

Aluminum Oxide Chloride (AlOCl)

(Crystal) Mol. Wt. = 78.437

ALUMINUM OXIDE CHLORIDE (AlOCl) (CRYSTAL) MOL. WT. = 78.437

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg ⁻¹	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
100							
200							
298	13.600	13.000	-0.000	-189.600	-176.208	-176.208	129.158
300	13.650	13.084	0.025	-189.600	-176.126	-176.126	128.301
400	13.570	12.984	0.025	-189.600	-176.126	-176.126	128.301
500	16.540	20.858	14.674	-189.519	-167.201	-167.201	73.080
600	17.360	23.952	15.968	-189.089	-162.799	-162.799	59.297
700	17.970	26.676	17.307	-188.836	-158.437	-158.437	49.464
800	18.710	29.384	18.633	-188.575	-154.113	-154.113	42.100
900	19.450	32.084	20.000	-188.312	-149.836	-149.836	36.169
1000	19.940	33.273	21.157	-188.058	-145.571	-145.571	31.766
1100	19.143	35.088	22.342	-187.804	-141.316	-141.316	27.886
1200	19.290	36.760	23.475	-187.550	-137.061	-137.061	24.840
1300	19.450	38.400	24.557	-187.296	-132.806	-132.806	22.182
1400	19.610	40.000	25.599	-187.042	-128.551	-128.551	19.942
1500	19.770	41.568	26.591	-186.788	-124.296	-124.296	17.942
1600	19.930	43.100	27.529	-186.534	-120.041	-120.041	16.224
1700	19.703	43.562	28.437	-186.280	-115.786	-115.786	14.712
1800	19.783	44.024	29.307	-186.026	-111.531	-111.531	13.370
1900	19.810	44.486	30.153	-185.772	-107.276	-107.276	12.106
2000	19.829	44.948	30.983	-185.518	-103.021	-103.021	10.924
2100	19.840	45.410	31.730	-185.264	-98.766	-98.766	9.242
2200	19.850	45.872	32.479	-185.010	-94.511	-94.511	7.439
2300	19.858	46.334	33.202	-184.756	-90.256	-90.256	5.833
2400	19.865	46.796	33.925	-184.502	-86.001	-86.001	4.439
2500	19.872	47.258	34.648	-184.248	-81.746	-81.746	3.209
2600	19.879	47.720	35.371	-183.994	-77.491	-77.491	2.109
2700	19.885	48.182	36.094	-183.740	-73.236	-73.236	1.109
2800	19.890	48.644	36.817	-183.486	-68.981	-68.981	0.209
2900	19.895	49.106	37.540	-183.232	-64.726	-64.726	-0.709
3000	19.899	49.568	38.263	-182.978	-60.471	-60.471	-1.709

Mar. 31, 1964

ΔH_f^o = Unknown

ΔH_f^o 298.15 = -189.6 ± 0.3 kcal. mole⁻¹

ΔH_m^o = Unknown

S_{298.15} = [13 ± 1] cal. deg⁻¹ mole⁻¹

T_m = Unknown

T_d = [500]°K.

Heat of Formation.

The heat of formation (ΔH_f^o 298.15) for AlOCl(c) was calculated from ΔH_f^o 298 = 21.05 kcal. mole⁻¹ for the reaction AlOCl(c) + Cl₂(g) = AlCl₃(c) + 1/2 O₂(g) reported by H. Schafer, F. E. Wittig, and W. Wilborn, Z. anorg. allgem. Chem. 297, 48 (1958). This reaction is the overall reaction of the following four separate reactions.

Chemical Reaction	ΔH _f ^o 298, kcal. mole ⁻¹
AlOCl(c) + 2(HCl·299.5 H ₂ O) = AlCl ₃ ·600 H ₂ O(l)	-46.9
AlCl ₃ ·600 H ₂ O(l) = AlCl ₃ (c) + 600 H ₂ O(l)	+79.3
H ₂ (g) + Cl ₂ (g) = 2(HCl·299.5 H ₂ O)	-79.67
H ₂ O(l) = H ₂ (g) + 1/2 O ₂ (g)	+68.32
AlOCl(c) + Cl ₂ (g) = AlCl ₃ (c) + 1/2 O ₂ (g)	+21.05

Heat Capacity and Entropy.

The heat capacities for AlOCl(c) were estimated based on the assumption that ΔC_p = 0 for the reaction AlCl₃(c) + Al₂O₃(c) = 3AlOCl(c). S_{298.15} was estimated by H. Schafer, F. E. Wittig, and W. Wilborn, loc. cit.

Temperature of Decomposition.

T_d is estimated as the temperature at which the free energy change of the reaction 6AlOCl(c) → 3Al₂O₃(c) + Al₂Cl₆(g) approaches zero.

Aluminum Oxide Chloride (AlOCl)

(Ideal Gas) Mol. Wt. = 78.437

T, °K.	C _p	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	7.749	48.785	68.944	-2.726	-82.698	-82.698	INFINITE
200	10.574	55.003	61.216	-2.016	-82.800	-83.178	181.778
298	11.567	58.471	61.324	-1.403	-83.030	-83.478	81.216
300	11.589	59.471	61.324	-1.403	-83.030	-83.478	81.216
400	12.935	63.135	59.054	1.272	-83.203	-83.667	60.948
500	13.511	66.089	56.805	2.597	-83.415	-83.912	36.676
600	13.877	68.587	61.074	3.968	-83.512	-84.003	20.506
700	14.120	70.745	63.076	5.368	-83.626	-84.076	12.648
800	14.288	72.642	64.156	6.789	-83.763	-84.131	6.983
900	14.409	74.333	65.194	8.224	-83.927	-84.167	20.438
1000	14.498	75.855	66.186	9.670	-84.114	-84.186	18.357
1100	14.565	77.241	67.139	11.123	-84.329	-84.194	16.635
1200	14.617	78.512	68.025	12.582	-84.564	-84.194	15.108
1300	14.658	79.682	68.877	14.046	-84.819	-84.186	13.681
1400	14.691	80.769	69.688	15.514	-85.094	-84.167	12.336
1500	14.718	81.784	70.461	16.984	-85.386	-84.131	11.073
1600	14.740	82.734	71.139	18.457	-85.691	-84.076	9.883
1700	14.758	83.629	71.804	19.932	-86.004	-84.003	8.748
1800	14.774	84.473	72.479	21.409	-86.331	-83.912	7.663
1900	14.787	85.272	73.156	22.887	-86.671	-83.799	6.628
2000	14.798	86.031	73.848	24.366	-87.024	-83.667	5.643
2100	14.808	86.753	74.545	25.846	-87.391	-83.512	4.708
2200	14.816	87.442	75.260	27.328	-87.771	-83.333	3.823
2300	14.824	88.101	75.975	28.810	-88.164	-83.131	2.988
2400	14.830	88.732	76.611	30.292	-88.571	-82.903	2.203
2500	14.836	89.337	77.267	31.776	-89.000	-82.648	1.468
2600	14.841	89.919	77.937	33.259	-89.451	-82.367	0.783
2700	14.846	90.479	78.611	34.744	-89.924	-82.060	0.148
2800	14.850	91.019	79.288	36.229	-90.419	-81.726	-0.437
2900	14.854	91.541	79.956	37.714	-90.936	-81.367	-1.062
3000	14.857	92.044	80.627	39.199	-91.474	-80.983	-1.737
3100	14.860	92.531	81.294	40.685	-92.034	-80.574	-2.462
3200	14.863	93.003	81.945	42.171	-92.614	-80.140	-3.237
3300	14.865	93.461	82.596	43.658	-93.214	-79.681	-4.062
3400	14.867	93.904	83.247	45.144	-93.834	-79.206	-4.937
3500	14.869	94.335	83.898	46.631	-94.474	-78.716	-5.862
3600	14.871	94.754	84.549	48.118	-95.134	-78.211	-6.837
3700	14.873	95.162	85.200	49.605	-95.814	-77.691	-7.862
3800	14.875	95.558	85.851	51.093	-96.514	-77.156	-8.937
3900	14.876	95.945	86.502	52.580	-97.234	-76.606	-10.062
4000	14.878	96.321	87.153	54.068	-97.974	-76.051	-11.237
4100	14.879	96.689	87.804	55.556	-98.734	-75.486	-12.462
4200	14.880	97.047	88.456	57.044	-99.514	-74.911	-13.737
4300	14.881	97.398	89.107	58.532	-100.314	-74.326	-15.062
4400	14.882	97.740	89.758	60.020	-101.134	-73.731	-16.437
4500	14.883	98.074	90.409	61.508	-101.974	-73.126	-17.862
4600	14.884	98.401	91.060	62.997	-102.834	-72.511	-19.337
4700	14.885	98.721	91.711	64.485	-103.714	-71.886	-20.862
4800	14.886	99.035	92.362	65.974	-104.614	-71.251	-22.437
4900	14.887	99.342	93.013	67.462	-105.534	-70.606	-24.062
5000	14.887	99.642	93.664	68.951	-106.474	-70.001	-25.737
5100	14.888	99.937	94.315	70.440	-107.434	-69.386	-27.462
5200	14.889	100.226	94.966	71.929	-108.414	-68.761	-29.237
5300	14.890	100.510	95.617	73.417	-109.414	-68.126	-31.062
5400	14.890	100.788	96.268	74.906	-110.434	-67.481	-32.937
5500	14.890	101.062	96.919	76.395	-111.474	-66.826	-34.862
5600	14.891	101.330	97.570	77.884	-112.534	-66.161	-36.837
5700	14.891	101.593	98.221	79.374	-113.614	-65.486	-38.862
5800	14.892	101.852	98.872	80.863	-114.714	-64.801	-40.937
5900	14.892	102.107	99.523	82.352	-115.834	-64.106	-43.062
6000	14.892	102.357	100.174	83.841	-116.974	-63.401	-45.237

Dec. 31, 1980; Sept. 30, 1964

AlOCl

MOL. WT. = 78.437

(IDEAL GAS)

Point Group C_{2v}
 $\Delta H_f^0 = [-82.7 \pm 5.0] \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = [-83.2 \pm 5.0] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm.⁻¹
 (450) (1)
 (350) (2)
 (900) (1)

Bond Distance: O-Al = [1.62] Å Al-Cl = [2.14] Å
 Bond Angle: O-Al-Cl = 180°
 Rotational Constant: B₀ = [0.097703] cm.⁻¹
 $\sigma^- = 1$

Heat of Formation.

The free energy change of the reaction $1/3 \text{ Al}_2\text{O}_3(\text{s}) + 1/3 \text{ AlCl}_3(\text{g}) = \text{AlOCl}(\text{g})$, $\Delta G^\circ_{2400^\circ\text{K.}} = 28 \pm 3 \text{ kcal. mole}^{-1}$, has been determined by M. A. Greenbaum, et al., Marenton Corporation, California, private communication, August 26, 1984. Incorporating appropriate auxiliary data the heat of reaction was derived to be 82.9 kcal. mole⁻¹, yielding $\Delta H_f^{298.15} = -83.2 \pm 5 \text{ kcal. mole}^{-1}$ for AlOCl(g).

Heat Capacity and Entropy.

Point group, ground state quantum weight and vibrational frequencies were obtained from J. Hilsenrath, W. H. Evans and H. M. Woolley, National Bureau of Standards Report 8484, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum and Their Compounds with Hydrogen, Oxygen, Nitrogen, Fluorine and Chlorine", July 1, 1959. The bond distances of $\text{F}_2\text{O-Al}$ and $\text{F}_2\text{O-Cl}$ were assumed to be the same as those in $\text{AlO}(\text{g})$ and $\text{AlCl}(\text{g})$ molecules, respectively. The three principal moments of inertia are: $I_A = 0$ and $I_B = I_C = 2.86467 \times 10^{-38} \text{ g. cm}^2$.

AlOCl

Aluminum Dichloride (AlCl₂)
(Ideal Gas) Mol. Wt. = 97.894

MOL. WT. = 97.894

(IDEAL GAS)

ALUMINUM DICHLORIDE (AlCl₂)

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	(H° - H° ₂₉₈)/T	ΔH _f ⁰	ΔH _f ⁰	Log K _p
0	0.000	0.000	INFINITE	2.012	- 74.724	- 74.724	INFINITE
100	9.134	57.108	78.936	2.183	- 74.702	- 75.720	105.497
200	11.016	68.815	88.815	1.861	- 74.843	- 76.719	83.850
298	12.571	75.461	95.461	1.600	- 75.000	- 77.611	50.888
300	12.356	68.892	88.815	1.291	- 75.003	- 77.628	56.549
400	12.943	72.536	92.536	1.291	- 75.162	- 78.478	42.876
500	13.260	75.461	95.461	2.003	- 75.330	- 79.287	34.055
600	13.444	77.897	97.897	3.238	- 75.510	- 80.062	29.141
700	13.554	79.079	99.079	5.280	- 75.733	- 80.803	25.227
800	13.642	81.796	101.796	8.650	- 75.975	- 81.512	22.267
900	13.697	83.406	103.406	12.468	- 76.245	- 82.186	19.057
1000	13.737	84.851	104.851	16.859	- 76.539	- 82.847	16.062
1100	13.766	86.162	106.162	21.764	- 76.861	- 83.507	13.489
1200	13.789	87.351	107.351	27.242	- 77.214	- 84.175	11.269
1300	13.807	88.445	108.445	33.222	- 77.605	- 84.833	9.331
1400	13.821	89.489	109.489	39.684	- 78.028	- 85.483	7.843
1500	13.832	90.443	110.443	46.585	- 78.481	- 86.128	6.753
1600	13.842	91.336	111.336	53.922	- 78.965	- 86.761	5.908
1700	13.850	92.175	112.175	61.697	- 79.480	- 87.380	5.218
1800	13.856	92.967	112.967	69.912	- 80.025	- 87.983	4.677
1900	13.862	93.716	113.716	78.567	- 80.600	- 88.570	4.237
2000	13.866	94.428	114.428	87.661	- 81.204	- 89.143	3.870
2100	13.871	95.104	115.104	97.193	- 81.839	- 89.693	3.571
2200	13.874	95.750	115.750	107.161	- 82.500	- 90.220	3.326
2300	13.877	96.366	116.366	117.564	- 83.187	- 90.729	3.127
2400	13.880	96.957	116.957	128.401	- 83.900	- 91.216	2.969
2500	13.882	97.524	117.524	139.661	- 84.639	- 91.683	2.843
2600	13.885	98.068	118.068	151.346	- 85.400	- 92.128	2.747
2700	13.886	98.592	118.592	163.461	- 86.183	- 92.550	2.677
2800	13.888	99.097	119.097	176.007	- 87.000	- 92.950	2.626
2900	13.890	99.585	119.585	189.984	- 87.850	- 93.328	2.590
3000	13.891	100.056	120.056	205.393	- 88.733	- 93.683	2.566
3100	13.892	100.511	120.511	222.236	- 89.643	- 94.016	2.552
3200	13.893	100.952	120.952	240.514	- 90.579	- 94.328	2.547
3300	13.894	101.380	121.380	260.236	- 91.540	- 94.619	2.550
3400	13.895	101.794	121.794	281.401	- 92.526	- 94.890	2.561
3500	13.896	102.197	122.197	304.007	- 93.539	- 95.140	2.576
3600	13.897	102.589	122.589	328.061	- 94.579	- 95.370	2.595
3700	13.898	102.970	122.970	353.561	- 95.643	- 95.580	2.618
3800	13.898	103.340	123.340	380.514	- 96.733	- 95.769	2.645
3900	13.899	103.701	123.701	408.929	- 97.848	- 95.936	2.676
4000	13.900	104.053	124.053	438.804	- 98.989	- 96.083	2.711
4100	13.900	104.396	124.396	469.149	- 100.156	- 96.210	2.750
4200	13.901	104.731	124.731	500.064	- 101.349	- 96.320	2.792
4300	13.901	105.058	125.058	531.549	- 102.569	- 96.414	2.838
4400	13.902	105.378	125.378	563.594	- 103.816	- 96.493	2.888
4500	13.902	105.690	125.690	596.199	- 105.089	- 96.558	2.942
4600	13.902	105.994	125.994	629.364	- 106.389	- 96.608	2.999
4700	13.903	106.295	126.295	663.089	- 107.714	- 96.645	3.059
4800	13.903	106.588	126.588	697.374	- 109.064	- 96.669	3.122
4900	13.903	106.874	126.874	732.219	- 110.439	- 96.680	3.188
5000	13.904	107.155	127.155	767.614	- 111.839	- 96.680	3.256
5100	13.904	107.431	127.431	803.559	- 113.264	- 96.669	3.326
5200	13.904	107.701	127.701	840.054	- 114.714	- 96.645	3.398
5300	13.904	107.965	127.965	877.109	- 116.189	- 96.608	3.472
5400	13.905	108.225	128.225	914.724	- 117.689	- 96.558	3.548
5500	13.905	108.480	128.480	952.899	- 119.214	- 96.493	3.626
5600	13.905	108.731	128.731	991.634	- 120.764	- 96.414	3.706
5700	13.905	108.977	128.977	1030.929	- 122.339	- 96.320	3.788
5800	13.906	109.219	129.219	1070.784	- 123.939	- 96.210	3.872
5900	13.906	109.457	129.457	1111.199	- 125.564	- 96.083	3.958
6000	13.906	109.690	129.690	1152.174	- 127.214	- 95.936	4.046

June 30, 1961/ Sept. 30, 1964

Point Group C_{2v}

ΔH_f⁰ = [-75 ± 20] kcal. mole⁻¹

ΔH_f⁰ 298.15 = [-75 ± 20] kcal. mole⁻¹

S_{298.15} = [68.815] cal. deg⁻¹ mole⁻¹

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	[430] (1)	[210] (1)	[540] (1)
298.15			

Bond Distance: Al-Cl = [2.14] Å

Bond Angle: Cl-Al-Cl = [120]°

Product of the Moments of Inertia: I_AI_BI_C = [6.62845 X 10⁻¹¹⁴] g.³ cm.⁶

Heat of Formation.

The value of ΔH_f⁰ 298.15 for AlCl₂(g) was calculated based on an assumption that ΔH_f⁰ = 0 for the reaction AlCl(g) + AlCl₃(g) = 2AlCl₂(g). The values of ΔH_f⁰ 298.15 for AlCl(g) and AlCl₃(g) used for calculation are -11.2 and -139.7 kcal. mole⁻¹, respectively.

Heat Capacity and Entropies.

The vibrational frequencies were calculated by valence force field method described by O. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950, using force constants, k₁ = 2.05 X 10⁵ and k_f/12 = 0.25 X 10⁵ dynes/cm., estimated from those for AlCl(g) and other similar compounds. The bond distance was assumed to be the same as that for AlCl(g). The bond angle and ground state quantum weight were estimated to be consistent with those for AlF₂(g). The three principal moments of inertia are I_A = 4.04243 X 10⁻³⁶, I_B = 3.7149 X 10⁻³⁹ and I_C = 4.41392 X 10⁻³⁸ g. cm.²

Aluminum Dichloride Unipositive Ion (AlCl₂⁺)

(Ideal Gas) GFW = 97.887

T, °K	Cp ^o	S ^o - (C ^o - H ^o)/T	H ^o - H ²⁹⁸	ΔH ^o	ΔG ^o	Log Kp
100						
200						
298	13.255	62.959	4.000	110.000	107.648	78.908
300	13.270	63.041	4.025	110.008	107.633	78.410
400	13.862	64.451	1.385	110.436	106.777	76.340
500	14.214	65.688	2.792	110.856	105.814	74.251
600	14.410	66.698	4.224	111.267	104.767	72.162
700	14.534	67.430	5.671	111.637	103.655	70.069
800	14.617	67.876	7.139	111.969	102.460	67.999
900	14.675	68.001	8.594	112.269	101.284	65.959
1000	14.716	68.150	10.064	112.539	100.128	63.905
1100	14.746	68.254	11.537	112.783	98.992	61.846
1200	14.773	68.339	13.013	113.000	97.877	59.786
1300	14.792	68.402	14.492	113.198	96.781	57.726
1400	14.808	68.451	15.972	113.368	95.701	55.666
1500	14.820	68.491	17.453	113.512	94.636	53.606
1600	14.830	68.523	18.936	113.633	93.586	51.546
1700	14.838	68.548	20.419	113.740	92.551	49.486
1800	14.845	68.568	21.903	113.834	91.531	47.426
1900	14.851	68.584	23.388	113.916	90.526	45.366
2000	14.856	68.600	24.873	113.987	89.536	43.306
2100	14.861	68.615	26.359	114.047	88.561	41.246
2200	14.864	68.628	27.846	114.096	87.601	39.186
2300	14.868	68.640	29.332	114.134	86.656	37.126
2400	14.871	68.650	30.819	114.162	85.726	35.066
2500	14.873	68.659	32.306	114.181	84.811	33.006
2600	14.875	68.667	33.794	114.191	83.911	30.946
2700	14.876	68.672	35.281	114.194	83.026	28.886
2800	14.879	68.675	36.768	114.191	82.156	26.826
2900	14.881	68.678	38.255	114.184	81.301	24.766
3000	14.883	68.680	39.745	114.172	80.461	22.706
3100	14.884	68.682	41.234	114.156	79.636	20.646
3200	14.885	68.684	42.722	114.136	78.826	18.586
3300	14.886	68.686	44.211	114.112	78.031	16.526
3400	14.887	68.688	45.699	114.084	77.251	14.466
3500	14.888	68.690	47.188	114.052	76.486	12.406
3600	14.889	68.691	48.677	114.016	75.736	10.346
3700	14.890	68.692	50.166	113.976	75.001	8.286
3800	14.891	68.693	51.655	113.932	74.281	6.226
3900	14.891	68.694	53.144	113.884	73.576	4.166
4000	14.892	68.695	54.633	113.832	72.886	2.106
4100	14.892	68.696	56.123	113.776	72.211	0.046
4200	14.893	68.697	57.612	113.716	71.551	-1.914
4300	14.893	68.698	59.101	113.652	70.906	-3.854
4400	14.894	68.699	60.590	113.584	70.276	-5.794
4500	14.894	68.700	62.080	113.512	69.661	-7.734
4600	14.895	68.701	63.571	113.436	69.061	-9.674
4700	14.895	68.702	65.062	113.356	68.476	-11.614
4800	14.895	68.703	66.554	113.272	67.906	-13.554
4900	14.896	68.704	68.046	113.184	67.351	-15.494
5000	14.896	68.705	69.539	113.092	66.811	-17.434
5100	14.896	68.706	71.034	113.000	66.286	-19.374
5200	14.897	68.707	72.529	112.908	65.776	-21.314
5300	14.897	68.708	74.024	112.816	65.281	-23.254
5400	14.897	68.709	75.519	112.724	64.791	-25.194
5500	14.897	68.710	77.014	112.632	64.316	-27.134
5600	14.898	68.711	78.509	112.540	63.856	-29.074
5700	14.898	68.712	80.004	112.448	63.411	-31.014
5800	14.898	68.713	81.499	112.356	62.981	-32.954
5900	14.898	68.714	83.000	112.264	62.566	-34.894
6000	14.898	68.715	84.495	112.172	62.166	-36.834

June 30, 1968



GFW = 97.887

(IDEAL GAS)

ALUMINUM DICHLORIDE UNIPOSITIVE ION (AlCl₂⁺)

Point Group [D_{2h}]

ΔH_f^o = [110 ± 40] kcal/mol

S_{298.15} = [63 ± 2] gibbs/mol

ΔH_f^o = [110 ± 40] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm⁻¹
[590] (1)
[180] (2)
[380] (1)

Bond Distance: Al-Cl = [2.17] Å

Bond Angle: Cl-Al-Cl = [180°]

Rotational Constant: B₀ = [0.0505] cm⁻¹

Heat of Formation

R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858 (1960), reported an appearance potential of 13.4 ± 0.5eV (309 ± 12 kcal) for AlCl₂⁺; they indicated that AlCl₂(g) was the probable parent molecule. Assuming the formation reaction to be AlCl₃ + e⁻ → AlCl₂⁺ + Cl + 2 e⁻, we obtain ΔH_f^o(AlCl₂⁺, g) = 140 kcal/mol or an ionization potential of 215 kcal or 9.3eV.

Since there is a possibility of the fragments containing excess kinetic energy, the ionization potential represents an upper limit to the true value. A comparison of the ionization potentials of BF₂ and BCl₂ indicates that the chloride is lower by 1eV per atom; on this basis we would obtain an ionization potential of 7eV using the value for AlF₂ of 9eV.

The National Bureau of Standards Report No. 6628, Jan. 1, 1965, gives an estimate of 8 ± 1eV (185 ± 25 kcal); we adopt this value as being representative of the probable range of values. The adopted ionization potential yields ΔH_f^o(AlCl₂⁺, g) = 110 ± 40 kcal/mol in conjunction with ΔH_f^o(AlCl₃, g) = -75 ± 20 kcal/mol.

Heat Capacity and Entropy

AlCl₂⁺ is isoelectronic with MgCl₂ and on this basis we assume the ground state to be singlet and linear in accordance with the predictions of A. D. Walsh, J. Chem. Soc. 2768 (1953). The vibrational frequencies are estimated to lie between those for AlCl₂ and MgCl₂. The bond length is estimated as the sum of the covalent radii of the atoms.

The enthalpy at 0°K is -3.128 kcal/mol.



Aluminum Dichloride Uninegative Ion (AlCl₂⁻)

(Ideal Gas) GFW = 97.888

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
100						
200						
298	12.289	67.441	67.441	0.000	- 80.714	59.165
300	12.304	67.517	67.442	0.023	- 80.719	59.403
400	12.906	71.149	67.933	1.286	- 80.854	44.177
500	13.233	74.067	68.877	2.595	- 81.347	35.327
600	13.426	76.498	69.950	3.929	- 82.038	29.377
700	13.548	78.578	71.038	5.278	- 82.748	25.091
800	13.629	80.392	72.056	6.637	- 83.489	21.848
900	13.687	82.001	73.109	8.003	- 84.272	19.302
1000	13.728	83.445	74.072	9.374	- 85.095	17.206
1100	13.759	84.755	74.884	10.748	- 85.954	15.458
1200	13.783	85.954	75.549	12.125	- 86.847	13.988
1300	13.801	87.058	76.070	13.504	- 87.773	12.733
1400	13.816	88.081	76.485	14.885	- 88.739	11.649
1500	13.828	89.035	76.790	16.268	- 89.739	10.700
1600	13.838	89.927	78.997	17.651	- 90.769	9.863
1700	13.846	90.767	79.569	19.035	- 91.830	9.119
1800	13.853	91.558	80.214	20.420	- 92.923	8.451
1900	13.859	92.307	80.831	21.806	- 94.048	7.849
2000	13.864	93.018	81.422	23.192	- 95.207	7.302
2100	13.868	93.695	81.991	24.578	- 96.412	6.804
2200	13.872	94.340	82.538	25.945	- 97.659	6.347
2300	13.875	94.957	83.064	27.333	- 98.944	5.926
2400	13.878	95.547	83.572	28.740	- 100.268	5.537
2500	13.880	96.114	84.063	30.128	- 101.630	5.177
2600	13.883	96.658	84.537	31.516	- 103.035	4.841
2700	13.885	97.182	84.995	32.905	- 104.478	4.529
2800	13.888	97.687	85.440	34.293	- 105.959	4.241
2900	13.889	98.175	85.870	35.682	- 107.478	3.976
3000	13.890	98.645	86.288	37.071	- 109.035	3.737
3100	13.891	99.101	86.694	38.460	- 110.630	3.522
3200	13.892	99.542	87.089	39.849	- 112.263	3.331
3300	13.893	99.969	87.473	41.238	- 113.935	3.161
3400	13.894	100.384	87.847	42.628	- 115.646	3.011
3500	13.895	100.787	88.211	44.017	- 117.396	2.879
3600	13.896	101.178	88.565	45.407	- 119.185	2.764
3700	13.897	101.559	88.911	46.796	- 121.013	2.667
3800	13.897	101.930	89.249	48.186	- 122.880	2.585
3900	13.898	102.291	89.579	49.576	- 124.785	2.515
4000	13.898	102.643	89.901	50.966	- 126.729	2.455
4100	13.899	102.986	90.216	52.355	- 128.712	2.403
4200	13.900	103.321	90.524	53.745	- 130.734	2.359
4300	13.900	103.648	90.826	55.135	- 132.795	2.324
4400	13.901	103.967	91.121	56.525	- 134.896	2.297
4500	13.901	104.280	91.411	57.915	- 137.036	2.276
4600	13.901	104.585	91.693	59.306	- 139.214	2.260
4700	13.902	104.884	91.970	60.696	- 141.430	2.248
4800	13.902	105.177	92.242	62.086	- 143.684	2.240
4900	13.902	105.464	92.509	63.476	- 145.976	2.234
5000	13.903	105.745	92.771	64.866	- 148.306	2.231
5100	13.903	106.020	93.028	66.257	- 150.674	2.230
5200	13.903	106.290	93.281	67.647	- 153.080	2.230
5300	13.904	106.555	93.529	69.037	- 155.524	2.230
5400	13.904	106.815	93.772	70.428	- 158.006	2.230
5500	13.904	107.070	94.012	71.818	- 160.526	2.230
5600	13.904	107.320	94.247	73.208	- 163.084	2.230
5700	13.904	107.566	94.479	74.599	- 165.680	2.230
5800	13.905	107.808	94.706	75.989	- 168.314	2.230
5900	13.905	108.046	94.931	77.380	- 170.986	2.230
6000	13.905	108.279	95.151	78.770	- 173.696	2.230

June 30, 1968

ALUMINUM DICHLORIDE UNINEGATIVE ION (AlCl₂⁻)

(IDEAL GAS)

GFW = 97.888

Point Group [C_{2v}]

ΔH_f^o = [-80 ± 40] kcal/mol

S_{298,15}^o = [67.4 ± 0.5] gibbs/mol

ΔH_f_{298,15}^o = [-80 ± 40] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\frac{\omega}{\text{cm}^{-1}}$	
[550] (1)	
[200] (1)	
[450] (1)	

Bond Distance: Al-Cl = [2.14] Å

Bond Angle: Cl-Al-Cl = [120°] σ = 2

Product of the Moments of Inertia: I_AI_BI_C = [6.634 × 10⁻⁴⁴] g³ cm⁶

Heat of Formation

AlCl₂⁻ is isoelectronic with SiCl₂ and an estimate of its heat of formation may be obtained by assuming the binding energy to be the same in the two molecules. This leads to ΔH_f^o₂₉₈(AlCl₂⁻, g) = -80 kcal/mol or an electron affinity of 5 kcal. An alternative route assumes that the heat of reaction is identical for the processes AlCl₃(g) + AlCl₂⁻(g) + Cl⁺(g) and AlCl(g) + Al⁺(g) + Cl⁺(g). Using the electron affinity of Al(g) given in National Bureau of Standards Report No. 8628, Jan. 1, 1965, we obtain ΔH_f^o₂₉₈(AlCl₂⁻, g) = -63 kcal/mol or an electron affinity of -12 kcal. In addition, using the correlation diagrams of A. D. Walsh, J. Chem. Soc. 2266 (1953), the electron must go into a non-bonding orbital; thus the binding energy should be close to that of AlCl₂. The dissociation energy of AlCl₂ is 211 kcal which leads to ΔH_f^o₂₉₈(AlCl₂⁻, g) = -87 kcal/mol or an electron affinity of 12 kcal. We adopt an intermediate value for the electron affinity of 5 ± 20 kcal/mol, or ΔH_f^o₂₉₈(AlCl₂⁻, g) = -80 ± 40 kcal/mol using ΔH_f₂₉₈(AlCl₂, g) = -75 ± 20 kcal/mol.

Heat Capacity and Entropy

As noted earlier, AlCl₂⁻ is isoelectronic with SiCl₂ and with 18 valence electrons, should be definitely bent according to the correlation scheme of A. D. Walsh, loc. cit. The vibrational frequencies are estimated to lie between those of SiCl₂ and AlCl₂. The bond length and angle are estimated as equal to those for AlCl₂(g). By analogy with SiF₂ (see G. Herzberg "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Company Inc., New York, 1966) we do not expect any low lying electronic levels. The enthalpy at 0°K is -3.006 kcal/mol. The three principal moments of inertia are: I_A = 3.7155 × 10⁻⁴⁹, I_B = 4.0430 × 10⁻⁴⁹, and I_C = 4.4154 × 10⁻⁴⁸ g cm².

AlCl₂⁻

Aluminum Dichloride Fluoride (AlCl₂F)

(Ideal Gas) Mol. Wt. = 116.894

T, °K.	C _p ^o	S ^o - (F ^o -H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	3.734	-187.991	-187.991	INFINITE	
100	11.238	59.274	7.828	-188.240	-187.449	409.849	
200	16.410	74.356	7.828	-188.400	-187.449	409.849	
298	16.410	74.356	7.828	-188.400	-187.449	136.072	
300	16.438	74.457	7.828	-188.403	-187.449	135.219	
400	17.582	79.357	7.828	-188.709	-187.449	100.862	
500	18.269	83.361	7.828	-188.797	-187.449	80.236	
600	18.700	86.732	7.828	-188.888	-187.449	66.481	
700	18.982	89.638	7.828	-188.993	-187.449	56.651	
800	19.176	92.186	7.828	-189.120	-187.449	49.273	
900	19.314	94.453	7.828	-189.270	-187.449	43.530	
1000	19.415	96.493	7.828	-189.442	-187.449	38.892	
1100	19.491	98.347	7.828	-189.632	-187.449	35.078	
1200	19.550	100.046	7.828	-189.842	-187.449	31.898	
1300	19.596	101.613	7.828	-189.993	-187.449	29.206	
1400	19.633	103.066	7.828	-190.120	-187.449	26.897	
1500	19.664	104.422	7.828	-190.224	-187.449	24.895	
1600	19.688	105.692	7.828	-190.322	-187.449	23.142	
1700	19.709	106.886	7.828	-190.420	-187.449	21.595	
1800	19.727	108.013	7.828	-190.520	-187.449	20.219	
1900	19.741	109.080	7.828	-190.621	-187.449	18.987	
2000	19.754	110.093	7.828	-190.725	-187.449	17.878	
2100	19.765	111.057	7.828	-190.832	-187.449	16.874	
2200	19.774	111.977	7.828	-190.942	-187.449	15.961	
2300	19.783	112.856	7.828	-191.056	-187.449	15.126	
2400	19.790	113.698	7.828	-191.174	-187.449	14.361	
2500	19.796	114.506	7.828	-191.295	-187.449	13.656	
2600	19.802	115.282	7.828	-191.419	-187.449	13.006	
2700	19.807	116.030	7.828	-191.546	-187.449	12.403	
2800	19.812	116.750	7.828	-191.675	-187.449	11.844	
2900	19.816	117.446	7.828	-191.806	-187.449	11.321	
3000	19.820	118.117	7.828	-191.938	-187.449	10.836	
3100	19.823	118.767	7.828	-192.071	-187.449	10.388	
3200	19.826	119.397	7.828	-192.206	-187.449	9.974	
3300	19.829	120.007	7.828	-192.342	-187.449	9.593	
3400	19.831	120.599	7.828	-192.479	-187.449	9.243	
3500	19.834	121.174	7.828	-192.617	-187.449	8.923	
3600	19.836	121.733	7.828	-192.756	-187.449	8.632	
3700	19.838	122.276	7.828	-192.896	-187.449	8.370	
3800	19.839	122.805	7.828	-193.037	-187.449	8.136	
3900	19.841	123.320	7.828	-193.179	-187.449	7.928	
4000	19.843	123.823	7.828	-193.322	-187.449	7.743	
4100	19.844	124.313	7.828	-193.466	-187.449	7.580	
4200	19.845	124.791	7.828	-193.611	-187.449	7.436	
4300	19.847	125.258	7.828	-193.756	-187.449	7.311	
4400	19.848	125.714	7.828	-193.902	-187.449	7.203	
4500	19.849	126.160	7.828	-194.048	-187.449	7.110	
4600	19.850	126.597	7.828	-194.194	-187.449	7.031	
4700	19.851	127.024	7.828	-194.341	-187.449	6.965	
4800	19.852	127.441	7.828	-194.488	-187.449	6.911	
4900	19.853	127.851	7.828	-194.635	-187.449	6.867	
5000	19.853	128.252	7.828	-194.782	-187.449	6.832	
5100	19.854	128.645	7.828	-194.929	-187.449	6.806	
5200	19.855	129.031	7.828	-195.076	-187.449	6.787	
5300	19.856	129.409	7.828	-195.223	-187.449	6.773	
5400	19.856	129.780	7.828	-195.370	-187.449	6.763	
5500	19.857	130.144	7.828	-195.517	-187.449	6.756	
5600	19.857	130.502	7.828	-195.664	-187.449	6.751	
5700	19.858	130.854	7.828	-195.811	-187.449	6.747	
5800	19.858	131.199	7.828	-195.958	-187.449	6.743	
5900	19.859	131.538	7.828	-196.105	-187.449	6.739	
6000	19.859	131.872	7.828	-196.252	-187.449	6.735	

Dec. 31, 1960; Sept. 30, 1964

Dec. 31, 1960; Sept. 30, 1964



ALUMINUM DICHLORIDE FLUORIDE (AlCl₂F) (IDEAL GAS)

MOL. WT. = 116.894

Point Group C_{2v}

S_{298.15}^o = [74.356] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[420] (1)	[200] (1)
[260] (1)	[650] (1)
[150] (1)	[820] (1)

Bond Distances: Al-F = [1.65] Å Al-Cl = [2.14] Å
Bond Angle: F-Al-Cl = [120]° Cl-Al-Cl = [120]°
Product of the Moments of Inertia: I_AI_BI_C = [4.64645 X 10⁻¹¹³] g.³ cm.⁶

σ⁻ = 2

Heat of Formation.

The value of ΔH_f^o 298.15 was calculated based on an assumption the ΔH_f^o = 0 for the reaction AlP₃(g) + 2AlCl₃(g) = 3AlCl₂F(g). The values of ΔH_f^o 298.15 for AlP₃(g) and AlCl₃(g) used for calculation are -286.5 and -139.7 kcal. mole⁻¹, respectively.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for AlP₃(g) and AlCl₃(g). The bond distances of Al-F and Al-Cl atoms were assumed to be the same as those in AlP₃(g) and AlCl₃(g), respectively. The bond angles and ground state quantum weight were estimated by comparison with those for AlP₃(g). The three principal moments of inertia are 4.04374 X 10⁻³⁶, 1.92508 X 10⁻³⁶, and 5.96882 X 10⁻³⁶ g.³ cm.⁶.



Aluminum Trichloride (AlCl₃)

(Crystal) GFW = 133.341

T, °K	Cp°	S°	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	.000	.000	INFINITE	-	4.058	-169.323	-169.323	INFINITE
100	11.260	7.361	53.251	-	3.589	-169.004	-169.004	355.405
200	16.930	17.990	88.035	-	2.015	-168.961	-168.961	171.115
298	21.760	26.120	109.621	-	.000	-168.950	-168.950	110.393
300	21.820	26.255	109.621	-	.040	-168.663	-150.476	109.621
400	23.920	32.620	127.001	-	2.001	-168.201	-145.482	78.922
500	26.020	38.383	142.734	-	4.824	-167.614	-138.617	60.589
600	28.120	43.313	160.760	-	7.531	-166.469	-132.885	48.403
700	30.220	47.805	180.879	-	10.248	-165.958	-127.291	39.792
800	32.320	51.977	203.008	-	13.575	-165.073	-121.641	33.295
900	34.420	55.905	231.114	-	16.912	-163.633	-116.538	28.298
1000	36.520	59.661	264.559	-	20.459	-161.760	-111.192	24.301
1100	38.620	63.220	303.205	-	24.216	-159.416	-105.916	21.093
1200	40.720	66.670	347.184	-	28.183	-156.625	-100.796	18.357
1300	42.820	70.012	396.510	-	32.360	-153.488	-95.840	16.112
1400	44.920	73.263	451.214	-	36.747	-150.012	-91.050	14.214
1500	47.020	76.433	511.344	-	41.344	-154.433	-86.432	12.593

Heat of Formation

Gross and Hayman (1) measured the enthalpy of direct combination of "spectrographically pure" aluminum and carefully purified chlorine and derived ΔH_f° 298.15 = -168.80 $\pm$ 0.16 kcal/mol. Siemsen (2) also reported the enthalpy of direct combination and is in agreement at -167.5 kcal/mol within his relatively large uncertainty interval of ± 1.1 kcal/mol.

Coughlin (3) determined the enthalpy of solution of 99.99+ pure Al in 4.360 M HCl and also (4) the enthalpy of solution of anhydrous AlCl₃ in the same solvent. Enthalpies of mixing were measured to close a thermochemical cycle at 303.15°K (adjusted to 1961 at. wts.):

Reaction	ΔH° , 303.15 cal.
(1) Al(c) + 3H ⁺ (sol) = Al ³⁺ (sol) + 3/2 H ₂ (g)	-127,057 $\pm$ 120
(2) 3(HCl·12.731 H ₂ O)(l) = 3H ⁺ (sol) + 3Cl ⁻ (sol) + 38.193 H ₂ O(sol)	0 $\pm$ 10
(3) AlCl ₃ (c) = Al ³⁺ (sol) + 3Cl ⁻ (sol)	-72,504 $\pm$ 50
(4) 38.193 H ₂ O(l) = 38.193 H ₂ O(sol)	-3,050 $\pm$ 20
(5) Al(c) + 3(HCl·12.731 H ₂ O)(l) = AlCl ₃ (c) + 38.193 H ₂ O(l) + 3/2 H ₂ (g)	-51,503 $\pm$ 140

With heat capacity data for Al, AlCl₃, and H₂ from the JANAF tables and for HCl(12.731 H₂O) from Parker et al. (5) reaction 5 at 298.15°K is -51,910 $\pm$ 140 cal/mol AlCl₃. Interpolation of data for ΔH_f° 298.15(HCl, aq) selected by Wagman et al. (6) yields ΔH_f° 298.15(AlCl₃, c) = -168.37 kcal/mol. The overall uncertainty is estimated as 300 cal/mol.

Earlier investigations on the enthalpies of solution of Al were adjusted to the conditions of Coughlin's experiments by means of the data of Smith and Bass (7) for the effects of HCl concentration and H₂O dilution on ΔH_f° (AlCl₃, aq) and estimates of ΔC_p of solution of Al of +20 gibbs/mol.

Investigator(s)	ΔH° (soln) as reported kcal/mol Al	ΔH° (soln) adjusted kcal/mol Al
Young (8)	-126.83	-126.79
Roth and Wolf (9)	-124.01	-127.29
Conneri and Rossi (10)	-125.40	-126.80
Sommerer (11)	-128.36	-126.42
Richards and Burgess (12)	-126.00	-124.06

Only Richards and Burgess deviate more than expected; they report a value for Mg in good agreement with modern values and it seems likely their sample of Al was impure.

Several values for the enthalpy of solution of AlCl₃(c) in water have also been published and are listed here along with Coughlin's value recalculated to solution in pure water at 20°K.

Investigator(s)	ΔH° (soln) in H ₂ O at 20°K (kcal/mol AlCl ₃)
Coughlin (3)	-78.22 (adjusted)
Thomsen (13)	-76.85
Berthelot (14)	-76.3
Saunders (15)	-77.6
Stoll (16)	-77.9
Roth and Böhner (14)	-79.3
Roth and Böger (15)	-77.7 (adjusted)
Klemm and Tanke (16)	-77.7 (adjusted)

Klemm and Tanke (16) measured the enthalpy of solution of AlCl₃ in HCl·20 H₂O at 0°K. A weighted average of this value of Gross and Hayman (1) and of Coughlin (3) is adopted for ΔH_f° 298.15(AlCl₃, c) = -168.65 $\pm$ 0.20 kcal/mol.

Heat Capacity and Entropy

Justice (17) reported low temperature heat capacity data (13° to 310°K) and presented smoothed thermodynamic functions, including $S_{298.15}^\circ$ = 26.12 gibbs/mol, of which 0.086 gibbs/mol is extrapolation below 13°K. Heat content relative to 273.15°K was measured by Fischer (18) from 298°K to 504°K and heat content relative to 298.15°K was measured by Holsen (19) from 310° to 493°K. The heat content data for the crystal can be fit within about 2% by integration of $C_p(c)$ (gibbs/mol) = 15.52 + 0.021T, which is an extrapolation of C_p data reported by Justice (17).

Melting Data

See table for AlCl₃(t).

Sublimation Data

See table for Al₂Cl₆(g).

References

1. P. Gross and C. Hayman, *Trans. Faraday Soc.*, **55**, 30 (1970).
2. H. Siemsen, *Z. Elektrochem.*, **55**, 327 (1951).
3. J. P. Coughlin, *J. Amer. Chem. Soc.*, **77**, 1191 (1955).
4. J. P. Coughlin, *J. Amer. Chem. Soc.*, **78**, 479 (1956).
5. V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-582, 1965.
6. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
7. M. B. Smith and G. E. Bass, *J. Chem. Eng. Data*, **9**, 342 (1963).
8. F. E. Young, *J. Amer. Chem. Soc.*, **55**, 777 (1944).
9. A. Roth and U. Wolf, *Z. Elektrochem.*, **45**, 232 (1940).
10. E. Conneri and R. Rossi, *Chim. Ind. (Milan)*, **36**, 201 (1954).
11. E. Sommerer, *Phys. Rev.*, **1**, 141 (1913).
12. T. W. Richards and L. L. Burgess, *J. Amer. Chem. Soc.*, **32**, 431 (1910).
13. F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of Chemical Substances*, Reinhold, New York, 1936, p. 331.
14. W. A. Roth and A. Böhner, *Z. Elektrochem.*, **40**, 87 (1934).
15. W. A. Roth and E. Böger, *Z. Elektrochem.*, **41**, 540 (1935).
16. W. Klemm and E. Tanke, *Z. Elektrochem.*, **41**, 540 (1935).
17. B. H. Justice, *J. Chem. Eng. Data*, **9**, 342 (1963).
18. W. Fischer, *Z. Anorg. Chem.*, **200**, 327 (1931).
19. R. A. Holsen, *The Dow Chemical Co., Midland, Mich.*, unpublished data.

Dec. 31, 1960; June 30, 1961; June 30, 1963; Mar. 31, 1964; June 30, 1970

Aluminum Trichloride (AlCl₃)

(Liquid) GFW = 133.341

AlCl₃

GFW = 133.341

(LIQUID)

ALUMINUM TRICHLORIDE (AlCl₃)

S^{298.15} = 41.326 ± 0.5 gibbs/mol

ΔHf^{298.15} = -161.28 ± 0.40 kcal/mol

Tm = 465.7 ± 0.2°K

ΔHm = 8.45 ± 0.20 kcal/mol

Heat of Formation

ΔHf^{298.15}(l) was obtained from ΔHf^{298.15}(c) by adding ΔHm and the difference between (H_{465.7-298.15}) for crystal and liquid.

Melting Point

Kendall et al. (1) observed AlCl₃ to melt "sharply" at 463.4°K, Foster (2) noted that AlCl₃ began melting and melted completely in the range 465.7 ± 0.2°K, Nisei'son et al. (3) reported Tm = 467.2°K, and Ostriкова et al. (4) reported Tm = 466°K. Smits and Meijering (5) and Treadwell and Terebesi (6) derived triple point temperatures of 465.8°K and 466.5°K, respectively, from intersection of vapor pressure curves for crystal and liquid. The value of Foster is adopted as most accurate. The vapor pressure at the triple point is 2.3 atm.

Heat of Fusion and Heat Capacity

Fischer (7) and McDonald (8) measured heat content data for the liquid over a short range (473°-504°K) of temperature. Their data can be represented within 21 by the heat capacity equation derived for the crystal [see AlCl₃(c) table], a heat of fusion of 8.45 kcal/mol, and a liquid heat capacity of 30.0 gibbs/mol. Fischer's data are high, while McDonald's points lie below the selected values.

References

1. J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Amer. Chem. Soc.* **45**, 963 (1923).
2. L. M. Foster, *J. Amer. Chem. Soc.* **72**, 1902 (1950).
3. L. A. Nisei'son, A. I. Pustil'nik, O. B. Gavrilov, and V. A. Rodin, *Zh. Neorg. Khim.* **10**, 2339 (1965).
4. M. V. Ostriкова, Z. A. Miroshnik, V. D. Kuleshova, N. P. Dudkina, and A. I. Ilyushchenko, *Zh. Neorg. Khim.* **14**, 2229 (1969).
5. A. Smits and J. L. Meijering, *Z. Physik. Chem.* **B11**, 88 (1938).
6. W. D. Treadwell and L. Terebesi, *Helv. Chim. Acta* **15**, 1053 (1932).
7. W. Fischer, *Z. Anorg. Chem.* **200**, 332 (1931).
8. R. A. McDonald, *The Dow Chemical Co., Midland, Mich.*, Unpublished measurements.

T, °K	Cp*	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	30,000	41.326	41.326	-	161.280	-167.751	106.304
300	30,000	41.512	41.327	0.055	-	-167.667	107.576
400	30,000	50.112	42.503	2.056	140.102	-133.313	76.303
500	30,000	56.836	44.725	6.056	159.013	-139.243	60.663
600	30,000	62.306	47.213	9.056	-	-135.387	49.315
700	30,000	66.931	49.708	12.056	-	-131.702	41.119
800	30,000	70.937	52.117	15.055	-	-128.158	35.011
900	30,000	74.470	54.408	18.055	-	-124.729	30.288
1000	30,000	77.631	56.575	21.055	-	-121.416	26.492
1100	30,000	80.490	58.621	24.056	-	-117.702	23.385
1200	30,000	83.100	60.554	27.056	-	-114.270	20.611
1300	30,000	85.502	62.362	30.056	-	-110.911	18.444
1400	30,000	87.725	64.114	33.056	-	-107.619	16.400
1500	30,000	89.795	65.756	36.056	-	-104.393	15.210

AlCl₃

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

T, °K	Cp ^a	gibbs/mol S ^b	-(C _p ^a - H ^o)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^c	ΔG ^c	Log K _p
0	0.000	INF INITE	-	3.959	-139.274	-139.274	INF INITE
100	12.113	56.002	99.004	3.958	-139.274	-139.274	130.103
200	15.103	71.116	116.116	3.958	-139.274	-139.274	99.671
300	17.176	75.116	116.116	3.958	-139.274	-139.274	99.671
400	18.166	75.224	75.116	3.958	-139.274	-139.274	99.671
500	18.708	75.224	75.116	3.958	-139.274	-139.274	99.671
600	19.034	75.224	75.116	3.958	-139.274	-139.274	99.671
700	19.242	75.224	75.116	3.958	-139.274	-139.274	99.671
800	19.383	75.224	75.116	3.958	-139.274	-139.274	99.671
900	19.481	75.224	75.116	3.958	-139.274	-139.274	99.671
1000	19.553	75.224	75.116	3.958	-139.274	-139.274	99.671
1100	19.607	75.224	75.116	3.958	-139.274	-139.274	99.671
1200	19.648	75.224	75.116	3.958	-139.274	-139.274	99.671
1300	19.681	75.224	75.116	3.958	-139.274	-139.274	99.671
1400	19.707	75.224	75.116	3.958	-139.274	-139.274	99.671
1500	19.728	75.224	75.116	3.958	-139.274	-139.274	99.671
1600	19.745	75.224	75.116	3.958	-139.274	-139.274	99.671
1700	19.759	75.224	75.116	3.958	-139.274	-139.274	99.671
1800	19.771	75.224	75.116	3.958	-139.274	-139.274	99.671
1900	19.781	75.224	75.116	3.958	-139.274	-139.274	99.671
2000	19.790	75.224	75.116	3.958	-139.274	-139.274	99.671
2100	19.798	75.224	75.116	3.958	-139.274	-139.274	99.671
2200	19.804	75.224	75.116	3.958	-139.274	-139.274	99.671
2300	19.810	75.224	75.116	3.958	-139.274	-139.274	99.671
2400	19.815	75.224	75.116	3.958	-139.274	-139.274	99.671
2500	19.819	75.224	75.116	3.958	-139.274	-139.274	99.671
2600	19.823	75.224	75.116	3.958	-139.274	-139.274	99.671
2700	19.827	75.224	75.116	3.958	-139.274	-139.274	99.671
2800	19.830	75.224	75.116	3.958	-139.274	-139.274	99.671
2900	19.833	75.224	75.116	3.958	-139.274	-139.274	99.671
3000	19.835	75.224	75.116	3.958	-139.274	-139.274	99.671
3100	19.838	75.224	75.116	3.958	-139.274	-139.274	99.671
3200	19.840	75.224	75.116	3.958	-139.274	-139.274	99.671
3300	19.842	75.224	75.116	3.958	-139.274	-139.274	99.671
3400	19.844	75.224	75.116	3.958	-139.274	-139.274	99.671
3500	19.845	75.224	75.116	3.958	-139.274	-139.274	99.671
3600	19.848	75.224	75.116	3.958	-139.274	-139.274	99.671
3700	19.848	75.224	75.116	3.958	-139.274	-139.274	99.671
3800	19.849	75.224	75.116	3.958	-139.274	-139.274	99.671
3900	19.850	75.224	75.116	3.958	-139.274	-139.274	99.671
4000	19.851	75.224	75.116	3.958	-139.274	-139.274	99.671
4100	19.852	75.224	75.116	3.958	-139.274	-139.274	99.671
4200	19.853	75.224	75.116	3.958	-139.274	-139.274	99.671
4300	19.854	75.224	75.116	3.958	-139.274	-139.274	99.671
4400	19.855	75.224	75.116	3.958	-139.274	-139.274	99.671
4500	19.855	75.224	75.116	3.958	-139.274	-139.274	99.671
4600	19.856	75.224	75.116	3.958	-139.274	-139.274	99.671
4700	19.857	75.224	75.116	3.958	-139.274	-139.274	99.671
4800	19.857	75.224	75.116	3.958	-139.274	-139.274	99.671
4900	19.858	75.224	75.116	3.958	-139.274	-139.274	99.671
5000	19.859	75.224	75.116	3.958	-139.274	-139.274	99.671
5100	19.859	75.224	75.116	3.958	-139.274	-139.274	99.671
5200	19.860	75.224	75.116	3.958	-139.274	-139.274	99.671
5300	19.860	75.224	75.116	3.958	-139.274	-139.274	99.671
5400	19.861	75.224	75.116	3.958	-139.274	-139.274	99.671
5500	19.861	75.224	75.116	3.958	-139.274	-139.274	99.671
5600	19.861	75.224	75.116	3.958	-139.274	-139.274	99.671
5700	19.862	75.224	75.116	3.958	-139.274	-139.274	99.671
5800	19.862	75.224	75.116	3.958	-139.274	-139.274	99.671
5900	19.862	75.224	75.116	3.958	-139.274	-139.274	99.671
6000	19.863	75.224	75.116	3.958	-139.274	-139.274	99.671

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
371 (1)	148 (2)	148 (2)
[106] (1)	810 (2)	810 (2)

Bond Distances: Al-Cl = 2.06 Å
Bond Angle: Cl-Al-Cl = 120°

Product of the Moments of Inertia: $I_A I_B I_C = 1.0618 \times 10^{-112}$ g cm⁶
 $\sigma = 8$

Heat of Formation

The heat of formation is calculated from the value adopted for Al₂Cl₆(g) and the heat of dissociation of Al₂Cl₆, derived from equilibrium P-V-T data on aluminum chloride vapor as listed below.

$\Delta H_{298.15}^\circ$, kcal/mol	2nd Law	3rd Law
29.28	30.12	30.12
30.82	30.82	30.82
30.22	30.22	30.40

Number of Data Points

6

16^a

16^b

30.40

Twenty six points reported, points at 838, 881, 944, 734, 605, and 688°K rejected by statistical test.
The three investigations are in reasonable agreement. Giving consideration also to equilibrium data on the reaction of AlCl₃(g) and Al(l) to form AlCl(g) [see AlCl(g) table], there is selected as a best value $\Delta H_{298.15}^\circ = 30.24$ kcal/mol AlCl₃(g), which yields $\Delta H_{298.15}^\circ(\text{AlCl}_3, g) = -139.70$ kcal/mol.

Heat Capacity and Entropy

Zaorin and Rambidi (4) carried out electron diffraction experiments on aluminum chloride vapor at 800°K where the monomer should predominate. They found a planar symmetrical structure with Al-Cl = 2.06 ± 0.01 Å and Cl-Al-Cl angles of 120°. The individual moments of inertia are $I_A = I_B = 3.7468 \times 10^{-38}$ g cm² and $I_C = 7.4932 \times 10^{-38}$ g cm². For aluminum chloride vapor at high temperatures (monomer predominant), Klemperer (5) observed a band at 610 cm⁻¹ in the infrared spectrum and Beattie and Hordner (6) reported Raman bands at 371 cm⁻¹ and 146 cm⁻¹. The remaining frequency should be infrared active but presumably was beyond the range of Klemperer's measurements. Zaorin and Rambidi (7) give 96 ± 15 cm⁻¹ based on amplitudes of vibration observed in electron diffraction measurements. However, this frequency gives thermodynamic functions clearly not compatible with the equilibrium P-V-T data. Force constant ratios in the boron halides also suggest a higher wavenumber. An estimate of 185 cm⁻¹ was therefore adopted as an optimum value for fitting both the Al₂Cl₆ dissociation data and the equilibrium data for AlCl₃(g) + 2Al(l) + 3AlCl(g) [see AlCl(g) table].

References

1. A. Smits and J. L. Maffering, Z. Phys. Chem. B11, 99 (1936).
2. W. Fischer, O. Rahlfs, and B. Benz, Z. Anorg. Chem. 205, 1 (1932).
3. E. Vrieland and D. R. Stull, J. Chem. Eng. Data 12, 632 (1967).
4. E. Z. Zaorin and N. G. Rambidi, Zh. Strukt. Khim. 9, 391 (1967).
5. W. Klemperer, J. Chem. Phys. 24, 353 (1956).
6. I. R. Beattie and J. R. Hordner, J. Chem. Soc. 1958, 2865.
7. E. Z. Zaorin and N. G. Rambidi, Zh. Strukt. Khim. 9, 531 (1967).

Potassium Tetrachloroaluminate (KAlCl₄)

(Crystal) Mol. Wt. = 207.908

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100							
200							
298	37.400	47.000	47.000	0.000	-286.000	-261.610	191.756
300	37.440	47.231	47.001	0.069	-285.985	-261.459	190.464
400	39.550	58.294	48.495	3.820	-285.705	-253.302	187.511
500	41.660	69.557	59.796	11.100	-285.210	-245.150	184.560
600	43.780	75.128	54.708	12.252	-283.569	-237.634	86.518
700	45.600	82.019	58.127	16.724	-282.256	-230.964	71.795
800	47.000	88.204	61.507	21.358	-280.822	-222.593	60.807
900	47.800	93.789	64.789	26.100	-279.319	-215.402	52.304
1000	48.300	98.654	67.946	30.808	-278.292	-208.199	45.500
1100	48.407	103.462	70.969	35.743	-277.588	-200.043	39.743
1200	48.500	107.678	73.854	40.589	-275.739	-191.257	34.831
1300	48.580	111.564	76.608	45.443	-273.886	-182.027	30.701
1400	48.647	115.166	79.235	50.304	-272.050	-174.136	27.183
1500	48.700	118.225	81.743	55.172	-270.171	-165.760	24.153
1600	48.763	121.670	84.142	60.045	-268.311	-157.547	21.519
1700	48.825	124.628	86.437	64.924	-266.448	-149.431	19.210
1800	48.885	127.420	88.637	69.810	-264.582	-141.427	17.171
1900	48.943	130.095	90.748	74.701	-262.715	-133.527	15.359
2000	49.000	132.577	92.777	79.599	-260.847	-125.717	13.737

AlCl₄K

MOL. WT. = 207.908

(CRYSTAL)

POTASSIUM TETRACHLOROALUMINATE (KAlCl₄)

ΔH_f^o 0 = Unknown

ΔH_f^o 298.15 = -286.0 ± 2.5 kcal. mole⁻¹

ΔH_m^o = Unknown

S_{298.15} = [47 ± 2] cal. deg.⁻¹ mole⁻¹

T_m = 529°K.

Heat of Formation.

The heat of reaction of aluminum chloride and potassium chloride was measured by E. Baud, Ann. Chim. Phys. 1, 8 (1904). From ΔH_f^o = -26.38 kcal. mole⁻¹ for the reaction: Al₂Cl₆(c) + 2KCl(c) = 2KAlCl₄(c), the value of ΔH_f^o 298.15 for KAlCl₄(c) was calculated to be -286 kcal. mole⁻¹.

Heat Capacity and Entropy.

Heat capacities were estimated by comparison with those for K₂SO₄(c), reported by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). S_{298.15} was estimated according to the method suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, 1958 and K. K. Kelley, private communication, June, 1960.

Temperature of Melting.

T_m was reported by W. Flacher and A.-L. Simon, Z. anorg. allgem. Chem. 306, 1 (1960).

AlCl₄K

Sodium Tetrachloroaluminate (NaAlCl₄)
(Crystal) Mol. Wt. = 191.799

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	-(F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF°	Log K _p
0								
100	37.040	45.000	45.000	-0.000	-273.000	-248.936	182.461	
200	37.080	45.229	45.001	-0.069	-272.984	-248.806	181.247	
300	37.090	45.299	45.002	-0.069	-272.964	-248.684	180.034	
400	37.090	45.309	45.002	-0.069	-272.964	-248.684	180.034	
500	37.090	45.309	45.002	-0.069	-272.964	-248.684	180.034	
600	43.800	73.001	52.864	12.203	-270.640	-225.285	82.056	
700	45.200	79.850	56.068	16.667	-269.345	-217.628	68.006	
800	46.250	85.960	59.430	21.224	-267.951	-210.563	57.520	
900	47.150	91.464	62.688	25.888	-266.494	-203.475	49.408	
1000	47.800	96.459	65.819	30.639	-265.503	-196.569	42.914	
1100	47.869	101.008	68.815	35.413	-265.019	-189.334	37.615	
1200	48.100	105.184	71.674	40.212	-264.560	-181.985	33.142	
1300	48.294	109.042	74.402	45.032	-264.126	-175.261	29.126	
1400	48.450	112.627	77.006	49.869	-263.706	-168.677	25.706	
1500	48.594	115.974	79.493	54.722	-263.225	-162.225	22.761	
1600	48.700	119.114	81.872	59.587	-262.713	-157.895	20.201	
1700	48.769	122.059	84.151	64.461	-262.169	-153.679	17.956	
1800	48.800	124.857	86.335	69.339	-261.594	-151.578	15.975	
1900	48.850	127.497	88.433	74.222	-260.994	-149.578	14.213	
2000	48.900	130.004	90.449	79.109	-260.369	-147.673	12.640	

SODIUM TETRACHLOROALUMINATE (NaAlCl₄) (CRYSTAL)

MOL. WT. = 191.799

ΔH_f° = Unknown

ΔH_f° 298.15 = -273 ± 1 kcal. mole⁻¹

ΔH_m° = Unknown

S° 298.15 = [45 ± 2] cal. deg.⁻¹ mole⁻¹

T_m = 424°K.

Heat of Formation.

The heat of formation at 298.15°K. was calculated from ΔH_f° = -11.9 kcal. mole⁻¹ for the reaction Al₂Cl₆(c) + 2NaCl(c) = 2NaAlCl₄(c) measured by E. Baud, Ann. chim. phys. 2, 8 (1904).

Heat Capacity and Entropy.

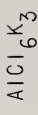
Heat capacities were estimated by comparison with those of KAlCl₄(c). S° 298.15 was estimated according to the methods suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, 1958 and K. K. Kelley, private communication, June, 1960.

Temperature of Melting.

T_m was reported by H. Fischer and A.-L. Simon, Z. anorg. allgem. Chem. 302, 1 (1960).

AlCl₄Na

AlCl₄Na



(Crystal) Mol. Wt. = 357.022

TRIPOTASSIUM HEXACHLOROALUMINATE (K_3AlCl_6) (CRYSTAL) MOL. WT. = 357.022

T. °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _f
0								
100								
200								
298								
300	59.450	90.000	90.000	0.000	- 500.000	- 463.325		339.610
400	59.580	90.368	90.001	11.0	- 499.085	- 443.098		337.350
500	61.940	107.949	92.931	6.227	- 500.897	- 450.001		297.295
600	64.450	122.043	96.947	12.548	- 499.991	- 438.126		191.496
600	66.800	134.004	102.151	16.112	- 498.868	- 425.854		155.110
600	68.900	144.523	107.493	22.892	- 497.550	- 413.787		139.184
800	72.300	162.193	117.720	40.626	- 496.887	- 390.742		104.759
1000	73.800	169.895	122.558	47.337	- 495.292	- 378.569		82.732
1100	75.175	176.995	127.188	54.787	- 495.000	- 363.913		72.299
1200	76.400	183.769	131.617	62.367	- 494.455	- 347.100		63.212
1300	77.400	189.978	135.814	70.067	- 493.667	- 330.110		55.681
1400	78.400	195.526	139.612	77.957	- 492.667	- 312.952		49.099
1500	79.188	200.961	143.802	85.737	- 491.444	- 297.997		43.416
1600	79.900	206.094	147.537	93.692	- 490.000	- 282.041		38.523
1800	80.750	210.958	151.126	101.715	- 488.455	- 266.279		34.231
1900	81.588	215.976	154.976	109.906	- 486.887	- 250.688		29.458
2000	82.000	224.171	161.115	126.112	- 485.292	- 235.297		24.046

ΔH_f^o = Unknown

ΔH_f^o 298.15 = -500 ± 1 kcal. mole⁻¹

ΔH_m^o = Unknown

S_{298.15} = [90 ± 2] cal. deg. ⁻¹ mole⁻¹

T_m = [800]°K.

Heat of Formation.

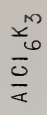
The heat of formation at 298.15°K. was recalculated from the same quantity given in National Bureau of Standards (U. S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952. The latter value was derived from the enthalpy change for the reaction $\text{Al}_2\text{Cl}_6(\text{c}) + 6\text{KCl}(\text{c}) = 2\text{K}_3\text{AlCl}_6(\text{c})$ measured by E. Baud, Ann. chim. phys. 1, 8 (1904).

Heat Capacity and Entropy.

Both C_p and S_{298.15} were estimated by comparison with the corresponding values of the sum of the constituent halides for $\text{Na}_3\text{AlF}_6(\text{c})$.

Temperature of Melting.

T_m was estimated by comparison with that for $\text{K}_2\text{AlF}_6(\text{c})$.



Ground State Configuration $1s^2$ $S_{298.15}^\circ = 51.40 \pm 0.01$ gibbs/mol $\Delta H_f^\circ = -63.4 \pm 0.8$ kcal/mol $\Delta H_f^\circ = -63.4 \pm 0.8$ kcal/mol

Electronic Levels and Quantum Weights

 $\epsilon_i, \text{cm}^{-1}$ g_i

0

1

2

1

43935

54251

 $\omega_e = 801.95 \text{ cm}^{-1}$ $\omega_e = 4.70 \text{ cm}^{-1}$ $\sigma = 1$ $\alpha_e = 0.00483 \text{ cm}^{-1}$ $r_e = 1.6547 \text{ \AA}$

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Heat of Formation

There have been several studies of the interaction of Al with AlF_3 to produce $\text{AlF}(g)$ and the results of 2nd and 3rd law analyses are given below.

Dec. 31, 1960; Sept. 30, 1961; June 30, 1969

(Ideal Gas) GFW = 45.9794

ALUMINUM MONOFLUORIDE UNIPOSITIVE ION (AlF⁺) (IDEAL GAS)

GFW = 45.9794

Ground State Configuration [2]

 $\Delta H_f^\circ = 161 \pm 12$ kcal/mol $S_{298.15}^\circ = (52.95 \pm 0.5)$ gibbs/mol $\Delta H_f^\circ_{298.15} = 161 \pm 12$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[2]
[28000]	[4]
[37000]	[2]
[45000]	[2]
$\omega_e x_e = [6]$ cm ⁻¹	$\sigma = 1$
$B_e = [0.5332]$ cm ⁻¹	$r_e = [1.71]$ Å
$\alpha_e = [0.0063]$ cm ⁻¹	

Heat of Formation

T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964) reported the ionization potential of AlF as 9.7 ± 0.5 eV (224 ± 12 kcal). The magnitude of the value has been confirmed by R. F. Porter, J. Chem. Phys. 33, 951 (1960) who found it between 9 and 10 eV. Using the above value in conjunction with $\Delta H_f^\circ(\text{AlF}, g) = -62.5$ kcal/mol, and the equation $\text{AlF}(g) \rightarrow \text{AlF}^+(g) + e^-$ yields $\Delta H_f^\circ(\text{AlF}^+, g) = 161 \pm 12$ kcal/mol.

Heat Capacity and Entropy

AlF⁺ is isoelectronic with MgF, and the electronic configuration of the ground and excited states we estimate to be those for MgF(g). The vibrational frequency, anharmonicity constant and bond length we estimate by comparison with those for MgF and AlF. The rotational constant is calculated from the bond length and atomic masses, and α_e is calculated from the other constants assuming a Morse potential function.

The enthalpy at 0°K is -2.139 kcal.

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG_f°	Log Kp
100				.000	161.000	152.967	-112.128
200	7.751	52.947	52.947	.000	161.000	152.967	-112.128
288				.014	161.005	152.917	-111.400
300	7.756	52.995	52.997	.011	161.315	150.175	-82.052
400	8.124	55.283	55.286	.044	161.605	147.355	-64.409
500	8.359	57.130	53.852	1.639	161.876	144.579	-52.679
600	8.559	58.677	54.531	2.488	162.125	141.806	-37.465
700	8.696	60.006	55.121	4.351	162.346	139.028	-22.251
800	8.766	61.156	55.550	5.705	162.523	136.248	-12.035
900	8.766	62.110	55.930	5.991	162.663	133.468	-2.821
1000	8.687	63.114	57.153	5.991	160.130	132.815	32.027
1100	8.928	63.993	57.737	6.882	160.313	130.075	25.843
1200	8.993	64.772	58.291	7.776	160.489	127.246	20.598
1300	9.019	65.458	58.818	8.670	160.667	124.416	15.353
1400	9.019	66.148	59.318	9.564	160.847	121.589	10.107
1500	9.043	66.781	59.795	10.478	161.052	118.758	4.861
1600	9.065	67.365	60.250	11.383	161.238	115.945	-1.385
1700	9.085	67.895	60.685	12.291	161.425	113.132	-7.629
1800	9.102	68.372	61.102	13.195	161.612	110.320	-13.873
1900	9.119	68.798	61.501	14.112	161.799	107.507	-20.117
2000	9.139	69.396	61.884	15.025	161.986	104.694	-26.361
2100	9.155	69.862	62.252	15.939	162.174	101.880	-32.605
2200	9.171	70.289	62.607	16.856	162.362	99.067	-38.849
2300	9.187	70.676	62.952	17.776	162.550	96.254	-45.093
2400	9.202	71.028	63.299	18.693	162.738	93.441	-51.337
2500	9.216	71.444	63.598	19.614	162.927	90.628	-57.581
2600	9.231	71.806	63.907	20.536	163.116	87.815	-63.825
2700	9.245	72.154	64.206	21.460	163.305	85.002	-70.069
2800	9.259	72.497	64.505	22.384	163.494	82.189	-76.313
2900	9.273	72.816	64.777	23.312	163.683	79.376	-82.557
3000	9.287	73.111	65.051	24.240	163.872	76.563	-88.801
3100	9.301	73.435	65.316	25.169	164.061	73.750	-95.045
3200	9.315	73.731	65.574	26.100	164.250	70.937	-101.289
3300	9.329	74.026	65.826	27.031	164.439	68.124	-107.533
3400	9.343	74.296	66.071	27.966	164.628	65.311	-113.777
3500	9.357	74.567	66.310	28.901	164.817	62.498	-119.999
3600	9.372	74.831	66.543	29.837	165.006	59.685	-126.243
3700	9.387	75.088	66.771	30.775	165.195	56.872	-132.487
3800	9.401	75.339	67.000	31.716	165.384	54.059	-138.731
3900	9.416	75.583	67.210	32.658	165.573	51.246	-144.975
4000	9.434	75.822	67.422	33.598	165.762	48.433	-151.219
4100	9.451	76.055	67.630	34.542	165.951	45.620	-157.463
4200	9.468	76.283	67.833	35.486	166.140	42.807	-163.707
4300	9.486	76.506	68.036	36.430	166.329	40.000	-169.951
4400	9.504	76.729	68.237	37.374	166.518	37.187	-176.195
4500	9.523	76.938	68.419	38.337	166.707	34.374	-182.439
4600	9.543	77.147	68.606	39.290	166.896	31.561	-188.683
4700	9.564	77.353	68.790	40.245	167.085	28.748	-194.927
4800	9.584	77.559	68.972	41.200	167.274	25.935	-201.171
4900	9.607	77.752	69.148	42.163	167.463	23.122	-207.415
5000	9.630	77.947	69.322	43.124	167.652	20.309	-213.659
5100	9.654	78.138	69.493	44.089	167.841	17.496	-219.903
5200	9.676	78.325	69.661	45.055	168.030	14.683	-226.147
5300	9.699	78.510	69.826	46.021	168.219	11.870	-232.391
5400	9.722	78.692	69.989	47.000	168.408	9.057	-238.635
5500	9.750	78.870	70.148	47.971	168.597	6.244	-244.879
5600	9.788	79.047	70.306	48.948	168.786	3.431	-251.123
5700	9.817	79.220	70.461	49.928	168.975	0.618	-257.367
5800	9.849	79.393	70.613	50.909	169.164	-2.195	-263.611
5900	9.889	79.560	70.763	51.894	169.353	-4.982	-269.855
6000	9.911	79.726	70.911	52.888	169.542	-7.769	-276.099

June 30, 1968

Aluminum Oxide Fluoride (AlOF)

(Ideal Gas) Mol. Wt. = 61.98

ALUMINUM OXIDE FLUORIDE (AlOF) (IDEAL GAS)

MOL. WT. = 61.98

Point Group $C_{\infty v}$ $\Delta H_f^0 = -139.5 \pm 2.6 \text{ kcal. mole}^{-1}$
 $S^0_{298.15} = [55.986] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^0_{298.15} = -140.2 \pm 2.6 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm.^{-1}
 [900](1)
 [500](2)
 [750](1)

Bond Distance: O-Al = $[1.62] \text{ \AA}$ Al-F = $[1.65] \text{ \AA}$
 Bond Angle: O-Al-F = $[180]^\circ$ $\sigma^- = 1$
 Rotational Constant: $B_0 = [0.180806] \text{ cm.}^{-1}$

Heat of Formation.

The equilibrium constants (2200-2225°K.) of the chemical reaction $\text{Al}_2\text{O}_3 (c) + \text{AlF}_3 (g) = 3\text{AlOF} (g)$ were measured by M. Farber and H. L. Petersen, Trans. Faraday Soc. 59, 836 (1963). Using this data, the heat of reaction at 298.15°K. was calculated by the third law method to be $266.2 \pm 1.7 \text{ kcal. mole}^{-1}$. The value of ΔH_f^0 298.15 for AlOF (g) was then derived.

Heat Capacity and Entropy.

The bond distances of Al-O and Al-F were estimated to be the same as those for AlO (g) and AlF (g), respectively. The point group, ground state quantum weight and vibrational frequencies were obtained from W. H. Evans, J. Hilsenrath and H. W. Woolley, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds," National Bureau of Standards Report 6926, July 1, 1960. The moment of inertia is $1.54800 \times 10^{-38} \text{ g. cm.}^2$

T, °K.	C_p^0	$S^0 - (F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K_p
0	0.000	INFINITE	2.448	-139.461	-139.461	INFINITE
100	7.116	46.705	64.207	-1.750	-139.574	305.886
200	8.839	52.095	56.008	0.963	-139.618	153.245
298	10.692	55.986	0.000	0.000	-140.200	102.872
300	10.722	56.052	0.020	-140.205	-140.348	102.838
400	12.018	59.328	5.256	-1.162	-140.200	76.689
500	12.846	62.105	12.846	-2.408	-140.550	61.338
600	13.381	64.498	58.296	3.721	-140.687	51.095
700	13.740	66.590	59.435	5.078	-140.831	43.771
800	14.057	68.401	60.450	6.461	-140.972	38.592
900	14.337	70.100	70.852	7.892	-141.110	34.519
1000	14.599	71.600	82.403	9.297	-143.680	30.510
1100	14.839	72.968	93.211	10.732	-144.010	27.660
1200	14.977	74.224	104.077	12.176	-144.139	25.274
1300	15.087	75.385	114.903	13.627	-144.269	23.254
1400	15.177	76.462	125.697	15.077	-144.398	21.504
1500	15.257	77.472	136.463	16.544	-144.527	20.018
1600	15.659	78.417	147.162	18.009	-144.659	18.701
1700	15.887	79.307	157.850	19.476	-144.791	17.538
1800	16.083	80.143	168.510	20.948	-144.921	16.504
1900	16.246	80.933	179.143	22.418	-145.051	15.594
2000	16.384	81.699	189.753	23.892	-145.180	14.743
2100	16.501	82.439	200.339	25.367	-145.306	13.987
2200	16.593	83.106	210.904	26.844	-145.432	13.299
2300	16.673	83.704	221.448	28.322	-145.557	12.671
2400	16.743	84.292	231.971	29.801	-145.681	12.099
2500	16.803	84.866	242.484	31.281	-145.805	11.562
2600	16.851	85.427	252.987	32.761	-145.929	11.071
2700	16.887	85.976	263.480	34.242	-146.053	10.616
2800	16.913	86.513	273.963	35.723	-146.177	10.194
2900	16.930	87.038	284.436	37.207	-146.301	9.800
3000	16.934	87.598	294.901	38.690	-146.425	9.435
3100	16.938	88.184	305.356	40.174	-146.549	9.095
3200	16.942	88.796	315.801	41.658	-146.673	8.779
3300	16.946	89.432	326.236	43.143	-146.797	8.487
3400	16.949	89.556	336.661	44.627	-146.921	8.219
3500	16.952	89.986	347.076	46.112	-147.045	7.973
3600	16.955	90.405	357.481	47.598	-147.169	7.747
3700	16.958	90.812	367.876	49.083	-147.293	7.540
3800	16.961	91.207	378.261	50.568	-147.417	7.351
3900	16.962	91.594	388.636	52.052	-147.541	7.179
4000	16.964	91.970	398.991	53.542	-147.665	7.024
4100	16.966	92.337	409.336	55.028	-147.789	6.885
4200	16.968	92.696	419.671	56.515	-147.913	6.761
4300	16.970	93.053	429.996	58.002	-148.037	6.651
4400	16.971	93.407	440.311	59.489	-148.161	6.554
4500	16.973	93.722	450.616	60.976	-148.285	6.471
4600	16.974	94.049	460.911	62.463	-148.409	6.399
4700	16.975	94.376	471.206	63.950	-148.533	6.337
4800	16.976	94.698	481.491	65.437	-148.657	6.284
4900	16.978	95.019	491.776	66.924	-148.781	6.241
5000	16.979	95.289	502.061	68.411	-148.905	6.207
5100	16.980	95.593	512.346	69.898	-149.029	6.182
5200	16.981	95.897	522.631	71.385	-149.153	6.166
5300	16.982	96.191	532.916	72.872	-149.277	6.158
5400	16.983	96.485	543.201	74.359	-149.401	6.156
5500	16.983	96.707	553.486	75.845	-149.525	6.159
5600	16.984	96.975	563.771	77.332	-149.649	6.166
5700	16.985	97.249	574.056	78.819	-149.773	6.177
5800	16.986	97.523	584.341	80.306	-149.897	6.191
5900	16.987	97.797	594.626	81.793	-149.999	6.207
6000	16.987	98.002	604.911	83.280	-150.101	6.224

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞	∞
100	6.777	52.784	2.779	-164.575	-164.575	INFINITE
200	9.504	59.228	7.387	-165.601	-165.601	361.904
298	10.949	63.381	1.024	-164.763	-166.586	182.028
300	10.967	63.449	∞	-165.000	-167.434	122.727
400	11.562	66.725	∞	-165.005	-167.450	121.981
500	12.375	69.424	2.372	-165.231	-168.629	75.912
600	13.261	71.717	6.667	-165.684	-169.633	61.786
700	13.924	73.705	4.920	-165.932	-170.271	53.159
800	13.210	75.457	6.232	-166.202	-170.874	46.678
900	13.445	76.832	8.500	-166.457	-171.438	41.629
1000	13.445	76.832	8.500	-166.457	-171.438	37.242
1100	13.521	79.718	10.249	-169.557	-172.024	34.176
1200	13.580	80.897	11.604	-169.799	-172.236	31.367
1300	13.627	81.986	12.964	-170.042	-172.430	28.987
1400	13.665	82.997	14.328	-170.284	-172.604	26.653
1500	13.695	83.941	15.697	-170.527	-172.761	25.170
1600	13.721	84.825	17.068	-170.771	-172.901	23.616
1700	13.742	85.658	18.441	-171.016	-173.027	22.243
1800	13.760	86.444	19.816	-171.263	-173.140	21.021
1900	13.775	87.186	21.191	-171.511	-173.241	19.936
2000	13.788	87.893	22.571	-171.759	-173.339	18.939
2100	13.799	88.568	23.950	-172.010	-173.434	18.044
2200	13.809	89.210	25.331	-172.262	-173.452	17.230
2300	13.818	89.824	26.712	-172.516	-173.500	16.485
2400	13.826	90.408	28.094	-172.771	-173.536	15.802
2500	13.832	90.977	29.477	-173.030	-173.565	15.172
2600	13.838	91.520	30.861	-173.289	-173.583	14.590
2700	13.843	92.042	32.245	-173.550	-173.588	14.050
2800	13.848	92.546	33.629	-173.811	-173.594	13.419
2900	13.852	93.032	35.014	-174.072	-173.600	12.743
3000	13.856	93.501	36.399	-174.334	-173.605	12.147
3100	13.859	93.956	37.785	-174.599	-173.613	11.573
3200	13.862	94.396	39.171	-174.868	-173.621	11.034
3300	13.865	94.822	40.558	-175.139	-173.628	10.528
3400	13.868	95.236	41.945	-175.411	-173.635	10.051
3500	13.870	95.638	43.331	-175.684	-173.641	9.601
3600	13.872	96.029	44.718	-175.959	-173.647	9.177
3700	13.874	96.409	46.106	-176.236	-173.652	8.775
3800	13.876	96.779	47.493	-176.514	-173.657	8.393
3900	13.877	97.146	48.881	-176.792	-173.662	8.033
4000	13.880	97.491	50.269	-177.070	-173.667	7.689
4100	13.881	97.834	51.657	-177.349	-173.672	7.362
4200	13.883	98.168	53.045	-177.628	-173.677	7.051
4300	13.885	98.495	54.433	-177.907	-173.682	6.754
4400	13.887	98.817	55.821	-178.186	-173.687	6.473
4500	13.888	99.126	57.210	-178.465	-173.692	6.199
4600	13.887	99.431	58.599	-178.744	-173.697	5.939
4700	13.888	99.730	59.988	-179.023	-173.702	5.691
4800	13.889	100.023	61.377	-179.302	-173.707	5.453
4900	13.890	100.310	62.766	-179.581	-173.712	5.224
5000	13.891	100.590	64.155	-179.860	-173.717	5.004
5100	13.892	100.865	65.544	-180.139	-173.722	4.793
5200	13.892	101.134	66.933	-180.418	-173.727	4.590
5300	13.893	101.399	68.322	-180.697	-173.732	4.394
5400	13.894	101.664	69.711	-180.976	-173.737	4.206
5500	13.894	101.914	71.101	-181.255	-173.742	4.023
5600	13.895	102.164	72.491	-181.534	-173.747	3.849
5700	13.895	102.410	73.880	-181.813	-173.752	3.680
5800	13.896	102.652	75.270	-182.092	-173.757	3.516
5900	13.896	102.899	76.659	-182.371	-173.762	3.358
6000	13.897	103.143	78.049	-182.650	-173.767	3.200

Dec. 31, 1960; Sept. 30, 1964

Point Group [C_{2v}]
S°_{298.15} = [63.381] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹
[917](1)
[236](1)
[750](1)

Bond Distance: Al-F = [1.65] Å
Bond Angle: F-Al-F = [120°]
Product of the Moments of Inertia: I_AI_BI_C = [3.367909 X 10⁻¹¹⁵] g.³ cm.⁶
σ = 2

Heat of Formation.

The selected heat of formation, -165 ± 20 kcal. mole⁻¹ is the weighted average of two estimates (a) [-163 ± 20 kcal. mole⁻¹] and (b) [-175 ± 30 kcal. mole⁻¹]. The first estimate (a) is based upon appearance potentials reported by T. C. Ehlert and J. L. Margrave, J. Am. Chem. Soc. 86, 3901 (1964).

- (1) AlF₃(g) → AlF₂(ion) + F(g) 15.2 ± 0.3 e.v.
(2) AlF₃(ion) → AlF₂(g) -9 ± 1.8 e.v.
(3) (1) + (2) or AlF₃(g) → AlF₂(g) + F(g) 6.2 ± 1.3 e.v.

The second estimate (b) is based upon the average Al-F bond strength of AlF₃(g) and AlF(g), i.e.

$$(4) \text{AlF}_3(\text{g}) + \text{AlF}(\text{g}) \rightarrow 2 \text{AlF}_2(\text{g}) \quad \Delta H_{\text{r}}^{\circ} = 0$$

Heat Capacity and Entropy.

The bond distance, 1.65 Å, was estimated from a consideration of the Al-F distance 1.63 and 1.65 Å in AlF₃(g) and AlF(g). The bond configuration and bond angle estimates were based on the correlations of A. D. Walsh, J. Chem. Soc., 2266, (1953). From the molecular constants the principal moments of inertia were found to be I_A = 1.7829 X 10⁻³⁹, I_B = 12.8817 X 10⁻³⁹ g. cm.². The vibrational frequencies were calculated assuming valence forces, [G. Herzberg, "Molecular Spectra and Molecular Structure II", D. Van Nostrand Co., 1945] and using force constants calculated from AlF₃(g).

Aluminum Difluoride Unipositive Ion (AlF₂⁺)

(Ideal Gas) GFW = 64.9778

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ²⁹⁸)/T	H ^o -H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0							
100							
200							
298	12.335	57.799	57.799	.000	42.000	39.743	- 29.132
300	12.355	57.875	57.799	.023	42.007	39.728	- 29.942
400	13.161	61.553	56.295	1.303	42.415	38.509	- 21.239
500	13.667	64.533	54.236	2.648	42.819	37.264	- 16.603
600	14.008	67.079	60.355	4.034	43.211	36.980	- 13.470
700	14.221	69.255	61.474	5.447	43.584	35.911	- 11.212
800	14.368	71.164	62.569	6.876	43.927	34.791	- 9.505
900	14.473	72.863	63.620	8.319	44.229	33.631	- 8.167
1000	14.551	74.392	64.622	9.770	44.559	32.622	- 7.130
1100	14.609	75.782	65.574	11.228	44.863	31.674	- 6.293
1200	14.655	77.055	66.479	12.692	45.148	30.698	- 5.591
1300	14.690	78.230	67.338	14.159	45.407	29.696	- 4.992
1400	14.719	79.319	68.155	15.629	45.644	28.673	- 4.476
1500	14.742	80.336	68.934	17.103	45.872	27.628	- 4.025
1600	14.761	81.288	69.677	18.578	46.100	26.559	- 3.628
1700	14.777	82.183	70.386	20.055	46.319	25.475	- 3.275
1800	14.791	83.028	71.065	21.533	46.531	24.372	- 2.959
1900	14.802	83.828	71.716	23.013	46.735	23.255	- 2.675
2000	14.812	84.588	72.341	24.493	46.940	22.121	- 2.417
2100	14.820	85.310	72.941	25.975	47.146	20.970	- 2.182
2200	14.828	86.000	73.519	27.457	47.353	19.808	- 1.968
2300	14.834	86.659	74.076	28.941	47.561	18.634	- 1.771
2400	14.840	87.291	74.634	30.424	47.769	17.444	- 1.599
2500	14.845	87.897	75.133	31.908	47.974	16.245	- 1.440
2600	14.849	88.479	75.635	33.393	48.184	15.036	- 1.294
2700	14.853	89.039	76.122	34.878	48.392	13.816	- 1.118
2800	14.857	89.580	76.593	36.364	48.601	12.593	- 1.047
2900	14.860	90.101	77.049	37.850	48.810	11.366	- 1.106
3000	14.863	90.605	77.493	39.336	49.019	10.137	- 1.180
3100	14.865	91.092	77.924	40.822	49.228	8.901	- 1.269
3200	14.868	91.564	78.343	42.309	49.437	7.657	- 1.294
3300	14.870	92.022	78.750	43.796	49.646	6.413	- 1.295
3400	14.872	92.466	79.147	45.283	49.854	5.169	- 1.332
3500	14.873	92.897	79.534	46.770	50.062	3.925	- 1.367
3600	14.875	93.316	79.911	48.257	50.270	2.681	- 1.399
3700	14.877	93.723	80.279	49.745	50.478	1.437	- 1.427
3800	14.878	94.120	80.638	51.233	50.686	0.193	- 1.454
3900	14.879	94.507	80.989	52.720	50.894	- 1.059	- 1.479
4000	14.881	94.883	81.331	54.208	51.102	- 2.315	- 1.501
4100	14.882	95.251	81.666	55.697	51.310	- 3.571	- 1.522
4200	14.883	95.610	81.994	57.185	51.518	- 4.827	- 1.542
4300	14.884	95.960	82.315	58.673	51.726	- 6.083	- 1.559
4400	14.885	96.302	82.629	60.162	51.934	- 7.339	- 1.576
4500	14.885	96.636	82.936	61.650	52.142	- 8.595	- 1.591
4600	14.886	96.964	83.238	63.139	52.350	- 9.851	- 1.605
4700	14.887	97.284	83.533	64.627	52.558	- 11.107	- 1.617
4800	14.888	97.597	83.823	66.116	52.766	- 12.363	- 1.629
4900	14.888	97.904	84.107	67.605	52.974	- 13.619	- 1.640
5000	14.889	98.205	84.386	69.094	53.182	- 14.875	- 1.650
5100	14.889	98.500	84.660	70.583	53.390	- 16.131	- 1.659
5200	14.890	98.789	84.929	72.072	53.598	- 17.387	- 1.668
5300	14.890	99.073	85.193	73.561	53.806	- 18.643	- 1.675
5400	14.891	99.351	85.453	75.050	54.014	- 19.899	- 1.682
5500	14.891	99.624	85.708	76.539	54.222	- 21.155	- 1.689
5600	14.892	99.892	85.959	78.028	54.430	- 22.411	- 1.695
5700	14.892	100.156	86.206	79.517	54.638	- 23.667	- 1.701
5800	14.893	100.415	86.448	81.006	54.846	- 24.923	- 1.706
5900	14.893	100.667	86.687	82.495	55.054	- 26.179	- 1.710
6000	14.893	100.920	86.922	83.985	55.262	- 27.435	- 1.714

June 30, 1968

ALUMINUM DIFLUORIDE UNIPosITIVE ION (AlF₂⁺)

(IDEAL GAS)

GFW = 64.9778

Point Group [D_{∞h}]

ΔH_f^o = [42.3 ± 10] kcal/mol

AlF₂⁺

S_{298.15}^o = [57.8 ± 2.0] gibbs/mol

ΔH_f^o_{298.15} = [42 ± 10] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm⁻¹

(850) (1)

(240) (2)

(500) (1)

Bond Distance: Al-F = [1.7] Å

Bond Angle: F-Al-F = [180°]

Rotational Constant: B₀ = [0.1535] cm⁻¹

σ = 2

Heat of Formation

T. C. Ehlert, G. D. Blue, J. W. Green and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964) report the appearance potential of AlF₂⁺ from AlF₃ as 15.2 ± 0.3 eV. Assuming the reaction to be AlF₃(g) + e⁻ → AlF₂⁺ + F + 2e⁻ ΔH = 350.5 ± 7 kcal we calculate ΔH_f^o (AlF₂⁺, g) = 42 ± 10 kcal/mol, or an ionization potential for AlF₂ of 9 eV. Due to the neglect of any kinetic energy of the fragments this probably is an upper limit.

Heat Capacity and Entropy

The linear configuration is estimated from the correlation diagrams of A. D. Walsh, J. Chem. Soc. 2268 (1953), however, it should be noted that the isoelectronic MgF₂ is considered to be bent. The vibrational frequencies are estimated to lie between those for AlF₂ and MgF₂. The bond distance is estimated by comparison with AlF and AlF₃.

The enthalpy at 0°K is -2.883 kcal/mol.

AlF₂⁺

Aluminum Difluoride Uninegative Ion (AlF₂⁻)

(Ideal Gas)

GF_W = 64.9788

ALUMINUM DIFLUORIDE UNINEGATIVE ION (AlF₂⁻)
(IDEAL GAS)

GT_W = 84.9788

Point Group [C_{2v}]

ΔH_f⁰ = [-174.5 ± 40] kcal/mol

S_{298.15}⁰ = [61.4 ± 0.5] gibbs/mol

ΔH_f⁰_{298.15} = [-175 ± 40] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_e, cm⁻¹

[820] (1)

[320] (1)

[900] (1)

Bond Distance: [1.85] Å

Bond Angle: F-Al-F = [120°]

Product of the Moments of Inertia: I_AI_BI_C = [3.36 × 10^{-11.5}] g³ cm⁶ σ = 2

Heat of Formation

AlF₂⁻ is isoelectronic with SiF₂ and an estimate of its heat of formation may be obtained by assuming the binding energy to be the same; this yields ΔH_f⁰₂₉₈(AlF₂⁻, g) = -191 kcal/mol, or an electron affinity for AlF₂ of 28 kcal/mol.

The binding energy should be close to that of AlF₂ since the extra electron should go into a non-bonding orbital according to the correlation diagrams of A. D. Walsh, J. Chem. Soc. 2266 (1953); using this approach yields ΔH_f⁰₂₉₈(AlF₂⁻, g) = -177 kcal/mol or an electron affinity for AlF₂ of 12 kcal. Another method of estimation assumes that the heats are identical for the two reactions AlF₃ + AlF₂⁻ + F⁺ and AlF₂⁻ + F⁺ which yields ΔH_f⁰₂₉₈(AlF₂⁻, g) = -161 kcal/mol or an electron affinity for AlF₂ of -4 kcal.

We adopt a median value for the electron affinity for AlF₂ of 10 ± 20 kcal, which leads to ΔH_f⁰₂₉₈(AlF₂⁻, g) = -175 ± 40 kcal/mol when combined with ΔH_f⁰₂₉₈(AlF₂, g) = -165 ± 20 kcal/mol.

Heat Capacity and Entropy

According to the predictions of A. D. Walsh, loc. cit., there is no doubt that the molecule is bent; the bond length is assumed to lie between those of AlF and AlF₃, the angle is that in AlF₃. The vibrational frequencies are estimated between those for SiF₂ and AlF₂. By analogy with SiF₂ no low electronic levels are expected (G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York 1966).

The enthalpy at 0°K is -2.698 kcal/mol.

The individual principal moments of inertia are I_A = 1.783 × 10⁻³⁹ g cm², I_B = 12.882 × 10⁻³⁹ g cm² and I_C = 14.565 × 10⁻³⁹ g cm².

T, °K	C _p ⁰	gibbs/mol S ⁰	-(G ⁰ -H ²⁹⁸)/T	kcal/mol ΔH ⁰	ΔG ⁰	Log K _p
0						
100						
200						
298	10.702	61.427	61.427	.000	-175.000	128.546
300	10.722	61.493	61.427	.020	-175.014	127.755
400	11.624	61.859	61.859	1.335	-175.365	124.588
500	12.145	62.103	62.103	2.335	-175.500	121.575
600	12.462	62.266	62.266	3.082	-175.582	118.692
700	12.622	62.366	62.366	3.682	-175.622	115.929
800	12.748	62.420	62.420	4.163	-175.633	113.266
900	12.846	62.451	62.451	4.557	-175.638	110.699
1000	12.904	62.468	62.468	4.871	-175.638	108.219
1100	12.937	62.473	62.473	5.107	-175.632	105.822
1200	12.951	62.476	62.476	5.269	-175.622	103.505
1300	12.958	62.477	62.477	5.452	-175.609	101.266
1400	12.960	62.477	62.477	5.652	-175.594	99.105
1500	12.960	62.477	62.477	5.865	-175.577	97.019
1600	12.958	62.476	62.476	6.087	-175.558	95.005
1700	12.954	62.474	62.474	6.316	-175.537	93.061
1800	12.948	62.471	62.471	6.549	-175.514	91.184
1900	12.940	62.467	62.467	6.782	-175.489	89.371
2000	12.930	62.462	62.462	7.012	-175.462	87.619
2100	12.918	62.456	62.456	7.237	-175.433	85.925
2200	12.904	62.449	62.449	7.456	-175.401	84.286
2300	12.888	62.441	62.441	7.668	-175.366	82.699
2400	12.870	62.432	62.432	7.872	-175.329	81.161
2500	12.850	62.422	62.422	8.068	-175.290	79.669
2600	12.828	62.411	62.411	8.256	-175.249	78.221
2700	12.804	62.399	62.399	8.436	-175.206	76.814
2800	12.778	62.386	62.386	8.608	-175.161	75.446
2900	12.750	62.372	62.372	8.772	-175.114	74.114
3000	12.720	62.357	62.357	8.928	-175.065	72.814
3100	12.688	62.341	62.341	9.076	-175.014	71.542
3200	12.654	62.324	62.324	9.216	-174.961	70.296
3300	12.618	62.306	62.306	9.348	-174.906	69.074
3400	12.580	62.287	62.287	9.472	-174.849	67.874
3500	12.540	62.267	62.267	9.588	-174.790	66.694
3600	12.498	62.246	62.246	9.696	-174.729	65.532
3700	12.454	62.224	62.224	9.796	-174.666	64.386
3800	12.408	62.201	62.201	9.888	-174.601	63.254
3900	12.360	62.177	62.177	9.972	-174.534	62.134
4000	12.310	62.152	62.152	10.048	-174.465	61.024
4100	12.258	62.126	62.126	10.116	-174.394	59.932
4200	12.204	62.099	62.099	10.176	-174.321	58.856
4300	12.148	62.071	62.071	10.228	-174.246	57.794
4400	12.090	62.042	62.042	10.272	-174.169	56.744
4500	12.030	62.012	62.012	10.308	-174.090	55.704
4600	11.968	61.981	61.981	10.336	-174.009	54.674
4700	11.904	61.949	61.949	10.356	-173.926	53.652
4800	11.838	61.916	61.916	10.368	-173.841	52.636
4900	11.770	61.882	61.882	10.372	-173.754	51.624
5000	11.700	61.847	61.847	10.368	-173.665	50.614
5100	11.628	61.811	61.811	10.356	-173.574	49.604
5200	11.554	61.774	61.774	10.336	-173.481	48.594
5300	11.478	61.736	61.736	10.308	-173.386	47.584
5400	11.399	61.697	61.697	10.272	-173.289	46.574
5500	11.318	61.657	61.657	10.228	-173.190	45.564
5600	11.234	61.616	61.616	10.176	-173.089	44.554
5700	11.148	61.573	61.573	10.116	-172.986	43.544
5800	11.060	61.528	61.528	10.048	-172.881	42.534
5900	10.969	61.481	61.481	9.972	-172.774	41.524
6000	10.875	61.432	61.432	9.888	-172.665	40.514

June 30, 1968

AlF₂⁻

Aluminum Trifluoride (AlF₃)

(Crystal)

GFW = 83.9767

AlF₃ALUMINUM TRIFLUORIDE (AlF₃)

(CRYSTAL)

GFW = 83.9767

$\Delta H_f^\circ = -359.5 \pm 0.3 \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = -361.0 \pm 0.3 \text{ kcal/mol}$
 $\Delta H_t^\circ = 0.1346 \text{ kcal/mol}$
 $\Delta H_s^\circ_{298.15} = 71.865 \pm 0.5 \text{ kcal/mol monomer}$
 $\Delta H_s^\circ_{298.15} = 92.55 \pm 4 \text{ kcal/mol dimer}$

$S^\circ_{298.15} = 15.89 \pm 0.1 \text{ gibbs/mol}$
 $T_t = 728^\circ\text{K}$
 $T_s = [1549]^\circ\text{K}$

Heat of Formation

The adopted value is from separate calorimetric studies of combustion in fluorine of aluminum (1) and aluminum-Teflon mixtures (2). More extensive auxiliary data (2) for Teflon bring the aluminum-Teflon study into exact agreement with the aluminum study (1). Calorimetric data relating AlF₃ to PbF₂ (1, 2) tend to confirm this value, but PbF₂ is probably more uncertain than is AlF₃.

Solid-state emf data (4) relating AlF₃ to HgF₂ via ThF₄ gave $\Delta G_f^\circ = -305.7 \text{ kcal/mol}$ for AlF₃(c) at 600°C. The adopted negative value indicated by entrainment data (3) for 2/3 AlF₃(c) + 1/3 Al₂O₃(c) + 2HF(g) in the range from 849° to 1312°K. Analysis of the equilibrium constants yields $\Delta H^\circ_{298.15} = 33.11 \pm 0.2 \text{ kcal/mol}$ (3rd law) and $33.33 \pm 0.22 \text{ kcal/mol}$ (2nd law) with an insignificant entropy difference, $\Delta S^\circ(2\text{nd law}) - \Delta S^\circ(3\text{rd law}) = 0.2 \pm 0.2 \text{ gibbs/mol}$. It has been suggested (1) that interaction of the condensed phases caused the equilibria to deviate from the standard-state reaction assumed above. An alternative may be that the reaction with water vapor produced Al₂O₃ in a metastable form; such forms require ignition temperatures greater than 1400°K for complete conversion to $\alpha\text{-Al}_2\text{O}_3$ (g).

Heat Capacity and Entropy

C_p° and S°_{298} are taken from Douglas and Dittmars (7), whose tables are based on heat capacity measurements from 54° to 298°K (g) and relative enthalpy measurements from 323° to 1173°K (7). The enthalpy data confirm earlier data (401°-1401°K) of O'Brien and Kelley (8) rather than the adjusted values proposed by Frank (10). Douglas and Dittmars (7) gave a detailed comparison with other data. The entropy is derived from C_p° using the extrapolation $S^\circ_{50} = 0.53 \pm 0.06 \text{ gibbs/mol}$.

Transition Data

T_t and ΔH_t° are from Douglas and Dittmars (7). The values were obtained from extensive enthalpy data for the transition region assuming the presence of a very small amount of impurity in solid solution.

Sublimation Data

T_s is the temperature at which the calculated total pressure (monomer plus dimer) reaches one atm; the mole fraction of dimer is calculated as 0.109 at T_s . Sublimation temperatures of 1533° and 1566°K were obtained in two sublimation-pressure studies (11, 22) at the Technische Hochschule, Breslau. The selected enthalpies of sublimation to AlF₃(g) and Al₂F₆(g) reproduce closely the entrainment data of Krause and Douglas (13). Selection of these values of ΔH_s° and comparisons with other vapor-pressure data are discussed on the gas-phase tables.

References

1. E. Rudzitis, H. M. Feder and W. N. Hubbard, *Inorg. Chem.*, **6**, 1716 (1967).
2. E. S. Domalski and G. T. Armstrong, *J. Res. Nat. Bur. Stand.*, **71A**, 105 (1967); **69A**, 137 (1965).
3. The JANAF Thermochemical Table for PbF₂(c), June 30, 1969.
4. R. J. Heus and J. J. Egan, *Z. Phys. Chem. (Frankfurt)*, **219**, 38 (1966).
5. V. P. Mashovets and B. F. Yudin, *Izv. Vyssh. Ucheb. Zaved.*, Tsvet. Met. **5** (4), 95 (1962).
6. T. Yokokawa and O. J. Kleppa, *J. Phys. Chem.*, **68**, 3246 (1964).
7. T. B. Douglas and D. A. Dittmars, *J. Res. Nat. Bur. Stand.*, **71A**, 185 (1967).
8. E. G. King, *J. Amer. Chem. Soc.*, **79**, 2036 (1957).
9. C. J. O'Brien and K. K. Kelley, *J. Amer. Chem. Soc.*, **79**, 5616 (1957).
10. W. B. Frank, *J. Phys. Chem.*, **65**, 2081 (1961).
11. O. Ruff and L. LeBoucher, *Z. Anorg. Allg. Chem.*, **219**, 376 (1934).
12. W. Olbrich, *Dissertation*, Technische Hochschule, Breslau, 1928.
13. R. F. Krause and T. B. Douglas, *J. Phys. Chem.*, **72**, 475 (1968).

Dec. 31, 1960; Sept. 30, 1963; Sept. 30, 1965; June 30, 1970

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	5.959	2.882	2.882	2.778	-359.519	-359.519	1.716
200	13.594	6.558	17.403	2.576	-360.465	-354.484	774.725
300	17.957	15.890	15.890	1.569	-360.951	-348.285	380.587
400	20.623	21.581	16.001	-0.33	-360.999	-341.936	249.100
500	22.054	26.349	16.112	1.979	-360.807	-335.604	183.365
600	23.258	30.472	19.636	4.119	-360.509	-329.338	143.953
700	24.244	34.084	23.419	6.262	-360.153	-323.136	117.029
800	25.066	37.283	26.419	8.331	-359.781	-317.093	90.962
900	25.763	40.073	28.419	10.331	-359.388	-311.211	65.296
1000	26.369	42.498	30.419	12.300	-358.888	-305.491	40.747
1100	26.903	44.597	32.419	14.250	-358.288	-299.926	26.404
1200	27.383	46.337	34.419	16.187	-357.596	-294.515	12.123
1300	27.823	47.767	36.419	18.115	-356.826	-289.255	7.710
1400	28.231	48.944	38.419	20.037	-355.986	-284.146	3.246
1500	28.613	50.000	40.419	21.956	-355.086	-279.186	-0.274
1600	28.973	51.044	42.419	23.873	-354.136	-274.376	-0.841
1700	29.313	52.076	44.419	25.789	-353.146	-269.716	-1.386
1800	29.633	53.100	46.419	27.706	-352.116	-265.206	-1.916
1900	29.933	54.116	48.419	29.623	-351.046	-260.846	-2.436
2000	30.213	55.126	50.419	31.540	-349.936	-256.636	-2.946
2100	30.473	56.131	52.419	33.457	-348.786	-252.576	-3.446
2200	30.713	57.131	54.419	35.374	-347.596	-248.666	-3.936
2300	30.933	58.126	56.419	37.291	-346.366	-244.906	-4.416
2400	31.133	59.116	58.419	39.208	-345.096	-241.296	-4.886
2500	31.313	60.101	60.419	41.125	-343.786	-237.836	-5.346

ALUMINUM TRIFLUORIDE (AlF₃)

(IDEAL GAS)

GFW = 83.9767

Point Group D_{3h}
 $S_{298.15}^\circ = 66.15 \pm 0.2$ gibbs/mol
 Ground State Quantum Weight = 1

$\Delta H_f^\circ = -288.14 \pm 0.6$ kcal/mol
 $\Delta H_f^\circ = -289.03 \pm 0.6$ kcal/mol

Aluminum Trifluoride (AlF₃)

(Ideal Gas)

GFW = 83.9767

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	Log Kp
0	0.000	INFINITE	-	3.368	-288.144	INFINITE
100	0.000	59.000	66.150	3.368	-288.144	312.687
200	12.924	60.591	67.552	3.373	-288.730	312.687
298	14.945	66.150	68.150	0.000	-289.035	208.964
300	14.977	66.283	68.151	0.028	-289.039	207.658
400	15.409	66.750	68.151	1.401	-289.220	155.000
500	17.352	74.530	69.945	3.292	-289.508	123.308
600	17.945	77.753	69.318	5.061	-289.508	102.303
700	18.418	80.560	70.727	6.883	-289.448	87.235
800	18.723	83.040	72.115	8.741	-289.806	75.994
900	18.943	85.259	73.544	10.624	-289.999	67.128
1000	19.107	87.136	74.736	12.527	-292.156	60.444
1100	19.232	89.091	75.960	14.445	-292.936	54.274
1200	19.329	90.769	77.125	16.373	-293.112	49.374
1300	19.406	92.319	78.235	18.310	-293.288	45.266
1400	19.468	93.760	79.293	20.254	-293.463	41.743
1500	19.516	95.103	80.302	22.212	-293.635	38.752
1600	19.560	96.365	81.267	24.157	-293.817	36.014
1700	19.594	97.552	82.191	26.115	-293.995	33.652
1800	19.624	98.673	83.074	28.076	-294.175	31.559
1900	19.649	99.735	83.925	30.039	-294.357	29.671
2000	19.670	100.743	84.741	32.000	-294.540	27.978
2100	19.688	101.703	85.526	33.973	-294.726	26.445
2200	19.704	102.620	86.289	35.943	-294.915	25.050
2300	19.718	103.496	87.012	37.914	-295.105	23.776
2400	19.731	104.335	87.716	39.886	-295.298	22.607
2500	19.742	105.141	88.397	41.860	-295.495	21.531
2600	19.751	105.916	89.056	43.835	-295.694	20.537
2700	19.760	106.661	89.694	45.810	-295.895	19.617
2800	19.766	107.380	90.313	47.787	-296.098	18.696
2900	19.775	108.074	90.914	49.764	-296.303	17.792
3000	19.781	108.744	91.497	51.742	-296.510	16.915
3100	19.787	109.393	92.064	53.720	-296.721	15.936
3200	19.792	110.021	92.615	55.699	-296.935	14.936
3300	19.797	110.630	93.152	57.678	-297.151	13.911
3400	19.801	111.221	93.675	59.658	-297.368	12.864
3500	19.805	111.795	94.184	61.639	-297.586	11.793
3600	19.809	112.353	94.681	63.619	-297.804	10.709
3700	19.812	112.896	95.166	65.600	-298.024	9.619
3800	19.815	113.425	95.640	67.582	-298.245	8.531
3900	19.818	113.939	96.103	69.563	-298.466	7.451
4000	19.821	114.441	96.555	71.545	-298.688	6.384
4100	19.823	114.931	96.997	73.527	-298.910	5.331
4200	19.825	115.408	97.430	75.510	-299.132	4.294
4300	19.827	115.875	97.853	77.492	-299.354	3.271
4400	19.829	116.331	98.268	79.475	-299.576	2.264
4500	19.831	116.776	98.674	81.458	-299.797	1.277
4600	19.833	117.212	99.073	83.442	-299.998	0.312
4700	19.835	117.639	99.463	85.425	-300.199	-0.719
4800	19.836	118.056	99.846	87.408	-300.399	-1.754
4900	19.838	118.465	100.222	89.392	-300.599	-2.799
5000	19.839	118.866	100.591	91.376	-300.799	-3.854
5100	19.841	119.259	100.953	93.360	-300.999	-4.919
5200	19.841	119.644	101.309	95.344	-301.199	-5.994
5300	19.842	120.022	101.658	97.328	-301.399	-7.079
5400	19.844	120.393	101.992	99.312	-301.599	-8.174
5500	19.846	120.757	102.340	101.297	-301.799	-9.279
5600	19.846	121.115	102.672	103.281	-301.999	-10.394
5700	19.846	121.466	102.998	105.266	-302.199	-11.519
5800	19.847	121.811	103.320	107.251	-302.399	-12.644
5900	19.848	122.151	103.636	109.235	-302.599	-13.769
6000	19.849	122.484	103.947	111.220	-302.799	-14.894

Dec. 31, 1980; Sept. 30, 1983; Sept. 30, 1986; June 30, 1970

Heat of Formation

ΔH_f° is calculated from that of the crystal by use of $\Delta H_{298.15}^\circ = 71.965 \pm 0.5$ kcal/mol. Sublimation studies by mass-spectrometric and entrainment techniques suggest the presence of a small amount of dimer in the saturated vapor. These studies are reviewed on the table for Al₂F₆(g). $\Delta H_{298.15}^\circ$ and $\Delta H_{298.15}^\circ$ are calculated by adopting (a) the JANAF entropies for crystal, monomer and dimer, (b) the mass spectrometric value of 2 $\Delta H_{298.15}^\circ$ (monomer) and $\Delta H_{298.15}^\circ$ (dimer), and (c) the entrainment data of Krause and Douglas (1). The resulting calculated pressures deviate by <0.5% from the entrainment data (1), by <0.1% from the mass-spectrometric equation (3) and by <3% from the mass-effusion equation (4).

Further comparisons with experimental data are given below. The adopted values favor the later (11) of two sublimation-point studies (11, 12); both show considerable scatter and smaller deviations from the calculated dP/dT . Torsion-effusion data suggest the possibility of more serious discrepancy. Although data of Witt and Barrow (3) are consistent with the JANAF pressures, Hildenbrand et al. (2, g) noted a trend toward increasing pressure with decreasing orifice area. They concluded (2) that the condensation coefficient <0.06, based on eightfold variation in the product of Clausius factor $\times$ orifice area. JANAF predictions for the pressure are 60 to 80% of the adjusted torsion values (2) and the discrepancy corresponds roughly to the ratios used in the adjustment. In contrast, the JANAF predictions agree closely with mass-effusion data of Ko et al. (4), who reported no significant effect from a twelvefold variation in orifice area.

Comparison of Calculated and Observed Total Pressures over AlF₃(c)

	T, °K	Method	Range	Calc. Range	Calc./Pobs	Difference ^a in dP/dT
(1) Krause (1968)		Entrainment	1194-1258	0.019-0.029	1.004-0.986	Very small (-)
(2) Naryshkin (1939)		Entrainment	1108-1273	0.010-0.032	0.73-2.22	Uncertain (?)
(3) Erokhin (1967)		Mass Spec. ^b	983-1165	0.003-0.016	1.09-0.91	Small (-)
(4) Ko (1965)		Mass Effusion	1027-1184	0.003-0.018	0.994-0.972	Very small (-)
(5) Blackburn (1965)		Mass Effusion	889-1006	0.001-0.004	1.42-1.66	Uncertain (+)
(6) Evans (1959)		Mass Effusion	980-1123	0.003-0.012	1.64-0.88	Large (-)
(7) Hildenbrand (1963)		Torsion Effusion ^c				
		Cell Gr-22	1004-1114	0.004-0.011	0.67-0.74	Very small (?)
		Cell Gr-7	989-1102	0.004-0.010	0.60-0.81	Medium (+)
		Cell Gr-9	972-1088	0.003-0.009	0.63-0.73	Small (+)
		Cell Gr-9	972-1088	0.003-0.009	0.60-0.72	Small (+)
		Cell Gr-12	949-1087	0.002-0.007	0.49-0.74	Medium (+)
(8) Hildenbrand (1961)		Torsion Effusion				
		Cell Gr-7	992-1101	0.004-0.010	0.89-1.01	Small (+)
		Cell Gr-9	938-1080	0.002-0.008	0.94-1.34	Medium (+)
(9) Witt (1959)		Torsion Effusion	955-1063	0.003-0.007	1.11-1.07	Small (-)
(10) Vetyukov (1959)		Dynamic B. P.	1335-1453	0.044-0.076	0.84-1.64	Large (+)
(11) Ruff (1934)		Dynamic B. P.	1367-1524	0.052-0.100	1.33-0.79	Large (-)
(12) Olbrich (1928)		Dynamic B. P.	1371-1567	0.053-0.116	2.70-1.28	Large (-)

^a Magnitude and sign of the difference, calculated minus observed, in dP/dT . ^b Absolute pressures of monomer were obtained by integration of the ion intensity during total sublimation. ^c Based on P calculated from the torsion pressure Pt by the equation given.

Heat Capacity and Entropy

The molecular structure is that derived from electron-diffraction data by Akishin et al. (13). Observed vibrational frequencies are those reported by Büchler et al. (14) from infrared spectra of the vapor at 1000-1200°K. These frequencies are confirmed by infrared spectra of AlF₃ isolated in matrices of neon, argon and krypton (15). The Raman-active fundamental ν_1 is estimated as 650 ± 50 cm⁻¹ by three methods: (a) calculation of the force constant k_1 from ν_3 and ν_4 ; (b) comparison of $k_1(XY)/k(XY)$ for X = B, Al and Y = F, Cl and Br; and (c) extrapolation of ν_1 (BY₃) to Y = F from Y = Cl, Br and I, using recent gas-phase Raman data (16) for AlY₃. Principal moments of inertia are $I_A = 12.572 \times 10^{-39}$ and $I_C = 25.14 \times 10^{-39}$ g cm².

References

1. I. Naryshkin, Zh. Fiz. Khim., **13**, 159 (1939).
2. E. V. Erokhin, N. A. Zhegul'skaya, L. N. Sidorov and P. A. Akishin, Izv. Akad. Nauk SSSR, **Moorg. Mater.**, **3** (5), 873 (1967).
3. H. C. Ko, H. A. Greenbaum, J. A. Blauer and M. Farber, J. Phys. Chem., **69**, 2311 (1965).
4. F. E. Blackburn, OAK Final Report, A. D. Little, Inc., May 31, 1965.
5. A. H. Eiselev, G. V. Pozharovskaya, An. N. Nemesyanov and Ya. I. Gerasimov, Zh. Neorg. Khim., **4**, 2136 (1959).
6. D. L. Hildenbrand, J. Chem. Phys., **33**, 1030 (1960).
7. D. L. Hildenbrand and L. F. Thieard, **Ad 25810**, 24 pp (1961).
8. M. P. Witt and R. F. Barrow, Trans. Faraday Soc., **55**, 730 (1959).
9. M. M. Vetyukov, M. L. Blyustein and V. P. Podymov, Izv. Vyssh. Ucheb. Zaved., **126** (1959).
10. O. Ruff and L. La Boucher, Z. Anorg. Allg. Chem., **213**, 376 (1934).
11. P. A. Akishin, Disertatsiya, Khimicheskoe Nauchnoye, Leningrad, 1928.
12. P. A. Akishin, Zh. Fiz. Khim., **2**, 186 (1928).
13. A. Büchler, E. P. Hargrave and J. L. Stauffer, J. Phys. Chem., **72**, 4139 (1967).
14. A. Snelson, J. Phys. Chem., **72**, 3202 (1967).
15. I. R. Beattie and J. R. Hordar, J. Chem. Soc. **A1963**, 2655.

Point Group $[C_{2v}]$ $\Delta H_f^\circ = -441.3 \pm 2 \text{ kcal/mol}$ $\Delta H_f^\circ = -443.0 \pm 2 \text{ kcal/mol}$ $S_{298.15}^\circ = [78.46] \pm 2 \text{ gibbs/mol}$

Ground State Quantum Weight = [1]

Lithium Tetrafluoroaluminate (LiAlF₄)

(Ideal Gas)

GFW = 109.9141

T, °K	Cp°	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔG°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	12.693	58.525	94.759	-4.755	-441.336	-439.336	INFINITE
200	19.601	69.682	80.545	-3.629	-439.336	-437.336	960.290
298	24.102	78.463	70.463	-2.537	-439.336	-435.336	476.992
300	24.163	78.612	70.466	-2.537	-439.336	-435.336	476.992
400	26.718	85.946	70.466	-2.537	-439.336	-435.336	315.699
500	28.243	92.066	81.377	-5.354	-439.336	-435.336	238.997
600	29.494	97.322	84.610	-8.230	-439.336	-435.336	194.524
700	30.429	101.922	86.603	-11.630	-439.336	-435.336	154.164
800	30.251	105.889	88.154	-14.184	-439.336	-435.336	113.093
900	30.056	109.670	89.427	-17.229	-439.336	-435.336	73.697
1000	30.760	112.702	92.407	-20.296	-439.336	-435.336	36.359
1100	30.949	115.648	94.384	-23.383	-439.336	-435.336	80.064
1200	31.080	118.544	96.275	-26.485	-439.336	-435.336	71.056
1300	31.193	120.835	98.067	-29.598	-439.336	-435.336	66.783
1400	31.265	122.849	99.777	-32.721	-439.336	-435.336	61.404
1500	31.332	124.508	101.407	-35.851	-439.336	-435.336	56.741
1600	31.387	125.932	102.945	-38.987	-439.336	-435.336	52.460
1700	31.432	127.236	104.455	-42.124	-439.336	-435.336	48.496
1800	31.471	128.434	105.945	-45.273	-439.336	-435.336	44.834
1900	31.504	129.536	107.421	-48.422	-439.336	-435.336	41.345
2000	31.532	130.553	108.866	-51.573	-439.336	-435.336	38.065
2100	31.554	131.592	109.831	-54.728	-439.336	-435.336	34.950
2200	31.577	132.640	110.819	-57.885	-439.336	-435.336	32.077
2300	31.595	133.764	111.828	-61.043	-439.336	-435.336	29.464
2400	31.611	134.869	112.858	-64.203	-439.336	-435.336	27.004
2500	31.626	135.954	113.914	-67.365	-439.336	-435.336	24.680
2600	31.638	137.024	114.984	-70.529	-439.336	-435.336	22.390
2700	31.646	138.076	116.064	-73.693	-439.336	-435.336	20.144
2800	31.650	139.116	117.157	-76.858	-439.336	-435.336	17.944
2900	31.659	140.197	118.260	-80.025	-439.336	-435.336	15.784
3000	31.677	141.271	119.380	-83.192	-439.336	-435.336	13.664
3100	31.684	142.316	120.520	-86.360	-439.336	-435.336	11.584
3200	31.689	143.336	121.679	-89.528	-439.336	-435.336	9.544
3300	31.697	144.336	122.859	-92.696	-439.336	-435.336	7.544
3400	31.703	145.316	124.041	-95.864	-439.336	-435.336	5.584
3500	31.708	146.276	125.229	-99.032	-439.336	-435.336	3.664
3600	31.713	147.216	126.424	-102.200	-439.336	-435.336	1.784
3700	31.717	148.136	127.624	-105.368	-439.336	-435.336	0.944
3800	31.721	149.036	128.824	-108.536	-439.336	-435.336	0.544
3900	31.725	149.916	129.996	-111.704	-439.336	-435.336	0.344
4000	31.728	150.776	131.156	-114.872	-439.336	-435.336	0.244
4100	31.731	151.616	132.304	-118.040	-439.336	-435.336	0.184
4200	31.734	152.436	133.444	-121.208	-439.336	-435.336	0.144
4300	31.737	153.236	134.576	-124.376	-439.336	-435.336	0.114
4400	31.740	154.016	135.704	-127.544	-439.336	-435.336	0.084
4500	31.742	154.776	136.824	-130.712	-439.336	-435.336	0.064
4600	31.744	155.516	137.936	-133.880	-439.336	-435.336	0.044
4700	31.747	156.236	139.044	-137.048	-439.336	-435.336	0.024
4800	31.749	156.936	140.144	-140.216	-439.336	-435.336	0.014
4900	31.750	157.616	141.236	-143.384	-439.336	-435.336	0.004
5000	31.751	158.276	142.316	-146.552	-439.336	-435.336	0.004
5100	31.752	158.916	143.384	-149.720	-439.336	-435.336	0.004
5200	31.753	159.536	144.444	-152.888	-439.336	-435.336	0.004
5300	31.754	160.136	145.496	-156.056	-439.336	-435.336	0.004
5400	31.755	160.716	146.536	-159.224	-439.336	-435.336	0.004
5500	31.756	161.276	147.564	-162.392	-439.336	-435.336	0.004
5600	31.757	161.816	148.584	-165.560	-439.336	-435.336	0.004
5700	31.758	162.336	149.596	-168.728	-439.336	-435.336	0.004
5800	31.759	162.836	150.596	-171.896	-439.336	-435.336	0.004
5900	31.760	163.316	151.584	-175.064	-439.336	-435.336	0.004
6000	31.761	163.776	152.564	-178.232	-439.336	-435.336	0.004
6100	31.762	164.216	153.536	-181.400	-439.336	-435.336	0.004
6200	31.763	164.636	154.496	-184.568	-439.336	-435.336	0.004
6300	31.764	165.036	155.444	-187.736	-439.336	-435.336	0.004
6400	31.765	165.416	156.376	-190.904	-439.336	-435.336	0.004
6500	31.766	165.776	157.296	-194.072	-439.336	-435.336	0.004
6600	31.767	166.116	158.204	-197.240	-439.336	-435.336	0.004
6700	31.768	166.436	159.096	-200.408	-439.336	-435.336	0.004
6800	31.769	166.736	159.976	-203.576	-439.336	-435.336	0.004
6900	31.770	167.016	160.844	-206.744	-439.336	-435.336	0.004
7000	31.771	167.276	161.696	-209.912	-439.336	-435.336	0.004
7100	31.772	167.516	162.536	-213.080	-439.336	-435.336	0.004
7200	31.773	167.736	163.364	-216.248	-439.336	-435.336	0.004
7300	31.774	167.936	164.176	-219.416	-439.336	-435.336	0.004
7400	31.775	168.116	164.976	-222.584	-439.336	-435.336	0.004
7500	31.776	168.276	165.764	-225.752	-439.336	-435.336	0.004
7600	31.777	168.416	166.536	-228.920	-439.336	-435.336	0.004
7700	31.778	168.536	167.296	-232.088	-439.336	-435.336	0.004
7800	31.779	168.636	168.044	-235.256	-439.336	-435.336	0.004
7900	31.780	168.716	168.776	-238.424	-439.336	-435.336	0.004
8000	31.781	168.776	169.496	-241.592	-439.336	-435.336	0.004
8100	31.782	168.816	170.204	-244.760	-439.336	-435.336	0.004
8200	31.783	168.836	170.896	-247.928	-439.336	-435.336	0.004
8300	31.784	168.846	171.576	-251.096	-439.336	-435.336	0.004
8400	31.785	168.846	172.244	-254.264	-439.336	-435.336	0.004
8500	31.786	168.836	172.896	-257.432	-439.336	-435.336	0.004
8600	31.787	168.816	173.536	-260.600	-439.336	-435.336	0.004
8700	31.788	168.776	174.164	-263.768	-439.336	-435.336	0.004
8800	31.789	168.716	174.776	-266.936	-439.336	-435.336	0.004
8900	31.790	168.636	175.376	-270.104	-439.336	-435.336	0.004
9000	31.791	168.536	175.964	-273.272	-439.336	-435.336	0.004
9100	31.792	168.416	176.544	-276.440	-439.336	-435.336	0.004
9200	31.793	168.276	177.104	-279.608	-439.336	-435.336	0.004
9300	31.794	168.116	177.644	-282.776	-439.336	-435.336	0.004
9400	31.795	167.936	178.164	-285.944	-439.336	-435.336	0.004
9500	31.796	167.736	178.664	-289.112	-439.336	-435.336	0.004
9600	31.797	167.516	179.144	-292.280	-439.336	-435.336	0.004
9700	31.798	167.276	179.604	-295.448	-439.336	-435.336	0.004
9800	31.799	167.016	180.044	-298.616	-439.336	-435.336	0.004
9900	31.800	166.736	180.464	-301.784	-439.336	-435.336	0.004
10000	31.801	166.436	180.864	-304.952	-439.336	-435.336	0.004

Sept. 30, 1962; Sept. 30, 1963; Dec. 31, 1963; Mar. 31, 1964; June 30, 1970

Vibrational Pre-energies and Degeneracies
 ω, cm^{-1} ω, cm^{-1} ω, cm^{-1} ω, cm^{-1}

800 (1)	[300] (1)	555 (1)	890 (1)
665 (1)	[195] (1)	450 (1)	330 (1)
[560] (1)	[180] (1)	240 (1)	285 (1)

Bond Distance: Al-F = [1.69] Å Li-F = [1.8] Å

Bond Angle: F-Al-F = [109.47°]

Product of the Moments of Inertia: $I_{ABC} = [2.0109 \times 10^{-11}] \text{ g}^2 \text{ cm}^2$

Heat of Formation

Mass spectrometric studies (1) of the two-phase systems LiF + Li₃AlF₆ and Li₃AlF₆ + AlF₃ suggested that the vapor contains small amounts of Li₂AlF₅ and Li₂(AlF₄)₂, but that LiAlF₄(g) constitutes of the order of 90%. Hildenbrand et al. (2) reported torsion effusion pressures for the compositions 3LiF·AlF₃ and LiF·AlF₃, as a first approximation, these total pressures should correspond to the reactions (A) Li₃AlF₆(g) = LiAlF₄(g) + 2LiF(g), and (B) 1/3 Li₃AlF₆(g) + 2/3 AlF₃(g) = LiAlF₄(g). Porter and Zeller (3) reported mass spectrometric equilibrium constants for the reaction (C) Li₂F₂ + AlF₃(g) = LiF(g) + LiAlF₄(g). Second-order and third-law analyses of these data are summarized below. Kumann and Tillessen (4) reported total vapor pressures over molten LiAlF₄·3H₂O (0.81 ≤ n ≤ 3), but we have made no attempt to establish the liquid phase activities necessary for use of these data.

The adopted ΔH_f is derived from reaction (B) which exhibits entropy deviations (68) and on the other area effects which are relatively minor. Data for reaction (A) yield a ΔH_f that is more negative by 1.5 kcal/mol, but the very large entropy deviation suggests the presence of systematic uncertainties. Combination of (B) and (A) into the reaction 3LiF(g) + AlF₃(g) + Li₃AlF₆(g) gives ΔH_f = -3.3 kcal/mol, which is fairly consistent with the calorimetric value (5) of ΔH_f = -5.4 ± 0.5 kcal/mol. Sidorov and Kolosov (6) suggested that the equilibrium constants for reaction (C) should be considered as lower limits since AlF₃ and LiAlF₄ are probably both precursors of AlF₂.

Reaction	Source	Method	Range T, °K	ΔS gibbs/mol	ΔH _f ^o kcal/mol	ΔH _f ^o kcal/mol
(1) Hildenbrand (1963)	A	Torsion effusion, Cell 7	987-1058	33 ± 1	103.3 ± 1.5	69.33
(2) Hildenbrand (1963)	B	Torsion effusion, Cell 9	899-980	74.3 ± 1.8	74.3 ± 1.8	-443.1 ± 2
(3) Porter (1960)	C	Torsion effusion, Cell 15X	873-976	2.7 ± 0.5	69.9 ± 0.5	67.35
		Mass spectrometry	1000-1100	4 ± 5	69.6 ± 0.9	67.48
					-1 ± 5	-438.4 ± 6

Heat Capacity and Entropy

The point group and molecular structure are assumed to be similar to those adopted for NaAlF₄. A discussion of the incomplete structural evidence is given on the table for NaAlF₄(g). The adopted structure consists of tetrahedral Al

Sodium Tetrafluoroaluminate (NaAlF₄)
(Ideal Gas) GFW = 125.9649

T, °K	C _p ^a	S ^b	(C _p ^a - H ^c)/T	H ^c - H ²⁹⁸	ΔH ^c	Log K _p
0	16.000	60.700	102.326	-5.158	-484.903	10.714
100	16.122	60.700	102.326	-4.85.723	-442.920	9.66.100
200	21.613	84.778	89.566	-4.46.311	-439.869	480.466
298	25.311	82.566	89.566	-4.46.400	-436.643	320.064
300	25.383	82.723	89.566	-4.46.404	-436.562	316.049
400	28.524	90.346	85.590	-4.47.597	-429.572	169.766
500	30.691	96.638	85.590	-4.47.597	-429.572	169.766
600	29.601	101.963	87.886	-4.47.714	-425.955	155.154
700	30.127	106.569	90.234	-4.47.823	-422.320	131.854
800	30.489	110.616	92.534	-4.47.935	-418.670	111.375
900	30.746	114.473	94.860	-4.48.046	-415.016	91.854
1000	30.938	117.478	96.860	-4.48.157	-411.337	69.854
1100	31.079	120.428	98.870	-4.48.271	-407.167	60.897
1200	31.189	123.138	100.781	-4.48.302	-402.725	73.346
1300	31.276	125.638	102.598	-4.48.340	-398.169	66.702
1400	31.345	127.958	104.298	-4.48.378	-393.504	59.107
1500	31.402	130.123	105.976	-4.48.419	-388.850	50.1073
1600	31.449	132.151	107.549	-4.48.462	-384.202	51.756
1700	31.487	134.058	109.053	-4.48.507	-379.564	51.756
1800	31.520	135.859	110.493	-4.48.554	-374.935	51.756
1900	31.548	137.566	111.968	-4.48.601	-370.311	51.756
2000	31.572	139.193	113.478	-4.48.649	-365.691	51.756
2100	31.592	140.724	114.974	-4.48.697	-361.074	51.756
2200	31.610	142.194	116.462	-4.48.746	-356.461	51.756
2300	31.625	143.599	117.942	-4.48.795	-351.849	51.756
2400	31.639	144.948	119.418	-4.48.844	-347.237	51.756
2500	31.651	146.238	119.727	-4.48.892	-342.625	51.756
2600	31.662	147.479	120.193	-4.48.940	-338.013	51.756
2700	31.672	148.679	121.226	-4.48.988	-333.401	51.756
2800	31.680	149.826	122.227	-4.49.036	-328.789	51.756
2900	31.688	150.926	123.194	-4.49.084	-324.177	51.756
3000	31.695	152.012	124.141	-4.49.131	-319.565	51.756
3100	31.701	153.052	125.057	-4.49.178	-314.953	51.756
3200	31.707	154.058	125.947	-4.49.225	-310.341	51.756
3300	31.712	155.034	126.814	-4.49.272	-305.729	51.756
3400	31.717	155.981	127.656	-4.49.319	-301.117	51.756
3500	31.721	156.901	128.481	-4.49.366	-296.505	51.756
3600	31.725	157.794	129.292	-4.49.412	-291.893	51.756
3700	31.729	158.663	130.085	-4.49.459	-287.281	51.756
3800	31.732	159.509	130.879	-4.49.506	-282.669	51.756
3900	31.735	160.333	131.655	-4.49.553	-278.057	51.756
4000	31.738	161.137	132.404	-4.49.600	-273.445	51.756
4100	31.741	161.921	133.117	-4.49.647	-268.833	51.756
4200	31.744	162.686	133.714	-4.49.694	-264.221	51.756
4300	31.746	163.433	134.296	-4.49.741	-259.609	51.756
4400	31.749	164.166	134.863	-4.49.788	-254.997	51.756
4500	31.750	164.876	135.419	-4.49.835	-250.385	51.756
4600	31.752	165.574	136.361	-4.49.882	-245.773	51.756
4700	31.754	166.257	137.090	-4.49.929	-241.161	51.756
4800	31.756	166.926	137.606	-4.49.976	-236.549	51.756
4900	31.758	167.581	138.111	-4.49.998	-231.937	51.756
5000	31.759	168.222	138.603	-4.50.000	-227.325	51.756
5100	31.760	168.851	139.368	-4.50.000	-222.713	51.756
5200	31.761	169.468	139.961	-4.50.000	-218.101	51.756
5300	31.763	170.073	140.523	-4.50.000	-213.489	51.756
5400	31.764	170.666	141.076	-4.50.000	-208.877	51.756
5500	31.765	171.249	141.619	-4.50.000	-204.265	51.756
5600	31.766	171.822	142.153	-4.50.000	-199.653	51.756
5700	31.767	172.384	142.679	-4.50.000	-195.041	51.756
5800	31.768	172.936	143.196	-4.50.000	-190.429	51.756
5900	31.769	173.479	143.704	-4.50.000	-185.817	51.756
6000	31.770	174.013	144.205	-4.50.000	-181.205	51.756

June 30, 1970

(IDEAL GAS)

SODIUM TETRAFLUOROALUMINATE (NaAlF₄)

AlF₄Na

GFW = 125.9649

ΔH_f⁰ = -444.9 ± 2.3 kcal/mol

Point Group [C_{2v}]

ΔH_f⁰ = -444.9 ± 2.3 kcal/mol

Ground State Quantum Weight = [1]

S_{298.15} = [82.571] ± 2 gibbs/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
800 (1)	[300] (1)	890 (1)	
890 (1)	[180] (1)	340 (1)	320 (1)
[390] (1)	[180] (1)	[190] (1)	[200] (1)

Bond Distance: Al-F = 1.69 ± 0.02 Å Na-F = 2.11 ± 0.02 Å

Bond Angle: F-Al-F = 109.47°

Product of the Moments of Inertia: I_AI_BI_C = 4.79396 × 10⁻¹¹³ g³ cm⁶ σ = [2]

Heat of Formation

ΔH_f⁰ is based on ΔH_f⁰_{298.15} = 69.36 kcal/mol for the reaction Na₃AlF₆(c) + NaAlF₄(g) + 2NaF(c). ΔH_f⁰ is calculated by third law analysis of the pressure equation reported for this reaction by Sidorov and Kolosov (1). The second law ΔH_f⁰ = 70.5 kcal/mol and the entropy deviation is 1.1 gibbs/mol. Sidorov and Kolosov obtained their pressure equation by combination of the temperature variation of ion intensities with integration of intensities during total sublimation at 931°K (2).

Sidorov et al. (2) concluded that the pressure of the dimer (NaAlF₄)₂ at 931°K is almost half of the monomer pressure over the two-phase system Na₃AlF₆·1/2NaAlF₄. In contrast, Büchler et al. (3) reported the approximate vapor composition of 97% monomer, 1% dimer, 1% NaAlF₄, and 1% AlF₃ over the same condensed phases at 931°K. The latter composition was obtained from a mass spectrometric study by the twin crucible method.

Vapor pressures over melts in the NaF-AlF₃ system have been measured by the entrainment and boiling point techniques (4-7). We have made no attempt to establish the liquid phase activities necessary for use of these data.

Heat Capacity and Entropy

The adopted structure (C_{2v} symmetry) consists of tetrahedral AlF₄ combined with Na to form a planar ring, AlF₂Na, through coordination with two fluorines. Experimental evidence available for NaAlF₄ and LiAlF₄ does not distinguish conclusively between this structure and the alternatives which have been seriously considered. Alternatives include a C_s structure, in which the ring is non-planar, and two C_{2v} structures, in which Na (or Li) is coordinated to one or three fluorines instead of two.

Electron diffraction data (8) for the vapor gave the adopted bond distances and showed that the AlF₄ group is essentially tetrahedral. Wave error at small scattering angles precluded the calculation of accurate non-bonded distances for Na.

Shelson (9) observed the infrared spectra of LiAlF₄ and NaAlF₄ isolated in matrices of neon and argon. Eight fundamentals were found above 200 cm⁻¹ for LiAlF₄ and six for NaAlF₄. Shelson chose a C_{2v} structure for LiAlF₄ on the basis of Redlich-Teller product-rule calculations for isotopic shifts due to Li.

Neither the infrared data nor the electron-diffraction data are conclusive so we apply these qualitative arguments. Coordination of Na to three fluorines seems less likely, since there are no known examples of this behavior. The C_{2v} structure, as suggested by Büchler and Berkowitz-Mattuck (3), is likely because it is a hybrid between the accepted structures of Na₂F₂ and Al₂F₆. C_{2v} symmetry (σ = 2) is a compromise which has an entropy effect intermediate between the other alternatives. The principal moments of inertia of the C_{2v} structure are I_A = 24.026 × 10⁻³⁹ and I_B = I_C = 44.559 × 10⁻³⁹ g cm².

The fundamental vibrations of 800 and 890 cm⁻¹ are average values from gas phase (10) and matrix (9) spectra. Four other observed values are from the matrix data. Six fundamentals are estimated by comparisons similar to those used for LiAlF₄(g).

References

1. L. N. Sidorov and E. N. Kolosov, Russ. J. Phys. Chem. (English transl.) 42, 1382 (1968); *ibid.*, p. 1384.
2. L. N. Sidorov, E. V. Erokhin, P. A. Akishin and E. N. Kolosov, Dokl. Akad. Nauk, SSSR 173 (2), 370 (1967).
3. A. Büchler, J. L. Stauffer and J. B. Berkowitz-Mattuck, unpublished results (1966), quoted in A. Büchler and J. B. Berkowitz-Mattuck, *AD 65163*, June, 1967.
4. U. Kumann and U. Tillessen, Z. Erzbau Metallhuettenw., 20, 147 (1967).
5. M. Rolin and J. Houriez, Bull. Soc. Chim. Fr. 1954, 891, 897, 900 (1964).
6. A. Vajna and R. Bacchiega, Met. Ital. 52, 491 (1960).
7. M. M. Vetyukov, M. L. Blyuststein and V. P. Podymov, Izv. Vyssh. Ucheb. Zaved., Tsvet. Met. 2 (6), 126 (1959).
8. V. P. Spiridonov and E. V. Erokhin, Dokl. Akad. Nauk 180 (1), 161 (1968); Proc. Acad. Sci. USSR (English transl.), 180 335 (1968).
9. A. Shelson, IIT Res. Inst. Report No. IITRI-UG6001-13, August 12, 1966.
10. L. D. McCarty, R. C. Paule and J. L. Margrave, J. Phys. Chem. 67, 1086 (1963).

AlF₄Na

Tripotassium Hexafluoroaluminate (K_3AlF_6)

(Crystal) Mol. Wt. = 258.28

T, °K.	C_p	$S^\circ - (F^\circ - H^\circ_{298})/T$	ΔH°_f	ΔF°	Log K_p
0					
100	53.250	68.000	0.000	-795.000	554.208
200	53.390	68.001	0.099	-794.993	550.614
300	57.620	84.425	5.704	-796.237	405.692
400	61.020	97.657	11.640	-795.578	318.720
500	63.910	109.046	17.891	-794.657	260.794
600	66.660	119.105	24.420	-793.516	219.472
700	69.230	128.182	31.220	-792.166	188.531
800	71.400	136.472	38.261	-790.637	164.508
900	73.000	144.081	45.484	-791.503	145.289
1000	74.400	151.106	52.856	-846.418	128.971
1100	75.600	157.633	60.358	-843.798	114.978
1200	76.600	163.725	67.969	-841.087	103.176
1300	77.400	169.432	75.671	-838.297	93.092
1400	78.038	174.794	83.444	-835.448	84.382
1500	78.400	179.849	91.276	-832.552	76.788
1600	79.088	184.629	99.161	-829.615	70.111
1700	79.500	189.161	107.091	-826.645	64.197
1800	79.800	193.468	115.057	-823.651	58.923
1900	80.000	197.567	123.048	-820.641	54.194

AlF_6K_3

MOL. WT. = 258.28

(CRYSTAL)

TRIPOTASSIUM HEXAFLUOROALUMINATE (K_3AlF_6)

ΔH°_f 0 = Unknown
 ΔH°_f 298.15 = [-795 + 5] kcal. mole⁻¹
 ΔH°_m = Unknown
 $S^\circ_{298.15}$ = [68.0 + 1.0] cal. deg.⁻¹ mole⁻¹
 T_m = 1233°K.

Heat of Formation.

The value of ΔH°_f 298.15 adopted was calculated based upon ΔH°_f = -30.2 kcal. mole⁻¹ for the reaction, $AlF_3(c) + 3KF(c) = K_3AlF_6(c)$, which was estimated by comparison with the values of ΔH°_f of the similar reactions for $Na_3AlF_6(c)$, $Na_3AlCl_6(c)$ and $K_3AlCl_6(c)$.

Heat Capacity and Entropy.

Both C_p and $S^\circ_{298.15}$ were estimated by the addition of a correction term, $3(M_{KF} - M_{NaF})$, to the corresponding values for $Na_3AlF_6(c)$, where M denotes either C_p or $S^\circ_{298.15}$.

Temperature of Melting.

T_m was obtained from P. F. Hall and H. Inaley, J. Am. Ceram. Soc. 21, 113 (1938).

AlF_6K_3

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	-0.000	INFINITE	INFINITE	7.683	-805.644	-805.644	INFINITE
100	16.965	9.136	79.746	7.061	-807.570	-795.583	1730.744
200	37.338	27.715	49.025	4.262	-808.633	-783.090	655.721
298	88.400	44.907	44.907	.000	-808.700	-770.517	564.804
300	88.550	45.207	44.908	.090	-808.696	-770.282	561.150
400	54.940	60.122	46.898	5.289	-804.269	-757.529	413.894
500	59.300	72.874	50.849	11.012	-805.852	-744.692	375.104
600	62.600	83.996	55.466	17.114	-805.040	-731.729	266.532
700	62.000	93.857	65.072	30.703	-803.178	-704.130	192.950
800	58.000	103.457	69.817	37.933	-804.417	-691.585	168.515
1000	73.000	119.624	74.416	45.206	-805.200	-681.585	148.940
1100	75.500	126.699	74.851	52.633	-803.274	-687.235	136.698
1200	60.500	139.717	87.231	69.233	-798.713	-684.336	108.691
1300	83.000	155.775	91.198	76.408	-794.073	-633.633	98.915
1400	85.500	151.586	95.031	84.833	-793.189	-622.130	90.644

Heat of Formation

ΔH_f° is derived from $\Delta H_r^\circ = -5.4 \pm 0.5$ kcal/mol at 298.15 K for the reaction $3 \text{LiF}(c) + \text{AlF}_3(c) + \text{Li}_2\text{AlF}_6(c, \beta \text{ mixture})$. Greena et al. (1) obtained this result by heating the fluorides under standardized conditions in a small electrical furnace contained in their calorimeter at 25°C. ΔH_r° includes a small endothermic effect observed during heating of the reaction product. The authors suggest that the enthalpy of conversion between the α - and β -forms is small and thus their result should apply to both forms.

Heat Capacity and Entropy

Furukawa et al. (2) measured C_p° (15-370 K) using a sample prepared by fusion of stoichiometric proportions of LiF and AlF_3 in graphite. X-ray diffraction and petrographic examination of separate portions of the sample indicated a single phase identified as $\beta\text{-Li}_3\text{AlF}_6$. The authors tabulated values of C_p° and S° based on their data and the extrapolation $S_{15}^\circ = 0.042$ gibbs/mol. These values are adopted.

Douglas and Neuffer (3) reported relative enthalpy data (323-973 K) for part of the same sample used in measurement of C_p° (2). Their study was made prior to discovery of the five crystalline phases, and their drop-calorimetric data reveal only the transition near 748 K. Reinterpretation of the data above 748 K is complicated by the proximity of the furnace temperatures to the transition temperatures and by the tendency of high-temperature forms to revert to both α - and β -forms under different conditions of cooling. Björge and Jensen (4) and Rolin et al. (5) also reported crystalline enthalpy data, but these are relatively imprecise and include similar uncertainties in the final state after the drop. These difficulties preclude the derivation of accurate heat capacities for the high-temperature forms.

C_p° for the β -form is adopted from (2, 3), since the two methods are in good agreement. The curve is extrapolated linearly above 748 K to obtain C_p° for the high-temperature forms. Obvious differences in C_p° are not apparent in the observed data for the different forms, so this should be an adequate approximation.

Transition Data

Existence of five polymorphic forms was shown by high-temperature X-ray diffraction (1, 2, 3) and differential thermal analysis (2, 3). Both α - and β -forms persisted at room temperature, but the α -form appeared only on quenching of high-temperature forms (1). The α -form transformed to β near 430 K (1, 2), but the reverse transformation was not observed. Single-crystal X-ray diffraction showed the α -form to be orthorhombic (3).

The adopted values of T_t are the lowest temperatures at which the high-temperature form was observed growing at the expense of the low-temperature form (1). DTA data (2, 3) were higher by roughly 30° for T_{t1} and 25° for T_{t2} . Combination of the observed enthalpies (3) with the adopted C_p° yields $\Delta H_{t1}^\circ = 0.76$ and $\Delta H_{t2}^\circ = 0.03$ or 0.15 kcal/mol; however, we prefer to adopt ΔH_{t1}° values (0.5 and 0.3 kcal/mol) which are more consistent with the areas of peaks in the DTA curve (2). Evidence suggests that ΔH_{t2}° is small, so we estimate 0.1 kcal/mol.

Melting Data

See the table for the liquid.

References

1. P. D. Greene, P. Gross and C. Heyman, Trans. Faraday Soc. **64**, 633 (1968).
2. G. T. Furukawa, W. G. Saba and J. C. Ford, Nat. Bur. Stand. Report 10074, p. 47, issued July 1, 1969.
3. T. B. Douglas and J. E. Neuffer, Nat. Bur. Stand. Report 8186, p. 68, issued January 1, 1964.
4. B. Björge and B. Jensen, Acta Chem. Scand. **22**, 1347 (1968).
5. M. Rolin, H. Latraille and H. Pham, Bull. Soc. Chim. Fr. **1969** (7), 2271.
6. G. Garton and B. M. Wanklyn, J. Inorg. Nucl. Chem. **27**, 2466 (1965).
7. J. L. Holm, Acta Chem. Scand. **20**, 1167 (1966).
8. J. H. Burns, A. C. Tennissen and G. D. Brunton, Acta Cryst. **B24**, 225 (1968).

Trilithium Hexafluoroaluminate (Li_3AlF_6)

(Liquid) $\text{GF}_W = 161.7889$

T, °K	C_p^0	S^0	$-(G^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	ΔH^0	ΔG^0	Log K _p
0							
100	48.400	58.759	58.759	.000	-792.935	-750.882	556.275
200	48.550	59.058	58.759	.090	-792.931	-750.673	552.692
300	54.940	73.973	60.750	5.289	-792.504	-747.304	406.308
400	59.300	86.725	64.701	11.012	-792.087	-743.852	321.641
500	63.450	97.828	69.318	17.118	-791.375	-740.375	263.817
600	66.000	107.728	74.112	23.531	-790.200	-737.558	222.564
700	68.000	119.212	79.048	32.131	-788.591	-734.746	191.708
800	69.000	129.341	84.084	40.731	-785.854	-731.028	167.605
900	69.000	136.402	89.071	46.331	-785.312	-730.475	148.714
1000	69.000	146.599	93.938	57.931	-782.211	-727.184	133.115
1100	69.000	156.082	98.630	66.531	-775.125	-720.091	120.219
1200	69.000	160.966	103.172	75.131	-776.050	-720.295	109.324
1300	69.000	167.339	107.531	83.731	-772.985	-716.735	100.073
1400	69.000	173.272	111.718	92.331	-769.926	-713.395	91.994
1500	69.000	178.823	115.761	100.931	-765.873	-709.259	84.997
1600	69.000	184.036	119.666	109.531	-760.967	-704.330	78.335
1700	69.000	188.952	123.323	118.131	-755.382	-698.159	72.141
1800	69.000	193.602	126.901	126.731	-749.180	-691.804	66.627
1900	69.000	198.013	130.387	135.331	-742.438	-684.238	61.675
2000	69.000	202.209	133.670	143.931	-735.087	-675.808	57.219
2100	69.000	206.210	136.877	152.531	-727.184	-666.570	53.184
2200	69.000	210.032	139.975	161.131	-718.822	-656.570	49.515
2300	69.000	213.683	142.971	169.731	-710.087	-645.887	46.166
2400	69.000	217.203	145.871	178.331	-700.981	-634.501	43.094
2500	69.000	220.576	148.680	186.931	-691.529	-622.629	40.274
2600	69.000	223.822	151.403	195.531	-681.740	-610.268	37.677
2700	69.000	226.949	154.045	204.131	-671.612	-597.551	35.207
2800	69.000	229.967	156.612	212.731	-661.146	-584.446	32.791
2900	69.000	232.883	159.106	221.331	-650.356	-570.922	30.545
3000	69.000	236.613	161.516	230.000	-639.146	-556.999	28.445

AlF_6Li_3

TRILITHIUM HEXAFLUOROALUMINATE (Li_3AlF_6) (LIQUID)

$\text{GF}_W = 161.7889$

$\Delta H_{298.15}^0 = -792.935 \text{ kcal/mol}$

$\Delta H_m^0 = 20.6 \pm 1.0 \text{ kcal/mol}$

Heat of Formation

$\Delta H_{298.15}^0$ is calculated from that of the crystal by addition of ΔH_m^0 and the difference of ($H_{1058}^0 - H_{298.15}^0$) for the crystal and liquid.

Heat Capacity and Entropy

Relative enthalpy data were measured by Björge and Jensen (1) from 1065 to 1088 K and by Rolin et al. (2) from about 1075 to 1145 K. The data are consistent with liquid heat capacities in the range from roughly 82 to 92 gibbs/mol. We adopt the mean value of 86 gibbs/mol and extrapolate this to higher and lower temperatures. A glass transition is assumed at 700 K and C_p^0 at lower temperatures is taken to be the same as that of $\beta\text{-Li}_3\text{AlF}_6$. S_{298}^0 is calculated in a manner analogous to that of the heat of formation.

Melting Data

T_m was observed at 780°C (3), 782°C (2, 4), 783°C (5, 8) and 785°C (1). The last and highest value is adopted for this table. Combination of the observed liquid enthalpies with the adopted crystal enthalpies yields values for ΔH_m^0 of 19.7 kcal/mol (1), authors gave 20.2 ± 1.0 and 21.5 ± 0.3 kcal/mol (2, authors gave 21.5). We adopt the mean value of 20.6 kcal/mol which is confirmed by values of 20.7 (8), 20.8 (4), 22.2 (4), 20.1 (4) and 22.0 (2) derived from crystal-liquid phase data for binary systems. The agreement among values for ΔH_m^0 seemingly excludes the possibility of large discrepancies in the enthalpies due to formation of the α -phase instead of β during drop-calorimetry from high temperatures.

Vaporization Data

Li_3AlF_6 vaporizes mainly to $\text{LiAlF}_4(\text{g})$ with small contributions from species such as $\text{Li}_2\text{AlF}_5(\text{g})$, $\text{Li}_2\text{F}_2(\text{g})$ and $\text{LiF}(\text{g})$ (5, 7).

References

1. B. Björge and B. Jensen, Acta Chem. Scand. **22**, 1347 (1968).
2. R. Rolin, H. Latreille and H. Pham, Bull. Soc. Chim. Fr. **1969** (7), 2271.
3. J. L. Holm, Acta Chem. Scand. **20**, 1167 (1967).
4. M. Malinovsky, Chem. Vestn. **21**, 783 (1967); ibid., p. 794.
5. G. Garton and B. Wanklyn, J. Inorg. Nucl. Chem. **27**, 2466 (1965).
6. A. Büchler and J. Berkowitz-Hattuck, AD 651633, pp 41-3, June, 1967.
7. R. F. Porter and E. E. Zeller, J. Chem. Phys. **33**, 858 (1960).
8. T. Matsushima, Denki Kagaku Oyobi Kogyo Butsuri Kagaku (Electrochemistry and Industrial Physical Chemistry) **37**, 778 (1969).

AlF_6Li_3

T, °K	Cp*	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	0.000	INFINITE		9.105	-788.058	-788.058	INFINITE
100	23.910	14.864	46.244	4.178	-781.685	-781.685	1.85
200	42.420	30.654	66.244	4.178	-771.685	-771.685	835.542
298	51.559	56.950	56.950	0.000	-791.000	-791.000	550.947
300	51.674	57.309	56.991	0.095	-790.994	-751.395	547.391
400	56.077	72.866	59.079	5.507	-792.523	-792.523	403.278
500	59.191	85.657	63.154	11.271	-792.034	-724.546	316.699
600	62.577	96.779	67.854	17.355	-791.268	-711.115	259.023
700	66.519	106.715	72.767	23.605	-790.174	-697.839	217.875
800	70.941	115.862	77.538	30.675	-788.704	-684.745	187.064
900	67.400	126.378	82.428	39.555	-785.284	-671.988	163.101
1000	67.400	133.479	87.184	46.295	-786.602	-657.283	144.066
1100	67.400	139.903	91.689	53.035	-785.385	-646.616	128.471
1200	65.000	146.548	95.972	60.891	-782.699	-632.699	115.210
1300	65.000	153.351	100.126	68.191	-784.457	-614.483	103.304
1400	65.000	159.651	104.157	77.691	-784.928	-596.541	93.124
1500	65.000	165.515	108.054	86.191	-784.411	-578.649	84.338
1600	65.000	171.001	111.819	94.691	-783.906	-561.394	76.683
1700	65.000	176.154	115.453	103.191	-783.407	-544.183	69.956
1800	65.000	181.012	118.962	111.691	-783.192	-527.125	64.002
1900	65.000	185.668	122.350	120.191	-782.444	-510.283	58.466
2000	65.000	189.968	125.622	128.691	-781.978	-493.620	53.941

Sept. 30, 1961; Sept. 30, 1963; Dec. 31, 1963; Dec. 31, 1968

Heat of Formation

The heats of solution of Al(c), NaCl(c), and Na₃AlF₆(c) in 4.36 M HCl acid solution were determined at 303.15°K by Coughlin (1). The enthalpy change for the reaction Al(c) + 2.96 NaCl(c) + 5.96 (HF·5.716 H₂O) + 3.617 H₂O(l) = Na₂96AlF₅96(c) + 2.96 (HCl·12.731 H₂O) + 3/2 H₂(g) was derived as ΔH_{298.15}° = -153.22 ± 0.14 kcal/mol. Using the ΔH₂₉₈° data on H₂O(l), HCl and HF solution from (2, 3) and NaCl from JANAF Table (4), we calculate the value ΔH₂₉₈° = -791.2 ± 0.7 kcal/mol for Na₃AlF₆(c). Baud (5) reported ΔH₂₉₈° = -40.7 kcal/mol for the reaction 2AlF₃(c) + 6NaF(c) = 2Na₃AlF₆(c). Based on JANAF ΔH₂₉₈° values for AlF₃(c) and NaF(c), we obtain ΔH₂₉₈°(Na₃AlF₆, c) = -793.7 ± 2 kcal/mol. Hashovets and Yudin (6) determined the equilibrium constants in the temperature range 1101-1239°K for the reaction 2/3 Na₃AlF₆(c) + H₂O(g) = 1/3 Al₂O₃(c) + 2HF(g) + 2NaF(c), using the transpiration method. Based on the reported K_p values, we evaluate ΔH₂₉₈° = 48.1 ± 0.8 and 46.6 kcal/mol by the second and third law methods, respectively. From the third law ΔH₂₉₈° value, we calculate ΔH₂₉₈°(Na₃AlF₆, c) = -791.3 kcal/mol. The equilibrium pressures of sodium vapor in the reaction 2NaF(c) + 1/3 Al(c) = Na(g) + 1/3 Na₃AlF₆(c) at temperatures 1020 - 1150°K were determined by Ono et al. (7), employing differential thermal analysis and X-ray analysis. Since the reported vapor pressures are the total pressures of Na(g) and Na₂(g), we calculate the partial pressures of Na(g) by use of the equilibrium constants for the reaction Na₂(g) = 2Na(g) derived from JANAF functions for Na₂(g) and Na(g). Based on the calculated Na(g) pressures we evaluate the enthalpy change of the above reaction by the third law method to be 109.2 kcal/mol, yielding ΔH₂₉₈°(Na₃AlF₆, c) = -791.1 kcal/mol.

The amounts of sodium over the mixtures of cryolite and aluminum were measured in the temperature range 1023 - 1373°K by the ultraviolet absorption method by Stokes and Frank (8). The enthalpy change for the reaction 6NaF(t) + Al(t) = 3Na(g) + Na₃AlF₆(t) is not evaluated due to lack of appropriate data on the activities of NaF(t) and Na₃AlF₆(t). The heat of formation (298°K) for cryolite(c) is adopted as -791 ± 1 kcal/mol. The heat capacity and entropy

The low temperature heat capacities, 53.66 - 296.00°K, were measured by King (9). The values of Cp below 53.66°K are extrapolated using the Cp equation given by King. S₂₉₈° is derived based on the adopted low temperature heat capacities. The high temperature enthalpies, 401.3 - 1370.5°K, determined by O'Brien and Kelley (10), are adopted to derive the heat capacities which join smoothly at 298°K with the low temperature Cp's. The heat capacity of Na₃AlF₆(γ) is estimated such that the calculated enthalpy at 1200.5°K is consistent with the measured value reported by O'Brien and Kelley. The heat capacity above the melting point is obtained by linear extrapolation.

Frank (21) commented that the enthalpies reported by O'Brien and Kelley were incorrect due to an apparent error in temperature measurement. However, his reported corrected enthalpy values are not used here (see NaF(c) table for details). The high temperature enthalpies have also been measured by the following investigators: July, 284.5 - 373.3°K (11); Baud, 289 - 328°K (12); Roth and Bertram, 369 - 1371°K (13); Krestovnikov and Karetnikov, 573 - 1773°K (14); Lyshenko, 290 - 1217°K (15); and Albright, 350.0 - 1311.8°K (16). Their data are not used for evaluation due to inconsistencies among the reported values.

Transition Data

Landon and Ubbelohde (17) determined the electrical conductance (σ) of crystals and melt of cryolite, and observed two transition temperatures from a plot of log σ vs 1/T, i.e. Tt(α + β) = 838°K and Tt(β + γ) = 1153°K, which are adopted here. Other values of Tt(α + β) reported are (°K): 823 (18), 833 (18), 834 (19), 835 (20), and 838 (13).

The values of ΔH^{*}(α + β) and ΔH^{*}(β + γ) are calculated as the difference between the adopted enthalpies for α and β at 838°K and β and γ at 1153°K, respectively. The value of ΔH^{*}(α + β) has also been reported as (kcal/mol): 1.24 (13), 2.16 (10), 2.24 (20), and 2.38 (16). Landon and Ubbelohde (17) estimated that ΔH^{*}(β + γ) = 0.01 x ΔH = 0.2 kcal/mol.

The cause of the discrepancies among the reported values for Tt, ΔH^{*} and the high temperature enthalpies may be due to differences in the sample composition.

Melting Data

See the Na₃AlF₆(t) table for details.

References

1. J. P. Coughlin, J. Am. Chem. Soc. 80, 1802 (1958).
2. U. S. Naval Res. Lab., Tech. Rep. No. 270-3, 1963.
3. ΔH₂₉₈° (HF·5.716 H₂O) is recalculated based on JANAF ΔH₂₉₈° (HF, g) value.
4. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan, Sept. 30, 1964.
5. E. Baud, Ann. Chim. Phys. 1, 8 (1904).
6. V. P. Hashovets and B. F. Yudin, Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met. 5, 95 (1962).
7. K. Ono, T. Matsushima, and T. Ito, Nippon Kinzoku Gakkaishi 29, 501 (1965).
8. J. J. Stokes, Jr. and W. B. Frank, "Extractive Metallurgy of Aluminum," Vol. II, Interscience Publishers, 1963, p. 3.
9. E. G. King, J. Am. Chem. Soc. 79, 2056 (1957).
10. J. O'Brien and K. A. Kelley, J. Am. Chem. Soc. 81, 250 (1959).
11. J. O'Brien and K. A. Kelley, J. Am. Chem. Soc. 81, 250 (1959).
12. M. E. Baud, J. Phys. Radium Ser. 4, 2, 569 (1903).
13. A. N. Krestovnikov and G. A. Karetnikov, Legkie Metal. 3, 29 (1934).
14. V. S. Lyshenko, Metallurg. 10, 85 (1935).
15. C. T. Inghram, J. Res. Natl. Bur. Stand. 68A, 160 (1963).
16. C. T. Inghram, J. Res. Natl. Bur. Stand. 68A, 160 (1963).
17. J. Landon and R. Ubbelohde, Phys. Rev. 152, No. 8, 495 (1960).
18. J. Brynestad, K. Griethelm, and S. Urnes, Metallurgia Ital. 52, No. 8, 495 (1960).
19. F. C. Knacke, Handbook of Physical Constants, Geological Society of America, Special Paper No. 36, 140, 1942.
20. A. J. Majumdar and R. Roy, J. Inorg. Nucl. Chem. 27, 1961 (1965).
21. W. B. Frank, J. Phys. Chem. 65, 2081 (1961).

GFW = 209.9413

(LIQUID)

CRYOLITE (Na₃AlF₆)Cryolite (Na₃AlF₆)

GFW = 209.9413

(Liquid)

S_{298.15} = 68.544 gibbs/mol $\Delta H_f^{\circ} 298.15 = -774.052$ kcal/molT_m = 1285°K $\Delta H_m^{\circ} = 25.64$ kcal/mol

T, °K	Cp°	gibbs/mol S° - (C° - H ₂₉₈)/T	kcal/mol H° - H ₂₉₈	ΔG°	Log Kp
0					
100					
200					
298	51.559	68.544	.000	- 736.137	541.069
300	51.674	68.863	- 0.095	- 737.913	537.569
400	56.077	84.400	5.507	- 755.575	396.544
500	59.191	97.250	11.271	- 775.086	311.816
600	62.577	108.333	17.355	- 791.099	255.375
700	66.519	118.269	23.605	- 806.979	215.109
800	94.700	127.436	30.676	- 823.226	184.959
900	94.700	136.590	40.146	- 840.481	161.591
1000	94.700	146.568	49.616	- 858.133	142.954
1100	94.700	157.593	59.086	- 876.286	127.767
1200	94.700	165.633	68.556	- 894.939	114.926
1300	94.700	173.413	78.026	- 914.178	103.354
1400	94.700	180.832	87.496	- 933.990	93.000
1500	94.700	188.965	96.966	- 954.302	84.967
1600	94.700	193.077	106.436	- 975.113	77.568
1700	94.700	196.616	115.906	- 996.425	71.095
1800	94.700	200.231	125.376	- 1018.238	65.357
1900	94.700	203.951	134.846	- 1040.550	60.250
2000	94.700	207.699	144.316	- 1063.363	55.660
2100	94.700	211.429	153.786	- 1086.675	51.568
2200	94.700	215.135	163.256	- 1110.488	47.951
2300	94.700	218.816	172.726	- 1134.701	44.806
2400	94.700	222.475	182.196	- 1159.314	42.139
2500	94.700	226.116	191.666	- 1184.327	39.966
2600	94.700	229.735	201.136	- 1209.740	38.293
2700	94.700	233.335	210.606	- 1235.553	37.020
2800	94.700	236.916	220.076	- 1261.766	36.145
2900	94.700	240.479	229.546	- 1288.379	35.670
3000	94.700	244.026	239.016	- 1315.392	35.500

Heat of Formation

The $\Delta H_f^{\circ} 298(\ell)$ is obtained from $\Delta H_f^{\circ} 298(c)$ by adding ΔH_m° and the difference between $H_{298}^{\circ} - H_{298}^{\circ}$ for crystal and liquid. Yudin and Mashovets (1) studied the dissociation of cryolite and reported $K_{1300} = 2.33 \times 10^{-5}$ for the reaction $\text{Na}_3\text{AlF}_6(\ell) = 3\text{NaF}(\ell) + \text{AlF}_3(\ell)$. Based on this K_{1300} value, we evaluated the enthalpy change by the third law method as 24.3 kcal/mol. Using $\Delta H_f^{\circ} 298 = -360.8$ and -130.6 kcal/mol for $\text{AlF}_3(\ell)$ and $\text{NaF}(\ell)$, respectively, we obtain $\Delta H_f^{\circ} 298 = -776.7 \pm 3$ kcal/mol for $\text{Na}_3\text{AlF}_6(\ell)$.

Heat Capacity and Entropy

The high temperature enthalpies, $1285.5 - 1370.5^\circ\text{K}$, were measured by O'Brien and Kelley (2). Using their data we derive a constant Cp, 94.7 gibbs/mol. For $\text{Na}_3\text{AlF}_6(\ell)$. A glass transition temperature is assumed at 800°K , and the heat capacities below 800°K are taken to be the same as those of the $\text{Na}_3\text{AlF}_6(c)$. The Cp values above 1370.5°K are obtained by linear extrapolation. The entropy, S_{298}° , is calculated in a manner analogous to that of the heat of formation.

Albright (3) measured the high temperature enthalpies of $\text{Na}_3\text{AlF}_6(\ell)$ in the temperature range $1298.1 - 1311.8^\circ\text{K}$. However, his data are systematically higher (about 4.91) than the values determined by O'Brien and Kelley (2), which is also true for the other sets of enthalpy data measured using this calorimeter. Therefore Albright's enthalpy data is not used for evaluation.

Melting Data

The melting point of cryolite has been reported as ($^\circ\text{K}$): 1273 (4), 1279 (3), 1281 (5), 1282 (6, 7), 1293 (9), and 1300 (2). The value of Tm adopted is that determined by Landon and Ubbelohde (9). This value is corrected from the original measured value 1286°K , due to the thermocouple standardization against the freezing points of assay gold giving a gold point of $1064.2 \pm 0.15^\circ\text{C}$ compared with the fixed value of 1063.0°C .

The value of ΔH_m° is calculated as the difference between the enthalpies at Tm for crystal and liquid. Other reported values of ΔH_m° are (in kcal/mol): 16.64 (4), 26.6 (10), 27.64 (2), and 27.91 (3).

References

1. B. F. Yudin and V. P. Mashovets, J. Appl. Chem. **35**, 1192 (1963).
2. C. J. O'Brien and K. K. Kelley, J. Am. Chem. Soc. **79**, 5616 (1957).
3. D. M. Albright, Ph.D. Thesis, Carnegie Institute of Technology, 1956.
4. W. A. Roth and W. Bertram, Z. Elektrochem. **35**, 297 (1929).
5. J. Brynestadt, K. Grjotheim, and S. Urnes, Metallurgia Ital. **52**, No. 8, 495 (1960).
6. M. Rolin, Bull. Soc. Chim. France, **1960**, 671 (1960).
7. N. W. F. Phillips, R. H. Singleton, and E. A. Hollingshead, J. Electrochem. Soc. **102**, 690 (1955).
8. G. J. Landon and A. R. Ubbelohde, Proc. Roy. Soc. (London) **240A**, 160 (1957).
9. F. C. Krack, Handbook of Physical Constants, Geological Society of America, Special Papers No. 36, 140, 1942.
10. M. Rolin and M. Bernard, Bull. Soc. Chim. France, **1962**, 423 (1962).

MOL. WT. = 27.988

(IDEAL GAS)

ALUMINUM MONOHYDRIDE (AIH)

$$\Delta H_f^0 = 62.0 \pm 5.0 \text{ kcal mole}^{-1}$$

$$\Delta H_f^0 = 62.0 \pm 5.0 \text{ kcal mole}^{-1}$$

Ground State Configuration $1s^2$

$$S_{298.15} = 44.875 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

Electronic Levels and Multiplicities

$$\frac{g_i}{\epsilon_i \text{ cm}^{-1}}$$

$$\omega_e = 1682.56 \text{ cm}^{-1} \quad \sigma = 1$$

$$B_e = 5.3907 \text{ cm}^{-1} \quad \alpha_e = 0.1858 \text{ cm}^{-1}$$

Heat of Formation

A. G. Gaydon, "Dissociation Energies", 2nd Ed., Chapman Hall, Ltd., London (1953), extrapolated the available $X^2\Sigma$ vibrational levels and also considered predissociation in the $A^1\Pi$ state and concluded that the best value of D_0^0 was 2.9 ± 0.2 e.v. The linear Birge-Sponer extrapolation gave a value of 3.05 e.v. while the predissociation limit was 3.07 e.v. Gaydon's recommended value is adopted here and leads to a value of ΔH_f^0 298.15 = 62.16 ± 5.0 kcal mole⁻¹ using JANAF auxiliary data.

Heat Capacity and Entropy

P. B. Zeeman and G. J. Ritter, Can. J. Phys. **32**, 555 (1954) examined the UV band system of AIH under high resolution and reported the molecular constants adopted above.

Aluminum Monohydride (AIH)

(Ideal Gas) Mol. Wt. = 27.988

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	2.071	62.034	62.034	INFINITE
100	6.961	37.259	51.081	1.382	62.238	59.897	-130.898
200	6.968	42.086	45.515	.686	62.191	57.560	-62.874
298	7.020	44.875	44.875	.000	62.000	55.291	-40.247
300	7.022	44.918	44.875	.013	61.995	55.249	-40.247
400	7.180	46.958	45.152	.722	61.761	53.036	-28.976
500	7.408	48.984	45.981	1.451	61.513	50.882	-22.240
600	7.650	49.956	46.282	2.204	61.260	48.760	-17.767
700	7.865	50.721	47.094	2.981	60.951	46.581	-13.216
800	8.054	51.312	47.694	3.778	60.727	44.659	-12.211
900	8.232	51.777	48.073	4.593	60.439	42.713	-10.372
1000	8.370	52.051	48.228	5.424	57.639	40.944	-8.948
1100	8.486	52.855	49.158	6.267	57.419	39.285	-7.805
1200	8.585	53.588	49.664	7.090	57.205	37.686	-6.856
1300	8.672	54.263	50.099	7.894	56.990	36.141	-6.059
1400	8.742	54.893	50.469	8.684	56.780	34.619	-5.373
1500	8.806	55.473	50.781	9.461	56.584	32.489	-4.783
1600	8.863	56.009	51.045	10.225	56.379	31.252	-4.269
1700	8.913	56.500	51.261	10.975	56.166	29.916	-3.816
1800	8.959	56.958	51.431	11.707	55.946	28.135	-3.416
1900	9.001	57.384	51.561	12.397	55.764	26.595	-3.059
2000	9.039	57.784	51.657	13.047	55.559	25.065	-2.739
2100	9.074	58.166	51.719	13.659	55.322	23.545	-2.450
2200	9.107	58.531	51.757	14.233	55.112	22.036	-2.189
2300	9.138	58.877	51.773	14.769	54.938	20.535	-1.951
2400	9.168	59.204	51.778	15.267	54.730	19.044	-1.734
2500	9.196	59.514	51.764	15.728	54.521	17.561	-1.535
2600	9.222	59.801	51.734	16.169	54.312	16.086	-1.352
2700	9.248	60.051	51.681	16.586	54.102	14.619	-1.183
2800	9.272	60.274	51.607	16.981	53.896	13.166	-1.028
2900	9.296	60.474	51.514	17.357	53.694	11.726	-0.886
3000	9.319	60.652	51.403	17.712	53.497	10.303	-0.753
3100	9.341	60.815	51.269	18.047	53.304	8.896	-0.628
3200	9.363	60.964	51.114	18.362	53.114	7.506	-0.511
3300	9.385	61.099	50.940	18.657	52.926	6.131	-0.401
3400	9.406	61.214	50.747	18.932	52.741	4.771	-0.296
3500	9.426	61.314	50.534	19.187	52.560	3.426	-0.205
3600	9.446	61.400	50.300	19.422	52.383	2.096	-0.128
3700	9.465	61.473	50.045	19.637	52.210	0.781	-0.064
3800	9.483	61.534	49.770	19.832	52.041	-0.520	0.000
3900	9.500	61.584	49.477	20.007	51.876	-1.826	0.084
4000	9.516	61.624	49.164	20.162	51.716	-3.141	0.189
4100	9.542	61.774	48.839	20.297	51.561	-4.466	0.314
4200	9.571	61.904	48.504	20.412	51.411	-5.801	0.459
4300	9.597	62.019	48.159	20.507	51.266	-7.146	0.624
4400	9.615	62.119	47.804	20.582	51.126	-8.501	0.809
4500	9.615	62.166	47.539	20.637	51.001	-9.866	1.014
4600	9.633	62.277	47.264	20.672	50.884	-11.241	1.239
4700	9.651	62.385	46.979	20.687	50.773	-12.626	1.484
4800	9.668	62.484	46.684	20.682	50.668	-14.021	1.749
4900	9.687	62.574	46.379	20.657	50.568	-15.426	2.034
5000	9.704	62.654	46.064	20.612	50.473	-16.841	2.339
5100	9.722	62.724	45.739	20.547	50.383	-18.266	2.664
5200	9.739	62.784	45.404	20.462	50.298	-19.701	3.009
5300	9.756	62.834	45.059	20.357	50.218	-21.146	3.374
5400	9.773	62.874	44.704	20.232	50.143	-22.601	3.759
5500	9.791	62.904	44.339	20.087	50.073	-24.066	4.164
5600	9.808	62.924	43.964	19.922	50.008	-25.541	4.589
5700	9.825	62.934	43.579	19.737	49.948	-27.026	5.034
5800	9.842	62.934	43.184	19.532	49.893	-28.521	5.499
5900	9.859	62.924	42.779	19.307	49.843	-30.026	5.984
6000	9.876	62.904	42.364	19.062	49.798	-31.541	6.489

Dec. 31, 1960 June 30, 1963

Aluminum Oxide Hydride (HA10)

(Ideal Gas) Mol. Wt. = 43.988

AlHO

MOL. WT. = 43.988

(IDEAL GAS)

ALUMINUM OXIDE HYDRIDE (HA10)

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	6.957	48.432	2.155	8.988	8.988	INFINITE
200	7.242	48.432	1.460	8.841	7.948	17.370
300	7.462	48.432	1.000	8.602	7.171	7.836
400	7.625	48.432	0.756	8.361	6.632	4.861
500	7.742	48.432	0.585	8.125	6.231	3.404
600	7.825	48.432	0.452	7.891	5.895	2.593
700	7.885	48.432	0.346	7.658	5.607	2.074
800	7.925	48.432	0.262	7.428	5.360	1.759
900	7.955	48.432	0.196	7.195	5.149	1.495
1000	7.975	48.432	0.144	6.958	4.970	1.265
1100	7.988	48.432	0.102	6.718	4.821	1.065
1200	7.995	48.432	0.070	6.475	4.691	0.885
1300	7.998	48.432	0.045	6.230	4.578	0.725
1400	7.998	48.432	0.026	5.985	4.480	0.585
1500	7.995	48.432	0.012	5.742	4.396	0.465
1600	7.988	48.432	0.004	5.500	4.325	0.365
1700	7.978	48.432	0.001	5.259	4.265	0.285
1800	7.965	48.432	0.000	5.018	4.215	0.215
1900	7.948	48.432	0.000	4.777	4.175	0.155
2000	7.928	48.432	0.000	4.536	4.145	0.105
2100	7.905	48.432	0.000	4.295	4.125	0.065
2200	7.878	48.432	0.000	4.054	4.115	0.035
2300	7.848	48.432	0.000	3.813	4.115	0.015
2400	7.815	48.432	0.000	3.572	4.125	0.005
2500	7.778	48.432	0.000	3.331	4.145	0.000
2600	7.738	48.432	0.000	3.090	4.175	0.000
2700	7.695	48.432	0.000	2.849	4.215	0.000
2800	7.648	48.432	0.000	2.608	4.265	0.000
2900	7.600	48.432	0.000	2.367	4.325	0.000
3000	7.550	48.432	0.000	2.126	4.396	0.000
3100	7.500	48.432	0.000	1.885	4.476	0.000
3200	7.448	48.432	0.000	1.644	4.566	0.000
3300	7.395	48.432	0.000	1.403	4.666	0.000
3400	7.340	48.432	0.000	1.162	4.776	0.000
3500	7.285	48.432	0.000	0.921	4.896	0.000
3600	7.230	48.432	0.000	0.680	5.026	0.000
3700	7.175	48.432	0.000	0.439	5.166	0.000
3800	7.120	48.432	0.000	0.198	5.316	0.000
3900	7.065	48.432	0.000	-0.043	5.476	0.000
4000	7.010	48.432	0.000	-0.284	5.646	0.000
4100	6.955	48.432	0.000	-0.525	5.826	0.000
4200	6.900	48.432	0.000	-0.766	6.016	0.000
4300	6.845	48.432	0.000	-1.007	6.216	0.000
4400	6.790	48.432	0.000	-1.248	6.426	0.000
4500	6.735	48.432	0.000	-1.489	6.646	0.000
4600	6.680	48.432	0.000	-1.730	6.876	0.000
4700	6.625	48.432	0.000	-1.971	7.116	0.000
4800	6.570	48.432	0.000	-2.212	7.366	0.000
4900	6.515	48.432	0.000	-2.453	7.626	0.000
5000	6.460	48.432	0.000	-2.694	7.896	0.000
5100	6.405	48.432	0.000	-2.935	8.176	0.000
5200	6.350	48.432	0.000	-3.176	8.466	0.000
5300	6.295	48.432	0.000	-3.417	8.766	0.000
5400	6.240	48.432	0.000	-3.658	9.076	0.000
5500	6.185	48.432	0.000	-3.899	9.396	0.000
5600	6.130	48.432	0.000	-4.140	9.726	0.000
5700	6.075	48.432	0.000	-4.381	10.066	0.000
5800	6.020	48.432	0.000	-4.622	10.416	0.000
5900	5.965	48.432	0.000	-4.863	10.776	0.000
6000	5.910	48.432	0.000	-5.104	11.146	0.000

Dec. 31, 1960; Mar. 31, 1964

Point Group [C_{2v}]
 $\Delta H_f^0 = [9 \pm 20] \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = [51.464] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 298.15 = [8 \pm 20] \text{ kcal. mole}^{-1}$
 Round State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	[900] (1)	[1000] (2)	[1600] (1)
------------------------------	-----------	------------	------------

Bond Distance: Al-O = [1.62] Å Al-H = [1.64] Å

Bond Angle: H-Al-O = [180°]

B₀ = [0.5271] cm.⁻¹

σ = 1

Heat of Formation.

The heat of formation was estimated by summing the constituent bond energies. The Al-O was taken as that in AlO(g) and the Al-H bond was taken as that in AlH(g), this gave a heat of atomization of 182 kcal.

Heat Capacity and Entropy.

Vibrational frequencies, bond lengths and angles and point group were taken from National Bureau of Standards Report 6297, Jan. 1, 1959, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and Their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine".

AlHO

Aluminum Monohydroxide (AlOH)
(Ideal Gas)

ALUMINUM MONOHYDROXIDE (AlOH)

(IDEAL GAS)

GFW = 43.9889

GFW = 43.9889

Point Group [C_{2v}]

$\Delta H_f^\circ = [-42 \pm 3] \text{ kcal/mol}$

$S_{298.15}^\circ = [51.7 \pm 0.5] \text{ gibbs/mol}$

$\Delta H_f^\circ = [-43 \pm 3] \text{ kcal/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega_e, \text{ cm}^{-1}$

[1000] (1)

[1300] (2)

[3600] (1)

Bond Distance: Al-O = [1.87] Å

Bond Angle: Al-O-H = [180°]

Rotational Constant: B₀ = [0.4256] cm⁻¹

O-H = [0.96] Å

$\sigma = 1$

Heat of Formation

From a mass-spectrometric investigation of the equilibrium

$1/3\text{Al}_2\text{O}_3(\text{g}) + 1/3\text{Al}(\text{g}) + 1/2\text{H}_2(\text{g}) = \text{AlOH}(\text{g})$

M. Farber et al. (1) report second law heats of reaction of 56.7 ± 0.6 kcal at 1800°K, 57.1 ± 2.8 kcal at 2060°K and 62.7 ± 1.4 kcal at 2000°K. Using JANAF auxiliary data, assuming AlOH to be AlOH, we obtain $\Delta H_f^\circ(298, \text{g}) = -44.6 \pm 1, -44.0 \pm 3.2$ and $-38.6 \pm 1.8 \text{ kcal/mol}$. A second equilibrium in the same investigation was

$\text{Al}_2\text{O}(\text{g}) + \text{D}_2\text{O}(\text{g}) = 2\text{AlOD}(\text{g})$

for which second law heats of reaction of 6.3 ± 2.1 kcal at 2060°K and 5.7 ± 0.8 kcal at 2000°K were reported. Farber et al. also measured the heat of reaction.

$1/3\text{Al}_2\text{O}_3(\text{g}) + 4/3 \text{Al}(\text{g}) = \text{Al}_2\text{O}(\text{g})$

at the same temperatures as $-10.7 \pm 2.8 \text{ kcal}$ at 2060° and $-10.3 \pm 10.2 \text{ kcal}$ at 2000°K. Combining these reactions and eliminating $\text{Al}_2\text{O}(\text{g})$ yields $\Delta H_f^\circ(2060) = -4.4 \pm 5.0 \text{ kcal}$ and $\Delta H_f^\circ(2000) = -5 \pm 11 \text{ kcal}$ for the reaction

$1/3\text{Al}_2\text{O}_3(\text{g}) + 4/3\text{Al}(\text{g}) + \text{D}_2\text{O}(\text{g}) = 2\text{AlOD}(\text{g})$.

Using auxiliary JANAF values for $\text{Al}_2\text{O}_3(\text{g})$ and $\text{Al}(\text{g})$, $\Delta H_f^\circ(298, \text{D}_2\text{O}, \text{g}) = -69.56 \text{ kcal/mol}$ (2), and functions for $\text{D}_2\text{O}(\text{g})$ from Friedman and Haar (3) we obtain $\Delta H_f^\circ(298, \text{AlOD}, \text{g}) = -43.9 \pm 6 \text{ kcal/mol}$ and $-43.4 \pm 3 \text{ kcal/mol}$. From all the above results we adopt a value of $\Delta H_f^\circ(298, \text{AlOD}, \text{g}) = -44 \pm 3 \text{ kcal/mol}$, assuming that AlOH is less stable than AlOD by 1 kcal/mol as is the case for H_2O , HDO and D_2O . We obtain $\Delta H_f^\circ(298, \text{AlOH}, \text{g}) = -43 \pm 3 \text{ kcal/mol}$.

Farber et al. (1) also performed weight loss experiments under molecular flow conditions by allowing hydrogen to flow over $\text{Al}_2\text{O}_3(\text{c})$. The products assumed were $\text{AlOH}(\text{g})$, $\text{Al}(\text{g})$, $\text{Al}_2\text{O}(\text{g})$, $\text{H}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ and the equilibrium amounts of $\text{H}(\text{g})$, $\text{Al}(\text{g})$ and $\text{Al}_2\text{O}(\text{g})$ were assumed to be those predicted by the free energies from the JANAF tables. A 3rd law analysis of the equilibrium constants given by Farber for the reaction $2\text{H}_2(\text{g}) + \text{Al}_2\text{O}_3(\text{c}) = 2\text{AlOH}(\text{g}) + \text{H}_2\text{O}(\text{g})$ yields $\Delta H_f^\circ(298, \text{g}) = 238 \pm 12 \text{ kcal/mol}$ and $\Delta H_f^\circ(298, \text{AlOH}, \text{g}) = -52 \pm 6 \text{ kcal/mol}$. However, the assumed equilibria involving $\text{Al}_2\text{O}(\text{g})$ and $\text{Al}(\text{g})$ may be significantly in error and thus the $\Delta H_f^\circ(298)$ should be considered as simply confirming the magnitude determined mass-spectrometrically.

References

1. M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Final Report, under USAF contract F0W611-67-C-0010, AFPR1-TR-67-244, November 1967.
2. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
3. A. S. Friedman and L. Haar, J. Chem. Phys. 22, 2051 (1954).

Heat Capacity and Entropy

The vibrational frequencies are estimated by using the $\text{AlO}(\text{g})$ fundamental as approximately the Al-O stretch; the O-H stretch is that in $\text{H}_2\text{O}(\text{g})$; and the bending frequency is approximately the OH bend in $\text{ODOH}(\text{g})$ reported by T. Shimanouchi, U. S. Natl. Bur. Std. NBS-RS-NBS 6, 1967.

The AlO bond length was taken from U. S. Natl. Bur. Std. Report No. 6297, Jan. 1, 1959, and the OH bond length is assumed to be that in $\text{H}_2\text{O}(\text{g})$. The bond angle is assumed to be 180° using the prediction of A. D. Walsh, J. Chem. Soc. 1953, 2788 (1953), for "HAB" molecules with less than 11 valence electrons. Confirmation of this prediction is scanty for molecules having a more electronegative than B; however, R. L. Kuczkowski, D. R. Lide, Jr., and L. C. Krishner, J. Chem. Phys. 44, 3131 (1966), have confirmed the linearity of KOH and CsOH which have 8 valence electrons.

Mar. 31, 1964; Dec. 31, 1967

T, °K	Cp ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log Kp
0	0.000	0.000	INFINITE	2.110	- 81.947	- 81.947	INFINITE
100	6.995	43.995	56.106	1.419	- 42.104	- 43.046	94.076
200	7.023	48.752	52.377	1.717	- 42.498	- 43.668	47.936
298	7.628	51.701	51.701	2.000	- 43.000	- 44.439	32.575
300	7.643	51.748	51.701	2.014	- 43.010	- 44.480	32.380
400	8.358	54.062	52.631	2.526	- 43.178	- 44.855	32.506
500	9.066	56.092	52.656	3.036	- 43.253	- 45.135	19.729
600	10.110	57.640	53.349	3.694	- 44.364	- 45.513	16.513
700	10.659	59.444	54.197	4.376	- 44.747	- 45.664	14.194
800	11.161	60.905	54.867	5.030	- 45.122	- 45.770	12.041
900	11.629	62.285	55.404	5.654	- 45.493	- 45.843	10.263
1000	12.069	63.645	55.910	6.254	- 45.857	- 45.886	8.916
1100	12.487	64.936	57.042	6.834	- 46.210	- 46.000	7.951
1200	12.887	66.172	57.720	7.390	- 46.558	- 46.084	7.141
1300	13.275	67.365	58.374	7.926	- 46.900	- 46.145	6.451
1400	13.653	68.527	59.002	8.444	- 47.236	- 46.188	5.861
1500	14.023	69.657	59.612	8.946	- 47.566	- 46.216	5.338
1600	14.381	70.758	60.199	9.434	- 47.890	- 46.236	4.868
1700	14.728	71.831	60.765	9.908	- 48.209	- 46.250	4.447
1800	15.065	72.876	61.312	10.369	- 48.523	- 46.259	4.064
1900	15.394	73.895	61.838	10.818	- 48.832	- 46.263	3.717
2000	15.715	74.889	62.343	11.256	- 49.136	- 46.263	3.403
2100	16.028	75.859	62.831	11.684	- 49.436	- 46.260	3.119
2200	16.334	76.805	63.296	12.102	- 49.731	- 46.255	2.863
2300	16.633	77.728	63.739	12.511	- 50.022	- 46.248	2.633
2400	16.926	78.629	64.161	12.911	- 50.309	- 46.239	2.426
2500	17.213	79.505	64.567	13.303	- 50.592	- 46.228	2.241
2600	17.495	80.359	64.948	13.687	- 50.871	- 46.215	2.076
2700	17.772	81.194	65.313	14.063	- 51.146	- 46.199	1.932
2800	18.045	82.009	65.665	14.432	- 51.417	- 46.181	1.807
2900	18.314	82.799	65.996	14.796	- 51.684	- 46.161	1.699
3000	18.579	83.564	66.308	15.155	- 51.947	- 46.139	1.606
3100	18.840	84.305	66.599	15.509	- 52.206	- 46.115	1.527
3200	19.097	85.022	66.870	15.858	- 52.461	- 46.089	1.460
3300	19.350	85.717	67.122	16.202	- 52.712	- 46.061	1.403
3400	19.599	86.394	67.356	16.541	- 52.959	- 46.031	1.354
3500	19.844	87.053	67.575	16.875	- 53.202	- 46.000	1.311
3600	20.085	87.694	67.783	17.204	- 53.441	- 45.968	1.273
3700	20.322	88.318	67.978	17.528	- 53.676	- 45.934	1.240
3800	20.555	88.927	68.160	17.847	- 53.907	- 45.898	1.211
3900	20.784	89.521	68.329	18.161	- 54.134	- 45.860	1.185
4000	21.009	90.100	68.485	18.470	- 54.357	- 45.820	1.162
4100	21.230	90.664	68.637	18.774	- 54.576	- 45.778	1.141
4200	21.447	91.214	68.785	19.073	- 54.791	- 45.734	1.121
4300	21.660	91.758	68.928	19.367	- 55.003	- 45.688	1.102
4400	21.869	92.297	69.066	19.656	- 55.211	- 45.640	1.084
4500	22.074	92.821	69.199	19.940	- 55.416	- 45.590	1.067
4600	22.275	93.331	69.327	20.219	- 55.618	- 45.538	1.051
4700	22.472	93.827	69.450	20.493	- 55.817	- 45.484	1.036
4800	22.666	94.310	69.568	20.762	- 56.013	- 45.428	1.021
4900	22.857	94.780	69.681	21.026	- 56.206	- 45.370	1.007
5000	23.044	95.237	69.789	21.285	- 56.396	- 45.311	0.993
5100	23.228	95.682	69.892	21.539	- 56.583	- 45.250	0.980
5200	23.408	96.116	69.990	21.788	- 56.767	- 45.187	0.967
5300	23.584	96.537	70.083	22.032	- 56.948	- 45.123	0.954
5400	23.757	96.945	70.171	22.271	- 57.126	- 45.058	0.942
5500	23.927	97.340	70.254	22.505	- 57.301	- 44.992	0.930
5600	24.093	97.722	70.332	22.734	- 57.473	- 44.925	0.918
5700	24.256	98.091	70.405	22.958	- 57.642	- 44.857	0.907
5800	24.416	98.447	70.473	23.177	- 57.808	- 44.788	0.896
5900	24.572	98.791	70.536	23.391	- 57.971	- 44.718	0.885
6000	24.725	99.123	70.594	23.600	- 58.131	- 44.647	0.875

Aluminum Monohydroxide Unipositive Ion (AlOH⁺)

GFW = 43.98832

(Ideal Gas)

T, °K	Cp ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	H ^o - H ^o ₂₉₈	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	8.015	54.632	54.632	.000	130.000	126.200	- 92.507
300	8.034	54.682	54.682	.015	130.000	126.176	- 91.919
400	9.079	57.138	54.960	1.811	130.052	125.866	- 86.566
500	9.962	59.262	55.613	1.825	130.156	123.596	- 54.024
600	10.643	61.142	56.381	2.857	130.299	122.270	- 44.537
700	11.167	62.823	57.183	3.948	130.461	120.919	- 37.753
800	11.566	64.343	57.984	5.087	130.628	119.545	- 32.458
900	11.933	65.728	58.768	6.263	130.776	118.151	- 28.551
1000	12.229	67.001	59.529	7.472	129.976	116.724	- 25.554
1100	12.487	68.179	60.263	8.708	128.548	115.270	- 23.001
1200	12.713	69.275	60.969	9.948	126.775	114.598	- 20.871
1300	12.913	70.301	61.648	11.249	124.964	113.406	- 19.065
1400	13.090	71.264	62.300	12.598	123.120	111.820	- 17.515
1500	13.248	72.173	62.929	13.867	121.260	110.795	- 16.169
1600	13.389	73.033	63.533	15.199	119.702	109.734	- 14.989
1700	13.514	73.848	64.116	16.544	118.480	108.480	- 13.946
1800	13.626	74.629	64.679	17.901	117.203	107.209	- 13.017
1900	13.726	75.378	65.222	19.268	115.876	105.876	- 12.197
2000	13.816	76.070	65.767	20.648	114.716	104.627	- 11.433
2100	13.897	76.746	66.255	22.032	113.975	103.314	- 10.752
2200	13.970	77.394	66.725	23.425	113.235	101.991	- 10.132
2300	14.036	78.017	67.223	24.826	111.496	100.657	- 9.565
2400	14.095	78.619	67.695	26.234	109.756	99.312	- 9.048
2500	14.149	79.192	68.134	27.648	108.014	97.952	- 8.563
2600	14.198	79.748	68.570	29.062	106.274	96.586	- 8.119
2700	14.242	80.284	68.994	30.484	104.531	95.209	- 7.707
2800	14.283	80.803	69.406	31.910	102.782	93.818	- 7.316
2900	14.321	81.305	69.806	33.338	101.033	92.413	- 6.947
3000	14.354	81.791	70.200	34.774	99.284	91.000	- 6.595
3100	14.386	82.262	70.581	36.211	97.536	89.581	- 6.260
3200	14.414	82.719	70.953	37.651	95.788	88.166	- 5.943
3300	14.441	83.163	71.317	39.094	94.040	86.751	- 5.644
3400	14.468	83.593	71.671	40.538	92.292	85.333	- 5.362
3500	14.488	84.014	72.018	41.987	90.544	83.916	- 5.097
3600	14.509	84.423	72.357	43.437	88.796	82.500	- 4.849
3700	14.528	84.821	72.689	44.889	87.048	81.083	- 4.615
3800	14.547	85.208	73.013	46.342	85.300	79.666	- 4.394
3900	14.564	85.585	73.330	47.795	83.552	78.249	- 4.184
4000	14.579	85.955	73.641	49.255	81.804	76.832	- 3.984
4100	14.594	86.315	73.946	50.714	80.056	75.415	- 3.794
4200	14.608	86.667	74.245	52.174	78.308	74.000	- 3.614
4300	14.620	87.011	74.538	53.635	76.560	72.583	- 3.443
4400	14.631	87.348	74.824	55.092	74.812	71.166	- 3.281
4500	14.644	87.676	75.107	56.562	73.064	69.750	- 3.127
4600	14.654	87.998	75.344	58.027	71.316	68.333	- 2.980
4700	14.664	88.314	75.656	59.493	69.568	66.916	- 2.840
4800	14.674	88.623	75.923	60.959	67.800	65.500	- 2.706
4900	14.683	88.926	76.174	62.426	66.032	64.083	- 2.578
5000	14.691	89.222	76.443	63.896	64.264	62.666	- 2.456
5100	14.699	89.513	76.696	65.366	62.496	61.250	- 2.339
5200	14.707	89.798	76.945	66.836	60.728	59.833	- 2.226
5300	14.714	90.079	77.190	68.307	58.960	58.416	- 2.117
5400	14.721	90.354	77.433	69.777	57.192	56.999	- 2.012
5500	14.727	90.624	77.666	71.251	55.424	55.582	- 1.911
5600	14.733	90.889	77.903	72.724	53.656	54.165	- 1.813
5700	14.739	91.150	78.133	74.197	51.888	52.748	- 1.718
5800	14.744	91.406	78.360	75.672	50.120	51.331	- 1.626
5900	14.749	91.657	78.583	77.145	48.352	49.914	- 1.536
6000	14.754	91.906	78.803	78.621	46.584	48.497	- 1.449

Dec. 31, 1967

AlHO⁺

ALUMINUM MONOHYDROXIDE UNIPOSITIVE ION (AlOH⁺)

(IDEAL GAS)

GFW = 43.98832

Point Group [C_{∞v}]

$\Delta H^\circ_f = [131 \pm 26] \text{ kcal/mol}$

S^o_{298.15} = [54.6 ± 0.5] gibbs/mol

$\Delta H^\circ_{298.15} = [130 \pm 26] \text{ kcal/mol}$

Ground State Quantum Weight = [4]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
[3000] (1)
[11000] (2)
[38000] (1)

Bond Distance: Al-O = [1.90] Å

Bond Angle: Al-O-H = [180°]

Rotational Constant: B₀ = [0.413] cm⁻¹

O-H = [0.96] Å

σ = 1

Heat of Formation

The heat of formation is obtained from $\Delta H^\circ_{f, \text{AlOH(g)}}$ and its ionization potential, which is estimated to be $7.5 \pm 1 \text{ eV}$ (173 ± 23 kcal). The ionization potential is estimated from a reported value of 7.5 eV for the appearance potential of AlOH⁺, presumably from the parent AlOH, by M. Farber, M. A. Frisch, G. Grenier, and H. C. Ko, Space Sciences, Inc., Final Report under USAF contract F04611-67-C-0010, AFRL-TR-67-244, November, 1967.

Heat Capacity and Entropy

According to the correlation diagram given by A. D. Walsh, J. Chem. Soc. 1953, 2286 (1953), for "HAg" molecules, a compound with 9 valence electrons would have the three outermost electrons in an unfilled π orbital. Thus, it would be a π state since the molecule ought to be linear if it has less than 11 valence electrons. The outermost orbital is a bonding orbital and thus the loss of an electron from it would weaken the bonding. The vibrational frequencies are estimated from those for AlOH(g) with somewhat lower frequencies due to the weaker bonding. Similarly, the Al-O bond length is slightly increased over that in AlOH(g). The enthalpy at 0°K is -2.138 kcal/mol.

AlHO⁺

T, °K	Cp°	S° -(G°-H° ₂₉₈)/T	kcal/mol ΔHf°	ΔGf°	Log Kp
0					
100					
200					
298	6.729	57.304	.000	- 56.622	41.505
300					
350	6.742	57.358	.016	- 56.632	41.257
400	6.754	57.372	.027	- 57.036	31.163
500	10.040	62.147	58.342	- 56.772	25.010
600	10.489	64.019	59.136	- 57.287	20.845
700	10.441	65.594	60.723	- 56.936	17.527
800	11.181	68.156	62.222	- 56.467	13.712
900	11.181	68.156	62.222	- 56.467	13.712
1000	11.603	69.667	62.296	- 55.814	12.198
1100	11.603	70.783	63.017	- 54.985	10.925
1200	11.984	71.635	63.106	- 54.905	9.926
1300	12.250	72.175	63.106	- 54.905	9.126
1400	12.496	73.489	65.003	- 52.050	8.125
1500	12.429	74.542	65.611	- 50.985	7.423
1600	12.550	75.348	66.195	- 49.785	6.800
1700	12.58	76.116	66.58	- 48.791	6.244
1800	12.644	77.531	67.616	- 47.308	5.744
1900	12.684	78.531	68.457	- 46.002	5.291
2000	12.923	78.192	68.319	- 44.652	4.879
2100	12.995	78.824	68.804	- 43.258	4.502
2200	13.119	80.012	69.728	- 41.797	4.154
2300	13.199	80.912	70.168	- 40.355	3.835
2400	13.172	80.571	70.168	- 38.850	3.538
2500	13.220	81.110	70.595	- 37.314	3.262
2600	13.265	81.629	71.009	- 35.739	3.004
2700	13.302	82.135	71.402	- 34.120	2.760
2800	13.332	82.615	71.802	- 32.471	2.537
2900	13.375	83.084	72.185	- 30.800	2.327
3000	13.406	83.538	72.555	- 29.126	2.131
3100	13.435	83.978	72.917	- 27.448	1.947
3200	13.461	84.400	73.263	- 25.764	1.764
3300	13.485	84.820	73.613	- 24.074	1.590
3400	13.507	85.223	73.949	- 22.375	1.410
3500	13.528	85.614	74.276	- 20.666	1.231
3600	13.547	85.992	74.597	- 18.947	1.052
3700	13.565	86.359	74.913	- 17.217	0.873
3800	13.581	86.729	75.216	- 15.478	0.694
3900	13.597	87.082	75.516	- 13.729	0.515
4000	13.611	87.427	75.809	- 11.970	0.336
4100	13.625	87.763	76.097	- 10.201	0.157
4200	13.639	88.081	76.379	- 8.422	- 0.022
4300	13.654	88.381	76.654	- 6.643	- 0.201
4400	13.660	88.726	76.925	- 4.864	- 0.380
4500	13.671	89.033	77.191	- 3.085	- 0.559
4600	13.680	89.334	77.452	- 1.306	- 0.738
4700	13.698	89.617	77.709	0.473	- 0.917
4800	13.706	90.199	78.206	2.254	- 1.096
4900	13.714	90.476	78.449	4.035	- 1.275
5000	13.721	90.748	78.687	5.816	- 1.454
5100	13.725	91.076	78.922	7.597	- 1.633
5200	13.729	91.404	79.154	9.378	- 1.812
5300	13.741	91.533	79.379	11.159	- 1.991
5400	13.747	91.785	79.602	12.940	- 2.170
5500	13.752	92.032	79.822	14.721	- 2.349
5600	13.759	92.275	80.035	16.502	- 2.528
5700	13.763	92.515	80.245	18.283	- 2.707
5800	13.767	92.751	80.441	20.064	- 2.886
5900	13.772	92.982	80.628	21.845	- 3.065
6000	13.772	92.982	80.628	21.845	- 3.065

ALUMINUM MONOHYDROXIDE UNINEGATIVE ION (AlOH⁻) (IDEAL GAS)

Point Group [C_s]
S°_{298.15} = [57.3 ± 0.5] gibbs/mol
Ground State Quantum Weight = [2]

ΔHf°₀ = [-54.33 ± 23] kcal/mol
ΔHf°_{298.15} = [-55 ± 23] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	[900] (1)	[1100] (1)	[3600] (1)
---------------------	-----------	------------	------------

Bond Distance: Al-O = [1.90] Å
Bond Angle: Al-O-H = [120°]
Product of the moments of Inertia: I_AI_BI_C = [4.554 × 10⁻¹¹⁷] g³ cm⁶ σ = 1

Heat of Formation

The heat of formation is obtained from ΔHf°(AlOH, g) and its electron affinity, which is estimated to be 0.5 ± 0.9 eV (12 ± 20 kcal). The electron affinity is estimated to be small, or even negative, since the additional electron must go into an antibonding orbital, according to the correlation diagram of A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

Heat Capacity and Entropy

Since the molecule now has 11 valence electrons, the Walsh correlation diagram predicts a bent molecule. The extra electron is antibonding thus making the bonds weaker than in AlOH(g). Thus the vibrational frequencies and bond lengths are taken to be the same as in AlOH⁻(g), which is also less strongly bound than AlOH(g). The bond angle is arbitrarily chosen as 120°. The principal moments of inertia are I_A = 6.536 × 10⁻³⁹ g cm², I_B = 0.105 × 10⁻³⁹ g cm² and I_C = 6.641 × 10⁻³⁹ g cm². The enthalpy at 0°K is -2.419 kcal/mol.

GFW = 59.98827

(IDEAL GAS)

ALUMINUM DIOXYDRIDE (AlO₂H)

Point Group [C_s]

$\Delta H_f^\circ = [-109 \pm 15] \text{ kcal/mol}$

$S_{298.15}^\circ [60.6 \pm 1.5] \text{ gibbs/mol}$

$\Delta H_f^\circ [298.15] = [-110 \pm 15] \text{ kcal/mol}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\frac{\omega}{\text{cm}^{-1}}$	$\frac{\omega}{\text{cm}^{-1}}$
(3400) (1)	(700) (1)
(1200) (1)	(500) (1)
(1100) (1)	(400) (1)

Bond Distances: Al-O = [1.62] Å Al-O = [1.87] Å O-H = [0.94] Å

Bond Angles: O-Al-O = [180°] Al-O-H = [105°] $\sigma = 1$

Product of the Moments of Inertia: $I_A I_B I_C = [37.349 \times 10^{-117}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

The hydroxyl group can often be considered as intermediate between F and Cl as is illustrated by the following examples of bond energies from these tables.

D(F-H) = 136 kcal, D(Cl-H) = 103 kcal and D(HO-H) = 119 kcal; also D(F-BO) = 163 kcal, D(Cl-BO) = 105 kcal and D(HO-BO) = 143 kcal. Thus from D(F-AlO) = 181 kcal and D(Cl-AlO) = 134 kcal we estimate D(HO-AlO) = 158 ± 20 kcal. This yields $\Delta H_f^\circ(\text{HOAlO}, g) = -127 \pm 20 \text{ kcal/mol}$.

Consider also D(FB-O) = 175 kcal and D(CIB-O) = 169 kcal; and D(FAl-O) = 138 kcal and D(ClAl-O) = 132 kcal; it is evident that the substituent F or Cl has little effect on the B-O and Al-O bonds. Thus, we assume that D(HOAl-O) = 135 ± 10 kcal/mol which leads to $\Delta H_f^\circ(\text{HOAlO}, g) = -119 \pm 10 \text{ kcal/mol}$.

M. Farber, M. A. Frisch, G. Grenier, and H. C. Ko, "Investigation of the Thermodynamic Properties of Rocket Combustion Products," AFRL-TR-67-244, Nov. 1967, found no evidence for the ion DOAlO⁺ when reacting D₂O(g) + Al₂O₃(c). From estimates of the pressure needed to ensure detection of DOAlO and a knowledge of the D₂O pressure, they calculated the most negative value of $\Delta H_f^\circ(\text{DOAlO}, g) = -104 \pm 10 \text{ kcal/mol}$. The absence of DOAlO⁺ may be caused by fragmentation by the ionizing electrons and thus the value quoted may not be a real limit.

We adopt $\Delta H_f^\circ(\text{HOAlO}, g) = -110 \pm 15 \text{ kcal/mol}$ which encompasses all the values.

Heat Capacity and Entropy

Vibrational Frequencies, bond distances, bond angles, and the product of the moments of inertia were taken from "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and Their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine," National Bureau of Standards Report No. 6797, January 1, 1959. The individual moments of inertia are: $I_A = 0.13 \times 10^{-39} \text{ g cm}^2$, $I_B = 16.9 \times 10^{-39} \text{ g cm}^2$, and $I_C = 17.0 \times 10^{-39} \text{ g cm}^2$.

Aluminum Dioxidehydride (AlO₂H)

(Ideal Gas) GFW = 59.98827

T, °K	Cp ^a	S ^b - (C ^a - H ²⁹⁸)/T	H ^c - H ²⁹⁸	ΔH_f°	Log Kp
0	8.000	INFINITE	-2.861	-108.620	INFINITE
100	9.000	71.131	-2.861	-108.620	217.131
200	10.137	56.367	-1.008	-109.526	117.787
298	11.983	60.770	0.000	-110.000	78.314
300	12.014	60.844	+0.022	-110.008	77.817
400	13.483	64.212	1.201	-110.363	57.479
500	14.266	67.643	2.766	-110.695	45.670
600	15.360	70.373	4.204	-110.959	37.597
700	15.961	72.788	5.771	-111.206	31.817
800	16.436	74.911	7.392	-111.453	27.673
900	16.825	76.910	9.056	-111.721	24.086
1000	17.154	78.700	10.755	-112.051	21.129
1100	17.436	80.349	12.485	-112.472	19.052
1200	17.681	81.877	14.241	-112.990	17.150
1300	17.894	83.300	16.020	-113.598	15.537
1400	18.081	84.634	17.819	-114.299	14.153
1500	18.246	85.887	19.636	-115.095	12.951
1600	18.391	87.069	21.468	-115.977	11.897
1700	18.519	88.188	23.313	-116.940	10.966
1800	18.632	89.250	25.171	-117.985	10.137
1900	18.733	90.250	27.039	-119.113	9.405
2000	18.823	91.193	28.917	-120.324	8.755
2100	18.904	92.143	30.804	-121.617	8.118
2200	18.976	93.025	32.698	-122.995	7.565
2300	19.041	93.870	34.599	-124.458	7.055
2400	19.099	94.682	36.506	-125.905	6.595
2500	19.151	95.462	38.418	-127.435	6.168
2600	19.199	96.214	40.336	-129.048	5.772
2700	19.242	96.939	42.258	-130.745	5.406
2800	19.282	97.640	44.184	-132.525	5.000
2900	19.316	98.317	46.114	-134.385	4.655
3000	19.351	98.977	48.058	-136.328	4.368
3100	19.381	99.608	49.984	-138.353	4.104
3200	19.408	100.223	51.924	-140.460	3.858
3300	19.434	100.821	53.866	-142.648	3.630
3400	19.457	101.402	55.810	-144.918	3.418
3500	19.479	101.966	57.757	-147.268	3.204
3600	19.499	102.515	59.706	-149.698	2.996
3700	19.518	103.049	61.657	-152.208	2.794
3800	19.535	103.570	63.610	-154.798	2.598
3900	19.551	104.078	65.564	-157.468	2.408
4000	19.566	104.573	67.520	-160.218	2.224
4100	19.580	105.056	69.477	-163.048	2.046
4200	19.593	105.528	71.436	-165.958	1.874
4300	19.605	105.989	73.396	-168.948	1.708
4400	19.616	106.440	75.356	-172.018	1.548
4500	19.627	106.881	77.316	-175.168	1.394
4600	19.637	107.313	79.282	-178.398	1.246
4700	19.647	107.735	81.246	-181.708	1.104
4800	19.656	108.149	83.211	-185.098	0.968
4900	19.665	108.556	85.171	-188.568	0.838
5000	19.672	108.952	87.134	-192.118	0.714
5100	19.679	109.341	89.112	-195.748	0.596
5200	19.687	109.723	91.090	-199.458	0.484
5300	19.693	110.098	93.069	-203.248	0.378
5400	19.699	110.468	95.049	-207.118	0.278
5500	19.705	110.828	97.034	-211.068	0.184
5600	19.711	111.183	99.020	-215.098	0.096
5700	19.717	111.532	101.011	-219.208	0.014
5800	19.722	111.875	103.006	-223.398	-0.072
5900	19.727	112.212	105.006	-227.668	-0.164
6000	19.731	112.546	107.011	-232.018	-0.262

Dec. 31, 1960; Mar. 31, 1968

T, °K.	C _p ^a	cal. mole ⁻¹ deg ⁻¹ S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ H° - H ₂₉₈ °	ΔH _f ^b	ΔF _f ^c	Log K _f
0						
200						
298	20.650	21.000	4.000	- 28.000	- 11.560	8.474
300	20.786	21.128	4.088	- 28.010	- 11.450	8.347
400	22.400	22.582	2.437	- 28.048	- 11.485	5.215
500	24.200	24.370	4.614	- 28.483	- 11.55	4.063
600	25.550	27.300	7.106	- 29.760	- 5.751	2.095
700	26.600	41.330	5.716	- 29.081	- 11.685	3.648
800	27.400	38.451	15.431	- 30.064	- 11.685	4.733
900	27.817	48.179	15.171	- 30.668	- 23.610	5.733
1000	28.150	51.128	33.157	- 32.766	- 29.775	6.507
1100	28.432	53.825	34.816	- 32.776	- 36.030	7.158
1200	28.620	56.308	23.654	- 32.779	- 42.285	7.701
1300	28.730	58.745	38.707	- 32.782	- 48.540	8.150
1400	28.830	60.745	49.212	- 32.786	- 54.796	8.550
1500	28.970	62.746	41.205	- 32.803	- 61.054	8.895
1600	29.200	64.626	42.410	- 32.827	- 67.309	9.194
1700	29.450	66.500	43.958	- 32.851	- 73.564	9.493
1800	29.680	68.350	45.453	- 32.875	- 79.819	9.792
1900	29.780	69.676	46.403	- 32.899	- 86.074	10.091
2000	29.700	71.197	47.693	- 32.923	- 92.329	10.390

June 30, 1963; Mar. 31, 1964

LITHIUM TETRAHYDROALUMINATE (LiAlH₄)

(CRYSTAL)

MOL. WT. = 37.952

ΔH_f° 0 = UnknownΔH_f° 298.15 = -28.0 ± 2.0 kcal. mole⁻¹

S° 298.15 = [21.0 ± 2.0]

T_d = [410 ± 10]°K.

Heat of Formation.

The heats of solution of LiAlH₄(c) in HCl(aq.) were measured calorimetrically by the following investigators: W. D. Davis, L. S. Maen and G. Stegeman, J. Am. Chem. Soc. 71, 2775 (1949), L. G. Fasolino, et al., "Heat of Formation of Lithium Aluminum Hydride," Special Report, National Research Corporation, Mo., April 26, 1963, and M. B. Smith and G. E. Bess, Jr., J. Chem. Eng. Data, 6, 342 (1963). The results are given in the following table. ΔH_f° 298.15, kcal. mole⁻¹

Chemical Reaction

(1) LiAlH₄(c) + 10(HCl·50H₂O) → (LiCl + AlCl₃ + 6HCl)·500H₂O + 4H₂(g) -165.87(2) (AlCl₃ + LiCl + 6HCl)·500 H₂O + 41020 H₂O(l) -4.43(3) (AlCl₃ + LiCl + 6HCl)·41520 H₂O → AlCl₃·5190 H₂O

(1) + (2) + (3) -170.30

(4) Al + 60(HCl·14H₂O) → (AlCl₃ + 57 HCl)·840 H₂O + 3/2 H₂ -128.14(5) Li + 80(HCl·14H₂O) → (LiCl + 59 HCl)·840 H₂O + 1/2 H₂ -87.05(6) LiAlH₄ + 80(HCl·14 H₂O) → (LiCl + AlCl₃ + 56 HCl)·840 H₂O + 4H₂ -170.52

(4) + (5) - (6) -24.67

(7) LiAlH₄(c) + 39.715(HCl·11.624 H₂O) → [LiCl + AlCl₃ + 35.715 (HCl·12.926 H₂O)] + 4H₂(g) -164.6(8) LiCl(c) + [AlCl₃ + 35.715(HCl·12.926 H₂O)] → [LiCl + AlCl₃ + 35.715 (HCl·12.926 H₂O)] -6.75

(7) - (8) -157.85

Smith and Bess

Fasolino, et al.

Incorporating appropriate auxiliary thermal data, the heats of formation (ΔH_f° 298.15) for LiAlH₄(c) were derived as -28.51 (recalculated value, by Smith and Bess, loc. cit.), -24.67 ± 1.31 and -28.4 ± 1.5 kcal. mole⁻¹, resp. The adopted value, -28.0 ± 2.0 kcal. mole⁻¹, is the weighted average of the above three values.

Heat Capacity and Entropy.

Heat capacities were estimated by comparison with those for LiBH₄(c), LiBO₂(c) and LiAlO₂(c). The entropy value (S° 298.15) was calculated from that for LiBH₄(c) by the substitution of the entropy contribution of B atom by that of Al atom in the LiAlH₄(c) molecule. The entropy values of the constituent B and Al atoms in crystalline compounds were taken from O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.

Temperature of Decomposition.

T_d was reported by A. E. Finholt, A. C. Bond, Jr. and H. I. Schlesinger, J. Am. Chem. Soc. 69, 1199 (1947). The decomposition products are aluminum, hydrogen, and lithium hydride. This reaction is apparently kinetically controlled since the free energy for the decomposition is negative even at room temperature.

AlH₄Li

Aluminum Moniodide (AlI)

(Ideal Gas) Mol. Wt. = 153.89

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.412	50.408	66.655	1.625	14.641	INFINITE
200	8.243	55.958	66.655	1.625	14.876	23.447
298	8.634	59.243	66.655	1.625	15.000	2.657
300	8.638	59.297	66.655	1.625	15.000	2.657
400	8.789	61.805	66.655	1.625	15.000	2.657
500	8.870	63.776	66.655	1.625	15.000	2.657
600	8.921	65.398	66.655	1.625	15.000	2.657
700	8.957	66.776	66.655	1.625	15.000	2.657
800	8.985	67.974	66.655	1.625	15.000	2.657
900	9.007	69.033	66.655	1.625	15.000	2.657
1000	9.027	69.983	66.655	1.625	15.000	2.657
1100	9.045	70.845	66.655	1.625	15.000	2.657
1200	9.061	71.632	66.655	1.625	15.000	2.657
1300	9.076	72.358	66.655	1.625	15.000	2.657
1400	9.091	73.031	66.655	1.625	15.000	2.657
1500	9.105	73.659	66.655	1.625	15.000	2.657
1600	9.119	74.247	66.655	1.625	15.000	2.657
1700	9.132	74.800	66.655	1.625	15.000	2.657
1800	9.145	75.323	66.655	1.625	15.000	2.657
1900	9.158	75.817	66.655	1.625	15.000	2.657
2000	9.171	76.288	66.655	1.625	15.000	2.657
2100	9.183	76.735	66.655	1.625	15.000	2.657
2200	9.196	77.153	66.655	1.625	15.000	2.657
2300	9.208	77.572	66.655	1.625	15.000	2.657
2400	9.221	77.964	66.655	1.625	15.000	2.657
2500	9.233	78.341	66.655	1.625	15.000	2.657
2600	9.245	78.703	66.655	1.625	15.000	2.657
2700	9.257	79.052	66.655	1.625	15.000	2.657
2800	9.269	79.389	66.655	1.625	15.000	2.657
2900	9.282	79.715	66.655	1.625	15.000	2.657
3000	9.294	80.029	66.655	1.625	15.000	2.657
3100	9.306	80.334	66.655	1.625	15.000	2.657
3200	9.318	80.630	66.655	1.625	15.000	2.657
3300	9.330	80.917	66.655	1.625	15.000	2.657
3400	9.342	81.196	66.655	1.625	15.000	2.657
3500	9.354	81.467	66.655	1.625	15.000	2.657
3600	9.366	81.730	66.655	1.625	15.000	2.657
3700	9.378	81.987	66.655	1.625	15.000	2.657
3800	9.390	82.237	66.655	1.625	15.000	2.657
3900	9.402	82.481	66.655	1.625	15.000	2.657
4000	9.414	82.720	66.655	1.625	15.000	2.657
4100	9.426	82.952	66.655	1.625	15.000	2.657
4200	9.438	83.179	66.655	1.625	15.000	2.657
4300	9.449	83.402	66.655	1.625	15.000	2.657
4400	9.461	83.619	66.655	1.625	15.000	2.657
4500	9.473	83.832	66.655	1.625	15.000	2.657
4600	9.485	84.040	66.655	1.625	15.000	2.657
4700	9.497	84.244	66.655	1.625	15.000	2.657
4800	9.509	84.444	66.655	1.625	15.000	2.657
4900	9.521	84.640	66.655	1.625	15.000	2.657
5000	9.533	84.833	66.655	1.625	15.000	2.657
5100	9.545	85.022	66.655	1.625	15.000	2.657
5200	9.556	85.207	66.655	1.625	15.000	2.657
5300	9.568	85.389	66.655	1.625	15.000	2.657
5400	9.580	85.568	66.655	1.625	15.000	2.657
5500	9.592	85.744	66.655	1.625	15.000	2.657
5600	9.604	85.917	66.655	1.625	15.000	2.657
5700	9.616	86.087	66.655	1.625	15.000	2.657
5800	9.628	86.255	66.655	1.625	15.000	2.657
5900	9.640	86.419	66.655	1.625	15.000	2.657
6000	9.651	86.581	66.655	1.625	15.000	2.657

Dec. 31, 1961; Sept. 30, 1964

ALUMINUM MONIODIDE (AlI)

(IDEAL GAS)

MOL. WT. = 153.89

Ground State Configuration Σ^+
 $S_{298.15}^o = [59.243] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = 14.6 \pm 2.0 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o = 14.3 \pm 2.0 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{\epsilon}{\text{cm.}^{-1}} = \frac{g_i}{1}$$

$$\omega_e x_e = 1.0 \text{ cm.}^{-1}$$

$$\alpha_e = [0.1156] \text{ cm.}^{-1}$$

$$r_e = [2.56] \text{ \AA}$$

$$\sigma = 1$$

Heat of Formation.

The dissociation energy (D_0^o) of AlI(ϵ) was reported by A. G. Gaydon¹, R. F. Barrow², and G. Herzberg³, respectively. Hence the corresponding values of ΔH_f^o 298.15 for AlI(ϵ) were derived. The results are given as follows.

Investigator	e.v.	D_0^o kcal. mole ⁻¹	ΔH_f^o 298.15 kcal. mole ⁻¹
Gaydon ¹	3.92	90.4	12.7
Barrow ²	—	87.0	16.0
Herzberg ³	2.9	66.9	36.2

¹ A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall Ltd., London, 1953.

² R. F. Barrow, Trans. Faraday Soc. 56, 952 (1960).

³ G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950.

The adopted value of ΔH_f^o 298.15 for AlI(ϵ) is the average of the first two ΔH_f^o 298.15 values listed in the above table.

Heat Capacity and Entropy.

The spectroscopic constants, ω_e and $\omega_e x_e$, and ground state configuration were taken from G. Herzberg, loc. cit. The values of B_e and α_e were estimated. The bond length (r_e) was estimated by comparison with those for $Al_2I_6(g)$ reported by K. J. Palmer and N. Elliott, J. Am. Chem. Soc. 80, 1852 (1958).

Aluminum Triiodide (AlI₃)
(Crystal) Mol. Wt. = 407.71

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0								
100	23.640	45.300	45.300	0.000	0.000	73.900	72.974	53.489
200	23.680	45.446	45.300	0.044	0.044	73.903	72.968	53.155
300	23.720	45.592	45.300	0.088	0.088	73.906	72.962	52.821
400	23.760	45.738	45.300	0.132	0.132	73.909	72.956	52.487
500	23.800	45.884	45.300	0.176	0.176	73.912	72.950	52.153
600	29.158	63.797	50.321	8.086	8.086	94.129	64.079	23.340
700	29.899	68.353	52.578	11.042	11.042	93.208	59.143	18.464
800	30.335	72.376	54.806	14.095	14.095	92.263	54.340	14.844
900	30.576	75.984	56.962	17.102	17.102	91.309	49.659	12.056
1000	30.700	79.152	59.026	20.166	20.166	90.384	45.011	9.811
1100	30.799	82.123	60.995	23.242	23.242	90.460	40.143	7.975
1200	30.870	84.806	62.869	26.325	26.325	90.540	35.485	6.402
1300	30.908	87.279	64.653	29.414	29.414	90.624	30.913	5.197
1400	30.928	89.541	66.351	32.511	32.511	90.711	26.434	4.284
1500	31.000	91.708	67.972	35.605	35.605	90.771	22.001	3.605

ALUMINUM TRIIODIDE (AlI₃) (CRYSTAL) MOL. WT. = 407.71

ΔH_f^o = Unknown
S_{298.15}^o = {45.3 ± 2.0} cal. deg.⁻¹ mole⁻¹
ΔH_f^o 298.15 = -73.9 ± 1.5 kcal. mole⁻¹
ΔH_m^o = 3.8 kcal. mole⁻¹
ΔH_a^o 298.15 (to dimer) = 28.8 ± 1.8 kcal. mole⁻¹

Heat of Formation.

J. D. Corbett and N. W. Gregory, J. Am. Chem. Soc. 76, 1446 (1954) reported the free energy change, ΔF_{298.15}^o = -8.7 ± 0.2 kcal. mole⁻¹, for the reaction AlI₃(c) + 3HCl(g) → AlCl₃(c) + 3HI(g). By the relationship ΔH = ΔF + TΔS the value of ΔH_f^o 298.15 was derived as -10.1 ± 0.2 kcal. mole⁻¹. The heat of formation (ΔH_f^o 298.15) for AlI₃(c) was evaluated to be -73.86 ± 0.30 kcal. mole⁻¹. The heat of solution of AlI₃(c) in water was measured by D. J. A. Dear and D. D. Eley, J. Chem. Soc., 4684 (1954). From the value, ΔH_f^o 298.15 = -91.4 ± 1.5 kcal. mole⁻¹ for the reaction AlI₃(c) → Al³⁺(aq.) + 3I⁻(aq.), the heat of formation for AlI₃(c) was calculated to be -74.1 ± 1.5 kcal. mole⁻¹. The adopted value of ΔH_f^o 298.15 for AlI₃(c) is the average of the above two values.

Heat Capacity and Entropy.

The heat capacities, S_{298.15}-464°K., were taken from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). They were derived from the enthalpy data measured by W. Fischer, Z. anorg. Chem. 200, 332 (1931). Above 464°K. the C_p values were obtained by graphical extrapolation. The entropy, S_{298.15}^o for AlI₃(c) was calculated from S_{298.15}^o for AlI₃(l) by subtracting ΔS_m^o and the difference between S_{298.15}^o for crystal and liquid.

Melting Data.

Temperature and heat of melting were reported by W. Fischer, loc. cit.

Heat of Sublimation.

Heat of sublimation was calculated from vapor pressure data reported by W. Fischer, O. Rahlfs, and B. Benze, Z. anorg. allgem. Chemie, 205, 1 (1932), by both the second and third law methods. See Al₂I₆(g) table for details.

Aluminum Triiodide (AlI₃)

(Liquid) Mol. Wt. = 407.71

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ° kcal. mole ⁻¹	ΔF _f ° kcal. mole ⁻¹	Log K _p
0						
100						
200						
298	29.000	52.450	0.000	- 70.770	- 71.976	52.757
300	29.000	52.639	- 0.54	- 70.763	- 71.983	52.437
400	29.000	60.972	2.954	- 70.218	- 72.237	39.487
500	29.000	67.443	5.536	- 68.330	- 68.834	30.523
600	29.000	72.731	8.754	- 65.331	- 65.641	23.909
700	29.000	77.019	11.524	- 61.837	- 61.595	19.230
800	29.000	81.273	14.254	- 58.437	- 57.848	15.254
900	29.000	84.489	17.054	- 55.237	- 54.248	11.975
1000	29.000	87.545	20.254	- 52.237	- 50.927	10.911
1100	29.000	90.309	23.254	- 49.427	- 48.005	9.140
1200	29.000	92.732	26.054	- 46.827	- 45.186	7.662
1300	29.000	94.852	28.654	- 44.427	- 42.586	6.412
1400	29.000	96.632	31.054	- 42.227	- 40.286	5.411
1500	29.000	98.133	33.254	- 40.227	- 38.286	4.519
1600	29.000	101.175	37.754	- 38.463	- 36.523	3.744
1700	29.000	102.590	40.054	- 36.963	- 35.023	3.068
1800	29.000	104.150	42.254	- 35.713	- 33.773	2.492
1900	29.000	106.158	44.254	- 34.693	- 32.753	1.946
2000	29.000	107.646	46.254	- 33.873	- 31.933	1.476

ALUMINUM TRIIODIDE (AlI₃)

(LIQUID)

MOL. WT. = 407.71

S°_{298.15} = [52.45] cal. deg.⁻¹ mole⁻¹
 T_m = 464.15°K.
 ΔH_f°_{298.15} = -70.77 ± 1.5 kcal. mole⁻¹
 ΔH_m° = 3.8 kcal. mole⁻¹

Heat of Formation.

ΔH_f°_{298.15}(l) was obtained from ΔH_f°_{298.15}(c) by adding ΔH_m° and the difference between H_{464.15}-H_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity, 464-500°K., was obtained from K. K. Kelley, U. S. Bur. Minea Bull. 584 (1960). It was derived based on the enthalpy data measured by W. Flacher, Z. anorg. Chem. 200, 332 (1931). The C_p values above 500°K. were assumed to be the same as that at 500°K. The entropy, S°_{298.15}, was estimated so that the values of ΔH_f° calculated from vapor pressure data by the second and third law methods were in reasonable agreement.

Melting Data.

T_m and ΔH_m° were reported by W. Flacher, loc. cit.

Aluminum Triiodide (AlI₃)
(Ideal Gas) Mol. Wt. = 407.71

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T cal. mole ⁻¹ deg. ⁻¹	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° _f	Log K _f
0	∞	∞	∞	∞	∞
100	13.828	69.035	102.015	-47.535	INFINITE
200	16.950	79.725	88.414	-52.224	114.130
300	18.281	86.776	86.776	-56.321	61.784
400	18.298	86.890	86.777	-60.440	44.302
500	18.017	82.249	87.503	-60.511	44.080
600	17.422	76.508	88.683	-64.033	34.084
700	16.654	70.051	90.464	-66.643	28.254
800	15.781	63.134	92.051	-68.265	23.043
900	14.857	55.951	93.456	-69.067	18.518
1000	13.895	48.502	94.686	-69.047	14.338
1100	12.834	40.918	95.779	-67.570	12.549
1200	11.718	33.228	96.746	-65.706	11.067
1300	10.578	25.553	97.593	-63.558	9.783
1400	9.437	17.904	98.326	-61.244	8.683
1500	8.307	10.268	98.958	-58.762	7.653
1600	7.198	2.649	99.491	-56.125	6.683
1700	6.122	-5.000	99.934	-53.368	5.769
1800	5.081	-12.611	100.295	-50.502	4.904
1900	4.075	-20.281	100.584	-47.535	4.080
2000	3.104	-27.999	100.809	-44.468	3.300
2100	2.168	-35.756	100.974	-41.316	2.569
2200	1.268	-43.549	101.089	-38.084	1.884
2300	0.404	-51.376	101.156	-34.783	1.244
2400	-0.422	-59.244	101.177	-31.437	0.649
2500	-1.244	-67.156	101.156	-28.062	0.094
2600	-2.062	-75.116	101.094	-24.668	-0.514
2700	-2.875	-83.126	101.000	-21.258	-1.064
2800	-3.683	-91.180	100.874	-17.837	-1.664
2900	-4.486	-99.276	100.719	-14.409	-2.314
3000	-5.284	-107.411	100.536	-10.978	-2.914
3100	-6.077	-115.584	100.326	-7.547	-3.464
3200	-6.865	-123.794	100.091	-4.116	-3.964
3300	-7.648	-132.041	99.822	-0.685	-4.414
3400	-8.426	-140.324	99.526	2.748	-4.814
3500	-9.199	-148.644	99.204	6.187	-5.164
3600	-9.968	-156.999	98.856	9.620	-5.464
3700	-10.732	-165.389	98.484	13.049	-5.714
3800	-11.491	-173.814	98.089	16.474	-5.914
3900	-12.245	-182.274	97.674	19.894	-6.064
4000	-12.994	-190.769	97.244	23.309	-6.164
4100	-13.738	-199.299	96.794	26.719	-6.214
4200	-14.477	-207.864	96.324	30.124	-6.214
4300	-15.211	-216.464	95.834	33.524	-6.164
4400	-15.940	-225.099	95.324	36.919	-6.064
4500	-16.664	-233.769	94.794	40.309	-5.914
4600	-17.383	-242.474	94.244	43.694	-5.714
4700	-18.097	-251.214	93.674	47.074	-5.464
4800	-18.806	-260.000	93.089	50.449	-5.164
4900	-19.510	-268.834	92.489	53.819	-4.814
5000	-20.209	-277.714	91.874	57.184	-4.414
5100	-20.904	-286.639	91.244	60.544	-3.964
5200	-21.594	-295.609	90.594	63.899	-3.464
5300	-22.279	-304.624	89.924	67.249	-2.914
5400	-22.959	-313.684	89.234	70.594	-2.314
5500	-23.634	-322.789	88.524	73.934	-1.664
5600	-24.304	-331.939	87.794	77.264	-0.964
5700	-24.969	-341.134	87.044	80.594	-0.214
5800	-25.629	-350.374	86.274	83.919	0.414
5900	-26.284	-359.659	85.494	87.239	1.014
6000	-26.934	-368.989	84.704	90.554	1.614

Dec. 31, 1961; June 30, 1964

ALUMINUM TRIIODIDE (AlI₃) (IDEAL GAS) MOL. WT. = 407.71

Point Group [D_{3h}]
S_{298.15} = [86.776] cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ = -47.5 ± 1.6 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -49.0 ± 1.6 kcal. mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies
[λ], cm.⁻¹ [λ], cm.⁻¹

[1210] (1) [95] (1)
[170] (1) [450] (2)

Bond Distance: Al-I = 2.44 ± 0.02 Å

Bond Angle: I-Al-I = [120]°K.

Product of the Moments of Inertia: I_AI_BI_C = 1.33213 X 10⁻¹¹⁰ g.³ cm.⁶

Heat of Formation.

The equilibrium pressures of the reaction Al₂I₆(g) → 2AlI₃(g) at several temperatures were determined by W. Fischer, O. Rehlfis and B. Benze, Z. anorg. allgem. Chem. 205, 1 (1932). The heats of dissociation of Al₂I₆(g) were calculated by both second and third law methods. The heats of vaporization, i.e. AlI₃(l) → AlI₃(g), were also evaluated using the calculated partial pressure of AlI₃(g) over AlI₃(l). See AlI₃(g) table for detail. The results obtained are summarized as follows:

Chemical Reaction or Process Temperature Range (°K.) Second Law Value Third Law Value Kcal. Mole⁻¹ ΔH_f⁰ 298.15, Kcal. mole⁻¹ ΔH_f⁰ 298.15(AlI₃, g)

Al₂I₆(g) → 2AlI₃(g) 614 - 744 25.18 23.34 -47.9
Al₂I₆(g) → 2AlI₃(g) 482.8 - 578.0 23.07 23.34 -49.0
AlI₃(l) → AlI₃(g) 493.8 - 645.2 21.45 22.69 -49.2

The three ΔH_f⁰ 298.15(AlI₃, g) values were calculated using the respective second law values of ΔH_f⁰ 298.15. The adopted value, ΔH_f⁰ 298.15 = -49.0 ± 1.6 kcal. mole⁻¹, is the weighted average of the above three values.

Heat Capacity and Entropy.

The molecular structure, bond distances and angle were obtained from P. A. Akshahin, N. G. Rambidi, and E. L. Zecorin, Kristallografiya, 4, 186 (1959). The vibrational frequencies were estimated such that the values of ΔH_f⁰ obtained by the third law method are in reasonable agreement with the corresponding values calculated by the second law method. The three principal moments of inertia are: I_A = I_B = 1.8815 X 10⁻³⁷ and I_C = 3.7630 X 10⁻³⁷ g.² cm.².

Lithium Aluminate (LiAlO₂)
(Crystal) Mol. Wt. = 65.92

T, °K.	C _p	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	0.000	INFINITE	2.1723	-282.779	-282.779	INFINITE
100	4.293	1.532	23.727	2.179	-283.573	-278.574	209.489
200	11.181	4.293	12.749	1.001	-284.329	-269.429	197.467
298	15.200	12.751	12.749	.001	-284.329	-269.429	197.467
300	16.283	12.851	12.749	.031	-284.334	-269.337	194.203
400	19.490	18.012	13.432	1.632	-284.462	-264.312	144.406
500	21.130	22.567	15.814	3.876	-285.194	-259.199	113.290
600	22.153	26.514	16.442	6.043	-285.151	-254.003	92.516
700	22.665	29.988	16.134	8.297	-285.062	-248.819	77.681
800	23.062	33.082	15.813	10.615	-284.950	-243.650	66.559
900	23.429	35.875	21.445	12.987	-284.830	-238.493	57.911
1000	23.760	38.421	23.017	15.403	-284.703	-233.106	50.756
1100	24.774	40.763	24.325	17.851	-286.972	-227.774	45.252
1200	25.143	42.935	25.970	20.337	-286.712	-222.404	40.503
1300	25.495	44.961	27.354	22.669	-286.423	-217.037	36.489
1400	25.834	46.883	28.660	25.456	-286.103	-211.733	33.051
1500	26.163	48.657	29.953	28.056	-285.759	-206.432	30.076
1600	26.485	50.355	31.175	30.686	-285.395	-201.155	27.475
1700	26.802	51.971	32.351	33.353	-285.029	-195.875	25.013
1800	27.115	53.511	33.484	36.059	-284.659	-190.582	22.730
1900	27.425	54.986	34.577	38.776	-284.276	-185.276	20.690
2000	27.733	56.400	35.633	41.534	-283.884	-179.959	18.859
2100	28.040	57.761	36.655	44.322	-283.480	-174.632	17.206
2200	28.340	59.065	37.644	47.126	-283.064	-169.294	15.705
2300	28.640	60.312	38.603	49.930	-282.636	-163.940	14.339
2400	28.940	61.505	39.532	52.734	-282.196	-158.572	13.089
2500	29.240	62.650	40.434	55.538	-281.744	-153.192	11.941
2600	29.540	63.749	41.310	58.342	-281.280	-147.796	10.885
2700	29.840	64.808	42.161	61.146	-280.804	-142.384	9.908
2800	30.140	65.827	42.988	63.950	-280.316	-136.956	9.044
2900	30.440	66.811	43.793	66.754	-279.816	-131.512	8.283
3000	30.740	67.762	44.576	69.558	-279.304	-126.052	7.624

LITHIUM ALUMINATE (LiAlO₂)

MOL. WT. = 65.92

(CRYSTAL)

AlLiO₂

ΔH_f° = -282.78 kcal. mole⁻¹
S_{298.15}° = 12.75 cal. deg.⁻¹ mole⁻¹
ΔH_m° = [6000] cal. mole⁻¹
T_m = 1663°K

Heat of Formation.
ΔH_f 298.15 was measured by J. P. Coughlin, J. Am. Chem. Soc. 79, 2397 (1957).

Heat Capacity and Extrapolation.

Thermodynamic Functions are based on the low temperature heat capacity data of E. O. King, J. Am. Chem. Soc. 77, 3189 (1955), and on the high temperature heat content results of A. O. Christensen, K. O. Conway, and K. K. Kelley, U. S. Bur. Mines Rept. Invest. 5565 (1960).

Melting.

R. Ballo and E. Dittler, Z. anorg. u. allgem. Chem. 76, 39 (1912), list the melting point as between 1900° to 2000°K. More recently, K. H. Kim and P. A. Hummel, J. Am. Ceram. Soc. 43, 611 (1960), determined the melting point as 1883° ± 15°K. by rapidly heating a small sample on a Pt-Rh strip furnace. The value, which was used in this report, was derived from an average of ten measurements by Kim and Hummel.

H. Prophet, The Dow Chemical Company, private communication March 9, 1961, using an arc-omega furnace reports the melting point to be about 1875°K. After seven successive runs on the same sample the melting point approached that of Al₂O₃ at 2308°K. The sample, therefore is decomposed upon fusion to Li₂O vapor and Al₂O₃(c). See O. N. Salmon and L. Marcus J. Am. Ceram. Soc. 43, 549 (1960), and P. A. Hummel, B. S. R. Sastry and D. Watring, Ibid., 41, 88 (1958).

INTERIM TABLE

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100							
200							
298	21.000	19.200	19.200	.000	-273.301	-260.323	190.613
300	21.000	19.330	19.200	-.039	-273.297	-260.244	189.578
400	21.000	25.371	20.024	2.139	-273.126	-255.920	159.021
500	21.000	30.037	21.560	4.239	-273.402	-251.253	109.946
600	21.000	33.686	23.321	6.339	-273.626	-247.101	90.002
700	21.000	37.123	25.066	8.439	-273.691	-242.643	75.753
800	21.000	40.451	26.754	10.539	-273.683	-238.163	62.984
900	21.000	43.681	28.391	12.639	-273.649	-233.764	51.464
1000	21.000	46.813	29.975	14.739	-273.636	-229.495	50.044
1100	21.000	49.853	31.507	16.839	-273.645	-224.205	44.543
1200	21.000	52.802	32.980	18.939	-273.670	-218.903	39.057
1300	21.000	55.661	34.403	21.039	-273.713	-213.589	33.574
1400	21.000	58.439	35.781	23.139	-273.793	-208.264	32.744
1500	21.000	61.126	37.112	25.239	-273.947	-202.928	29.657
1600	21.000	63.723	38.397	27.339	-277.705	-200.060	27.320
1700	21.000	66.237	39.640	29.439	-312.018	-193.696	24.926
1800	21.000	68.669	40.843	31.539	-312.002	-187.863	20.001
1900	21.000	71.025	42.006	33.639	-312.690	-172.695	16.692
2000	21.000	73.307	43.130	35.739	-312.690	-172.695	16.692
2100	21.000	75.514	44.215	37.839	-312.694	-165.696	17.264
2200	21.000	77.647	45.261	39.939	-312.906	-156.695	15.764
2300	21.000	79.706	46.267	42.039	-312.947	-144.692	13.194
2400	21.000	81.689	47.234	44.139	-312.947	-137.690	12.054
2500	21.000	83.595	48.160	46.239	-312.979	-137.690	12.054
2600	21.000	85.427	49.047	48.339	-313.017	-130.687	11.002
2700	21.000	87.182	49.790	50.439	-313.064	-123.682	10.027
2800	21.000	88.859	50.491	52.539	-313.112	-116.676	9.091
2900	21.000	90.462	51.141	54.639	-313.162	-109.670	8.191
3000	21.000	91.994	51.741	56.739	-313.212	-102.664	7.321
3100	21.000	93.457	52.291	58.839	-313.262	-95.658	6.481
3200	21.000	94.851	52.791	60.939	-313.312	-88.652	5.671
3300	21.000	96.184	53.241	63.039	-313.362	-81.646	4.891
3400	21.000	97.457	53.641	65.139	-313.412	-74.640	4.151
3500	21.000	98.671	53.991	67.239	-313.462	-67.634	3.451
3600	21.000	99.825	54.291	69.339	-313.512	-60.628	2.791
3700	21.000	100.929	54.541	71.439	-313.562	-53.622	2.171
3800	21.000	101.973	54.741	73.539	-313.612	-46.616	1.591
3900	21.000	102.967	54.891	75.639	-313.662	-39.610	1.051
4000	21.000	103.911	54.991	77.739	-313.712	-32.604	0.551
4100	21.000	104.805	55.041	79.839	-313.762	-25.598	0.091
4200	21.000	105.649	55.091	81.939	-313.812	-18.592	-0.409
4300	21.000	106.443	55.091	84.039	-313.862	-11.586	-0.909
4400	21.000	107.187	55.041	86.139	-313.912	-4.580	-1.409
4500	21.000	107.881	54.941	88.239	-313.962	2.426	-1.909
4600	21.000	108.525	54.791	90.339	-314.012	9.420	-2.409
4700	21.000	109.119	54.591	92.439	-314.062	16.414	-2.909
4800	21.000	109.663	54.341	94.539	-314.112	23.408	-3.409
4900	21.000	110.157	53.991	96.639	-314.162	30.402	-3.909
5000	21.000	110.601	53.591	98.739	-314.212	37.396	-4.409
5100	21.000	111.005	53.141	100.839	-314.262	44.390	-4.909
5200	21.000	111.369	52.641	102.939	-314.312	51.384	-5.409
5300	21.000	111.693	52.091	105.039	-314.362	58.378	-5.909
5400	21.000	111.977	51.491	107.139	-314.412	65.372	-6.409
5500	21.000	112.221	50.841	109.239	-314.462	72.366	-6.909
5600	21.000	112.425	50.141	111.339	-314.512	79.360	-7.409
5700	21.000	112.589	49.391	113.439	-314.562	86.354	-7.909
5800	21.000	112.713	48.591	115.539	-314.612	93.348	-8.409
5900	21.000	112.797	47.741	117.639	-314.662	100.342	-8.909
6000	21.000	112.841	46.841	119.739	-314.712	107.336	-9.409
6100	21.000	112.845	45.891	121.839	-314.762	114.330	-9.909
6200	21.000	112.809	44.891	123.939	-314.812	121.324	-10.409
6300	21.000	112.733	43.841	126.039	-314.862	128.318	-10.909
6400	21.000	112.617	42.741	128.139	-314.912	135.312	-11.409
6500	21.000	112.461	41.591	130.239	-314.962	142.306	-11.909
6600	21.000	112.265	40.391	132.339	-315.012	149.300	-12.409
6700	21.000	112.029	39.141	134.439	-315.062	156.294	-12.909
6800	21.000	111.753	37.841	136.539	-315.112	163.288	-13.409
6900	21.000	111.437	36.491	138.639	-315.162	170.282	-13.909
7000	21.000	111.081	35.091	140.739	-315.212	177.276	-14.409
7100	21.000	110.685	33.641	142.839	-315.262	184.270	-14.909
7200	21.000	110.249	32.141	144.939	-315.312	191.264	-15.409
7300	21.000	109.773	30.591	147.039	-315.362	198.258	-15.909
7400	21.000	109.257	28.991	149.139	-315.412	205.252	-16.409
7500	21.000	108.701	27.341	151.239	-315.462	212.246	-16.909
7600	21.000	108.105	25.641	153.339	-315.512	219.240	-17.409
7700	21.000	107.469	23.891	155.439	-315.562	226.234	-17.909
7800	21.000	106.793	22.091	157.539	-315.612	233.228	-18.409
7900	21.000	106.077	20.241	159.639	-315.662	240.222	-18.909
8000	21.000	105.321	18.341	161.739	-315.712	247.216	-19.409
8100	21.000	104.525	16.391	163.839	-315.762	254.210	-19.909
8200	21.000	103.689	14.391	165.939	-315.812	261.204	-20.409
8300	21.000	102.813	12.341	168.039	-315.862	268.198	-20.909
8400	21.000	101.897	10.241	170.139	-315.912	275.192	-21.409
8500	21.000	100.941	8.091	172.239	-315.962	282.186	-21.909
8600	21.000	100.045	5.891	174.339	-316.012	289.180	-22.409
8700	21.000	99.109	3.641	176.439	-316.062	296.174	-22.909
8800	21.000	98.133	1.391	178.539	-316.112	303.168	-23.409
8900	21.000	97.117	-0.891	180.639	-316.162	310.162	-23.909
9000	21.000	96.061	-3.091	182.739	-316.212	317.156	-24.409
9100	21.000	94.965	-5.291	184.839	-316.262	324.150	-24.909
9200	21.000	93.829	-7.491	186.939	-316.312	331.144	-25.409
9300	21.000	92.653	-9.691	189.039	-316.362	338.138	-25.909
9400	21.000	91.437	-11.891	191.139	-316.412	345.132	-26.409
9500	21.000	90.181	-14.091	193.239	-316.462	352.126	-26.909
9600	21.000	88.885	-16.291	195.339	-316.512	359.120	-27.409
9700	21.000	87.549	-18.491	197.439	-316.562	366.114	-27.909
9800	21.000	86.173	-20.691	199.539	-316.612	373.108	-28.409
9900	21.000	84.757	-22.891	201.639	-316.662	380.102	-28.909
10000	21.000	83.301	-25.091	203.739	-316.712	387.096	-29.409
10100	21.000	81.805	-27.291	205.839	-316.762	394.090	-29.909
10200	21.000	80.269	-29.491	207.939	-316.812	401.084	-30.409
10300	21.000	78.693	-31.691	210.039	-316.862	408.078	-30.909
10400	21.000	77.077	-33.891	212.139	-316.912	415.072	-31.409
10500	21.000	75.421	-36.091	214.239	-316.962	422.066	-31.909
10600	21.000	73.725	-38.291	216.339	-317.012	429.060	-32.409
10700	21.000	71.989	-40.491	218.439	-317.062	436.054	-32.909
10800	21.000	70.213	-42.691	220.539	-317.112	443.048	-33.409
10900	21.000	68.397	-44.891	222.639	-317.162	450.042	-33.909
11000	21.000	66.541	-47.091	224.739	-317.212	457.036	-34.409
11100	21.000	64.645	-49.291	226.839	-317.262	464.030	-34.909
11200	21.000	62.709	-51.491	228.939	-317.312	471.024	-35.409
11300	21.000	60.733	-53.691	231.039	-317.362	478.018	-35.909
11400	21.000	58.717	-55.891	233.139	-317.412	485.012	-36.409
11500	21.000	56.661	-58.091	235.239	-317.462	492.006	-36.909
11600	21.000	54.565	-60.291	237.339	-317.512	499.000	-37.409
11700	21.000	52.429	-62.491	239.439	-317.562	506.000	-37.909
11800	21.000	50.253	-64.691	241.539	-317.612	513.000	-38.409
11900	21.000	48.037	-66.891	243.639	-317.662	520.000	-38.909
12000	21.000	45.781	-69.091	245.739	-317.712	527.000	-39.409
12100	21.000	43.485	-71.291	247.839	-317.762	534.000	-39.909
12200	21.000	41.149	-73.491	249.939	-317.812	541.000	-40.409
12300	21.000	38.773	-75.691	252.039	-317.862	548.000	-40.909
12400	21.000	36.357	-77.891	254.139	-317.912	555.000	-41.409
12500	21.000	33.901	-80.091	256.239	-317.962	562.000	-41.909
12600	21.000	31.405	-82.291	258.339	-318.012	569.000	-42.409
12700	21.000	28.869	-84.491	260.439	-318.062	576.000	-42.909
12800	21.000	26.293	-86.691	262.539	-318.112	583.000	-43.409
12900	21.000	23.677	-88.891	264.639	-318.162	590.000	-43.909
13000	21.000	21.021	-91.091	266.739	-318.212	597.000	-44.409
13100	21.000						

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	0.000	INFINITE	-0.925	-74.795	-74.795	INFINITE
100	1.360	0.519	9.388	-0.887	-75.205	-73.187	159.942
200	4.913	2.435	5.399	-0.589	-75.701	-70.979	77.558
298	7.221	4.816	4.816	-0.000	-76.000	-68.595	50.279
300	7.225	4.861	4.816	-0.13	-76.004	-68.549	49.935
400	8.700	7.155	5.119	0.814	-76.149	-66.038	36.080
500	9.701	9.210	5.736	1.737	-76.204	-63.503	27.756
600	10.439	11.048	6.471	2.747	-76.207	-60.942	22.204
700	10.915	12.696	7.245	3.816	-76.188	-58.423	18.240
800	11.255	14.177	8.020	4.926	-76.166	-55.887	15.267
900	11.495	15.518	8.780	6.064	-76.155	-53.352	12.955
1000	11.660	16.738	9.516	7.222	-76.055	-50.834	11.065
1100	11.769	17.855	10.224	8.394	-76.577	-47.835	9.504
1200	11.836	18.882	10.903	9.575	-78.497	-45.044	8.203
1300	11.876	19.831	11.554	10.760	-78.417	-42.260	7.104
1400	11.901	20.712	12.177	11.949	-78.339	-39.482	6.163
1500	11.923	21.534	12.774	13.140	-78.262	-36.709	5.348
1600	11.955	22.304	13.345	14.334	-78.186	-33.940	4.636
1700	12.000	23.030	13.894	15.532	-78.110	-31.178	4.008
1800	12.023	23.717	14.421	16.733	-78.033	-28.420	3.450
1900	12.035	24.367	14.927	17.936	-77.957	-25.664	2.952
2000	12.065	24.985	15.415	19.141	-77.881	-22.914	2.504
2100	12.092	25.575	15.885	20.349	-77.804	-20.169	2.099
2200	12.115	26.138	16.338	21.559	-77.727	-17.419	1.731
2300	12.135	26.677	16.776	22.772	-77.649	-14.687	1.396
2400	12.152	27.194	17.199	23.986	-77.570	-11.951	1.088
2500	12.165	27.690	17.609	25.202	-77.491	-9.218	0.806
2600	12.183	28.167	18.006	26.420	-77.412	-6.490	0.545
2700	12.199	28.628	18.391	27.639	-77.333	-3.763	0.305
2800	12.215	29.072	18.765	28.859	-77.254	-1.033	0.068
2900	12.231	29.500	19.127	30.082	-77.175	1.703	-0.175
3000	12.245	29.915	19.480	31.305	-77.096	4.445	-0.445
						11.196	-0.816

$$\Delta H_f^o = -74.8 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = -76.0 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 4.816 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_D = [2790^\circ \text{K}]$$

Heat of Formation.

The selected heat of formation is the average of two independent calorimetric determinations. The heat of formation was reported to be $-76.5 \pm 0.2 \text{ kcal. mole}^{-1}$ and $-75.6 \pm 0.4 \text{ kcal. mole}^{-1}$. The former value was reported by C. A. Neugebauer and J. L. Margrave, *Z. Anorg. Allgem. Chem.* **290**, 82 (1957). The latter value was reported by A. D. Mah, E. G. King, W. W. Weller, and A. V. Christensen, U. S. Bureau of Mines Report of Investigations **5716** (1961).

Vapor pressure measurements agree with the selected heat of formation. For instance $\Delta H_f^o 298.15 = -75.5 \text{ kcal. mole}^{-1}$ for AlN(c) was calculated from the heat for the reaction $2\text{AlN(c)} \rightarrow 2\text{Al(g)} + \text{N}_2(\text{g})$ and the heat of sublimation, $78.0 \text{ kcal. mole}^{-1}$, for Al(c). This heat of reaction was obtained from a third law calculation using JANAP values for the free energy functions and torsion effusion pressures measured by D. L. Hildenbrand and L. P. Theard, *Aeronutronic Technical Report U-1497* (1961). Vapor pressure measurements with a microbalance in a vacuum system by L. H. Dreger, V. V. Dedape, and J. L. Margrave, *J. Phys. Chem.* **66**, 1556 (1962) agree with the selected $\Delta H_f^o 298.15$. When recalculated with the sublimation coefficient ($Q \times 2.2 \times 10^{-5}$) reported by Hildenbrand and Theard, some of the Knudsen cell measurements by M. Hoch and D. White, "The Vaporization of Boron Nitride and Aluminum Nitride," *ASTIA Unclassified Report 142616*, October 29, 1956, agree with the selected heat of formation.

Earlier determinations of the heat of formation which apparently are in error are summarized by C. A. Neugebauer and J. L. Margrave (*loc. cit.*) and by L. H. Dreger et al. (*loc. cit.*).

Heat Capacity and Entropy.

The heat capacity and entropy were reported by A. D. Mah et al. (*loc. cit.*). They measured the low temperature (51-298.15°K) and high temperature (298.15-1800°K) heat capacities and extrapolated the heat capacity from 0 to 51°K using the T^3 law. A smooth extrapolation of the heat capacity was made from 1800° to 3000°K. The heat content of AlN(c) was recently determined from 300 to 1200°K by R. Mezaki, "Heat Contents of Inorganic Substances at High Temperatures," M. S. Thesis, University of Wisconsin (1961). The enthalpies reported by Mezaki are about 1% greater than those of Mah et al.

Decomposition Data.

P. O. Schissel and W. S. Williams, *Bull. Am. Phys. Soc. II*, **4**, 139 (1959) studied the vaporization of AlN with the mass spectrometer and detected only the gaseous species Al and N_2 . The temperature at which the ΔH_f^o of AlN(c) and Al(g) were equal, 2788.9°K, was taken as the temperature of decomposition.

(Ideal Gas)

GFW = 40.9882

ALUMINUM NITRIDE (AlN)

(IDEAL GAS)

OPW = 40.9882

T, °K	C _p ^o	S ^o - (C _p ^o - H _f ²⁹⁸)/T	H ^o - H _f ²⁹⁸	ΔH _f ^o	Log K _p
0	0.000	INFINITE	- 2.104	104.024	INFINITE
100	6.997	42.840	56.950	104.266	102.056
200	7.079	47.683	51.242	104.176	99.653
298	7.444	50.573	0.000	104.000	97.763
300	7.452	50.620	0.074	103.926	97.724
400	7.748	52.416	20.371	103.814	95.724
500	8.134	54.801	51.444	103.631	93.644
600	8.347	56.104	52.099	103.440	91.664
700	8.500	57.402	52.766	103.234	89.718
800	8.612	58.545	53.418	103.022	87.802
900	8.694	59.584	54.054	102.806	85.914
1000	8.763	60.584	54.684	102.586	84.231
1100	8.815	61.322	55.214	102.359	82.701
1200	8.858	62.001	55.755	102.126	81.176
1300	8.894	62.601	56.270	101.888	79.654
1400	8.925	63.128	56.762	101.645	78.132
1500	8.952	63.578	57.228	101.398	76.615
1600	8.976	64.057	57.674	101.148	75.293
1700	8.997	64.520	58.101	100.893	74.068
1800	9.017	64.917	58.510	100.632	72.882
1900	9.034	65.248	58.898	100.366	71.734
2000	9.052	65.568	59.272	100.094	70.616
2100	9.067	65.871	59.642	99.816	69.528
2200	9.082	66.153	59.991	99.532	68.468
2300	9.096	66.417	60.328	99.242	67.434
2400	9.110	66.666	60.657	98.946	66.424
2500	9.123	66.896	60.967	98.644	65.436
2600	9.135	67.054	61.271	98.336	64.468
2700	9.147	67.239	61.566	98.022	63.520
2800	9.159	67.432	61.852	97.702	62.592
2900	9.170	67.642	62.132	97.376	61.684
3000	9.182	67.865	62.398	97.044	60.796
3100	9.193	68.066	62.666	96.706	59.928
3200	9.204	68.258	62.915	96.362	59.080
3300	9.215	68.442	63.163	96.012	58.252
3400	9.226	68.618	63.401	95.656	57.444
3500	9.236	68.784	63.640	95.294	56.656
3600	9.247	68.945	63.870	94.926	55.888
3700	9.257	69.098	64.095	94.552	55.140
3800	9.267	69.245	64.314	94.172	54.412
3900	9.276	69.386	64.528	93.786	53.704
4000	9.287	69.521	64.737	93.394	53.016
4100	9.297	69.651	64.942	92.996	52.348
4200	9.307	69.775	65.143	92.592	51.698
4300	9.317	69.894	65.339	92.182	51.068
4400	9.326	69.998	65.531	91.766	50.448
4500	9.336	70.118	65.720	91.344	49.838
4600	9.346	70.233	65.905	90.916	49.238
4700	9.356	70.344	66.086	90.482	48.648
4800	9.365	70.451	66.264	90.042	48.068
4900	9.374	70.554	66.438	89.596	47.498
5000	9.383	70.653	66.610	89.144	46.938
5100	9.394	70.749	66.778	88.686	46.388
5200	9.404	70.842	66.944	88.222	45.848
5300	9.413	70.932	67.106	87.752	45.308
5400	9.422	71.018	67.264	87.276	44.768
5500	9.432	71.101	67.423	86.794	44.228
5600	9.441	71.171	67.578	86.306	43.688
5700	9.451	71.238	67.730	85.812	43.148
5800	9.460	71.302	67.880	85.312	42.608
5900	9.469	71.363	68.028	84.806	42.068
6000	9.479	71.423	68.173	84.294	41.528

Dec. 31, 1960; Mar. 31, 1964; Mar. 31, 1967

Ground State Configuration [1Σ⁺]ΔH_f^o = 104 ± 20 kcal/molS_{298.15} = [50.573] gibbs/molΔH_f^o_{298.15} = 104 ± 20 kcal/mol

Electronic Levels and Quantum Weights

$$\frac{e_1, \text{ cm}^{-1}}{0} \frac{g_1}{1}$$

$$w_{e_e} = [930] \text{ cm}^{-1}$$

$$w_{e_e} = [6.9] \text{ cm}^{-1}$$

$$\sigma = 1$$

$$B_e = [0.6748] \text{ cm}^{-1}$$

$$\alpha_e = [0.0064] \text{ cm}^{-1}$$

$$r_e = [1.65] \text{ Å}$$

Heat of Formation.

The heat of formation is calculated from the estimated w_e and w_{e_e} using $D_0 = w/2w_{e_e}$, as 89 kcal/mol.J. L. Margrave and P. Stephitanonda, J. Phys. Chem. 59, 1231 (1955) estimated values of the bond length as 1.23 - 1.65 Å and calculated from an ionic model D_0 values of 137 - 82 kcal/mol. Using an estimated bond length of 1.65 Å and a $D_0 = 87$ kcal/mol leads to ΔH_f^o₂₉₈ = 104 kcal/mol.

Heat Capacity and Entropy.

The bond length is estimated as 1.65 Å from a comparison with the bond lengths of SO, PO, SiO, AlO, MgO, S₂, SiS, AlS, PN, SiN, and the sums of covalent radii. This bond length is then used with Ouggenheimer's Relation[K. M. Ouggenheimer, Proc. Phys. Soc. (London), 59, 456 (1946)] to calculate a value for w_e . By analogy with SiN(g) it is taken to closely approach the multiple bonding case, which gives $w_e = 960 \text{ cm}^{-1}$. The anharmonicity correction x_e is calculated by assuming the product $x_e \mu_e^{1/2}$ equal to that for AlO(g). The value of α_e is calculated using the relation:

$$\alpha_e = 6(w_e x_e \mu_e^{3/2})^{1/2} / 2 - B_e^2 / w_e$$

Sodium Aluminate (NaAlO₂)

(Crystal) Mol. Wt. = 81.971

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	4.754	3.586	2.844	-268.974	-268.974	-268.974	INFINITE
200	13.011	10.583	2.597	-265.866	-265.866	-265.866	579.869
298	17.610	16.826	2.548	-270.526	-260.557	-260.557	284.687
300	17.660	16.935	2.548	-270.843	-255.466	-255.466	187.322
400	19.936	22.347	2.499	-271.609	-250.058	-250.058	186.098
500	21.608	26.868	2.464	-271.654	-244.937	-244.937	107.052
600	22.531	30.973	2.436	-271.568	-239.591	-239.591	87.267
700	23.492	34.520	2.413	-271.436	-234.272	-234.272	72.140
800	24.502	38.085	2.396	-271.260	-228.999	-228.999	62.557
900	25.566	40.889	2.384	-271.050	-223.718	-223.718	54.378
1000	26.684	43.442	2.378	-270.815	-218.437	-218.437	47.117
1100	27.854	45.792	2.376	-270.564	-213.156	-213.156	42.292
1200	29.074	47.975	2.376	-270.300	-207.875	-207.875	37.591
1300	30.342	50.017	2.376	-270.026	-202.594	-202.594	33.048
1400	31.658	51.938	2.376	-269.745	-197.313	-197.313	30.004
1500	33.024	53.757	2.376	-269.460	-192.032	-192.032	26.957
1600	34.442	55.485	2.376	-269.171	-186.751	-186.751	24.259
1700	35.914	57.135	2.376	-268.878	-181.470	-181.470	21.802
1800	37.442	58.714	2.376	-268.582	-176.189	-176.189	19.611
1900	39.024	60.230	2.376	-268.283	-170.908	-170.908	17.659
2000	40.664	61.688	2.376	-267.981	-165.627	-165.627	15.929
2100	42.364	63.094	2.376	-267.676	-160.346	-160.346	14.375
2200	44.124	64.451	2.376	-267.368	-155.065	-155.065	13.000
2300	45.944	65.761	2.376	-267.057	-149.784	-149.784	11.811
2400	47.824	67.026	2.376	-266.743	-144.503	-144.503	10.797
2500	49.764	68.249	2.376	-266.426	-139.222	-139.222	9.950
2600	51.764	69.434	2.376	-266.106	-133.941	-133.941	9.267
2700	53.824	70.581	2.376	-265.783	-128.660	-128.660	8.711
2800	55.944	71.693	2.376	-265.457	-123.379	-123.379	8.267
2900	58.124	72.769	2.376	-265.128	-118.098	-118.098	7.929
3000	60.364	73.822	2.376	-264.796	-112.817	-112.817	7.697

SODIUM ALUMINATE (NaAlO₂)

(CRYSTAL)

MOL. WT. = 81.971

$$\Delta H_f^0 = -268.97 \pm 0.17 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = -270.84 \pm 0.17 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 0.310 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = \text{Unknown}$$

$$S_{298.15}^0 = 16.826 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_c = 740^\circ \text{K.}$$

$$T_m = \text{above } 1925^\circ \text{K.}$$

Heat of Formation.

ΔH_f^0 298.15 was reported by J. P. Coughlin, J. Am. Chem. Soc. 79, 2397 (1957). The value was calculated from the measured heat of solution of NaAlO₂(c) at 303.15°K. in 4.36M hydrochloric acid solution.

Heat Capacity and Entropy.

The low temperature heat capacities, below 350°K., were measured by E. F. Westrum, University of Michigan, Ann Arbor, Michigan, private communication, May 19, 1960. Heat capacities above 350°K. 399.4 - 1698.6°K., were measured by A. U. Christensen, K. C. Conway, and K. K. Kelley, U. S. Bur. Mines Rept. Invest. 5565 (1960).

These two sets of C_p data were plotted graphically and joined smoothly at 350°K. Low temperature heat capacities $S_{298.15}^0$ were also determined by E. O. King, J. Am. Chem. Soc. 77, 3189 (1955), which agree very well with those reported by E. F. Westrum, loc. cit. $S_{298.15}^0$ was reported by E. F. Westrum, loc. cit., using $S_{298.15}^0(\text{extrap.}) = 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Transition Data.

T_c and ΔH_f^0 were obtained from A. U. Christensen, K. C. Conway, and K. K. Kelley, loc. cit.

Temperature of Melting.

T_m was taken from K. Kammermeyer and A. B. Peck, J. Am. Ceram. Soc. 15, 363 (1933).

ALUMINUM MONOXIDE UNIPosITIVE ION (AlO⁺) (IDEAL GAS) GFW = 42.9804

ΔHf₀[°] = 239 ± 15 kcal/mol

ΔHf_{298.15}[°] = 239 ± 15 kcal/mol

Ground State Configuration [1²]

S_{298.15}[°] = [51.1 ± 3] gibbs/mol

Electronic Levels and Degeneracies

E _i , cm ⁻¹	g _i
0	(1)
[2300]	(6)
[2300]	(3)
[3600]	(2)
[20000]	(1)

ω_eX_e = [6.0] cm⁻¹
ω_e = [0.0053] cm⁻¹
σ = 1
r_e = [1.7] Å

Heat of Formation

The ionization potential of AlO has been reported as 9.5 ± 0.5eV(219 kcal) by J. Drowart, G. DeMaria, R. P. Burns, and M. G. Inghram, J. Chem. Phys. 32, 1366 (1960), and by G. DeMaria, J. Drowart and M. G. Inghram, J. Chem. Phys. 30, 318 (1959). Using this value in conjunction with ΔHf₀[°](AlO, g) = 20 ± 4 kcal/mol, we obtain ΔHf₂₉₈[°](AlO⁺) = 239 ± 15 kcal/mol.

Heat Capacity and Entropy

AlO⁺ is isoelectronic with MgO and we estimated the electronic ground state and excited states by comparison with those for MgO as reported by H. G. Richards, G. Verhaegen and C. M. Moser, J. Chem. Phys. 45, 3226 (1966). The bond length is estimated to be longer than that in AlO since the dissociation energy of AlO⁺ is less than that of AlO. The vibrational frequency and anharmonicity are estimated between those for MgO and AlO and the rotational constant, α_e, is derived from the above quantities assuming a Morse potential function.

The enthalpy at 0°K is -2.118 kcal/mol.

Aluminum Monoxide Unipositive Ion (AlO⁺)

GFW = 42.9804

(Ideal Gas)

T, °K	Cp [°]	gibbs/mol S [°]	-(G [°] -H [°] ₂₉₈)/T	H [°] -H [°] ₂₉₈	kcal/mol ΔHf [°]	ΔGf [°]	Log Kp
0							
100							
200							
298	7.591	51.064	51.064	0.000	239.000	231.612	-169.776
300	7.601	51.111	51.064	0.018	239.006	231.565	-168.495
400	8.271	51.330	51.369	1.605	239.339	229.037	-125.140
500	9.274	55.330	51.970	1.680	239.714	226.419	-98.967
600	10.523	57.129	52.681	2.669	240.164	223.718	-81.489
700	11.566	58.584	53.440	3.783	240.720	220.745	-68.579
800	12.398	59.814	54.099	5.087	241.429	217.522	-58.241
900	13.048	61.083	54.698	6.287	241.913	215.132	-52.241
1000	13.141	63.365	55.767	7.599	239.975	212.308	-46.400
1100	12.984	64.612	56.515	8.906	240.601	209.510	-41.626
1200	12.659	65.730	57.237	10.141	241.200	206.956	-37.637
1300	12.284	66.741	57.931	11.311	241.766	204.622	-34.254
1400	11.864	67.633	58.591	12.459	242.283	202.613	-31.348
1500	11.450	68.448	59.222	13.640	242.767	197.832	-28.824
1600	11.351	69.191	59.822	14.900	243.216	194.822	-26.611
1700	11.069	70.001	60.393	16.111	243.635	191.795	-24.656
1800	10.669	71.080	61.056	17.285	244.036	188.748	-22.954
2000	10.504	71.623	61.951	19.344	244.739	182.539	-19.947
2100	10.363	72.132	62.424	20.387	245.068	179.420	-18.672
2200	10.243	72.611	62.809	21.417	245.360	176.268	-17.512
2300	10.144	73.068	63.114	22.436	245.626	173.082	-16.456
2400	10.054	73.494	63.375	23.446	245.866	169.982	-15.479
2500	9.974	73.903	63.124	24.447	246.241	166.807	-14.582
2600	9.915	74.293	64.508	25.442	246.508	163.625	-13.754
2700	9.861	74.666	64.877	26.431	246.766	160.433	-12.986
2800	9.774	75.368	65.577	28.394	247.062	157.354	-12.282
3000	9.740	75.698	65.908	29.369	247.609	156.629	-11.410
3100	9.710	76.017	66.229	30.342	247.952	155.889	-10.990
3200	9.685	76.325	66.540	31.311	248.192	155.135	-10.595
3300	9.664	76.621	66.846	32.274	248.426	154.362	-10.227
3400	9.630	77.190	67.413	34.208	248.954	153.574	-9.872
3500	9.618	77.461	67.692	35.170	249.103	152.773	-9.540
3600	9.618	77.461	67.692	35.170	249.103	151.962	-9.225
3700	9.609	77.425	67.650	36.132	249.173	151.131	-8.927
3800	9.592	77.230	67.473	36.051	249.003	150.283	-8.643
3900	9.567	76.873	67.020	35.010	248.362	148.575	-8.118
4000	9.563	76.710	66.961	34.969	248.320	147.697	-7.873
4100	9.560	76.640	66.927	34.927	248.276	146.815	-7.640
4200	9.550	76.540	66.846	34.846	248.192	145.927	-7.416
4300	9.537	76.386	66.689	34.683	247.954	145.013	-7.203
4400	9.579	79.601	69.868	43.801	185.628	144.092	-6.998
4500	9.560	79.812	70.082	44.759	186.076	143.168	-6.802
4600	9.562	80.018	70.377	45.717	186.519	142.224	-6.613
4700	9.568	80.417	70.696	47.634	187.401	140.325	-6.256
4800	9.592	80.611	70.892	48.593	187.836	139.359	-6.091
4900	9.596	80.601	71.085	49.552	188.270	138.384	-5.930
5000	9.601	80.470	71.256	50.512	188.701	137.401	-5.775
5100	9.612	81.350	72.433	52.433	189.554	135.412	-5.460
5200	9.618	81.526	71.818	53.395	189.975	134.404	-5.341
5300	9.624	81.700	71.993	54.357	190.391	133.388	-5.206
5400	9.637	82.019	72.335	55.280	190.806	132.369	-5.075
5500	9.644	82.203	72.500	57.247	191.620	130.304	-4.827
5600	9.652	82.365	72.663	58.212	192.020	129.266	-4.708

Aluminum Dioxide (AlO₂)

GFW = 58.9803

(Ideal Gas)

ALUMINUM DIOXIDE (AlO₂)

(IDEAL GAS)

GFW = 58.9803

Point Group [D_{∞h}] $\Delta H_f^\circ = [-44 \pm 20] \text{ kcal/mol}$ $S_{298.15}^\circ = [56.7 \pm 4] \text{ gibbs/mol}$ $\Delta H_f^\circ = [-44 \pm 20] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	[4]
[20000]	[4]
[25000]	[2]

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}	
[680] (1)	
[295] (2)	
[1005] (1)	

Bond Distance: Al-O = [1.66] Å
 Bond Angle: O-Al-O = [180]°

Rotational Constant: $B_0 = [0.1912] \text{ cm}^{-1}$
 $\sigma = 2$

Heat of Formation

The OH bond strength in H₂O is 119 kcal and in HOBO it is 118 kcal. Thus, it appears very reasonable to assume 118 kcal for the value in HOAlO. This assumption leads to $\Delta H_f^\circ \text{g}(\text{AlO}_2, g) = -44 \pm 20 \text{ kcal/mol}$, using the JANAF $\Delta H_f^\circ \text{g}(\text{HOAlO}, g) = -110 \text{ kcal/mol}$. This value is consistent with the independently estimated $\Delta H_f^\circ \text{g}(\text{AlO}_2, g) = -130 \pm 15 \text{ kcal/mol}$, since it yields an electron affinity for AlO₂ of 46 kcal in good agreement with the value 98 kcal for BO₂.

Heat Capacity and Entropy

The electronic ground and excited states and molecular configuration are estimated to be similar to those for BO₂. The AlO bond length is assumed to be equal to that in Al₂O₃. The vibrational frequencies are estimated from a valence force field treatment using k_1 from BO₂ modified by the ratio $K(\text{AlO})/K(\text{BO})$ and using the same ratio of bending to stretch force constants as in BO₂.

The adopted molecular configuration and electronic ground state are in accord with the predictions of A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0	6.000	INFINITE	-	2.707	43.538	43.538	INFINITE
100	8.023	46.101	59.973	1.987	43.618	44.124	56.433
200	10.160	58.373	59.723	1.070	43.839	44.556	48.688
298	11.561	58.707	58.707	0.000	44.000	44.875	32.894
300	11.583	58.779	58.708	.021	44.003	44.881	32.686
400	12.550	62.624	61.113	1.515	44.115	45.115	22.418
500	13.191	65.127	60.086	2.520	44.176	45.411	19.689
600	13.619	67.572	61.135	3.662	44.248	45.652	16.629
700	13.912	69.695	62.210	5.240	44.333	45.879	14.324
800	14.119	71.567	63.265	6.462	44.446	46.093	12.592
900	14.269	73.239	64.282	7.118	44.561	46.283	11.162
1000	14.381	74.748	65.254	8.494	44.687	46.436	10.115
1100	14.466	76.123	66.181	10.937	47.485	46.172	9.174
1200	14.532	77.385	67.062	12.387	47.462	46.046	8.366
1300	14.585	78.550	67.902	13.643	47.601	45.906	7.118
1400	14.627	79.643	68.602	14.768	47.601	45.806	6.142
1500	14.661	80.683	69.164	15.768	48.129	45.591	5.463
1600	14.690	81.590	70.193	16.236	48.997	45.416	4.920
1700	14.714	82.482	70.890	19.706	48.468	45.231	4.437
1800	14.734	83.323	71.557	21.178	48.483	45.034	3.970
1900	14.751	84.109	72.196	22.452	48.483	44.826	3.518
2000	14.766	84.877	72.813	24.126	49.066	44.614	3.075
2100	14.778	85.598	73.405	25.605	49.193	44.392	2.640
2200	14.790	86.286	73.975	27.084	49.385	44.159	2.213
2300	14.800	86.943	74.524	28.563	49.560	43.915	1.793
2400	14.809	87.575	75.055	30.042	49.715	43.661	1.379
2500	14.817	88.178	75.568	31.525	49.866	43.409	0.970
2600	14.825	88.759	76.064	33.007	50.195	43.139	0.566
2700	14.833	89.319	76.545	34.490	50.409	42.865	0.166
2800	14.840	89.859	77.011	35.974	50.637	42.581	-0.233
2900	14.847	90.380	77.463	37.453	50.879	42.286	-0.636
3000	14.855	90.883	77.902	38.931	51.196	41.981	-1.037
3100	14.863	91.370	78.329	40.429	51.603	41.666	-1.437
3200	14.871	91.842	78.743	41.916	52.093	41.341	-1.837
3300	14.879	92.300	79.147	43.403	52.667	41.006	-2.237
3400	14.886	92.744	79.541	44.881	53.337	40.661	-2.637
3500	14.888	93.176	79.924	46.361	54.100	40.306	-3.037
3600	14.908	93.596	80.298	47.871	54.957	39.941	-3.437
3700	14.919	94.004	80.663	49.363	55.900	39.566	-3.837
3800	14.930	94.402	81.019	50.855	56.937	39.181	-4.237
3900	14.943	94.790	81.368	52.348	58.067	38.786	-4.637
4000	14.956	95.169	81.708	53.844	59.289	38.381	-5.037
4100	14.970	95.538	82.041	55.340	60.603	37.966	-5.437
4200	14.984	95.899	82.366	56.837	62.000	37.541	-5.837
4300	15.000	96.252	82.685	58.337	63.483	37.106	-6.237
4400	15.016	96.597	83.000	59.837	65.050	36.661	-6.637
4500	15.033	96.935	83.304	61.340	66.693	36.206	-7.037
4600	15.050	97.265	83.603	62.844	68.421	35.741	-7.437
4700	15.068	97.589	83.898	64.350	70.236	35.266	-7.837
4800	15.087	97.907	84.186	65.858	72.140	34.781	-8.237
4900	15.107	98.216	84.469	67.367	74.133	34.286	-8.637
5000	15.127	98.523	84.747	68.879	76.216	33.781	-9.037
5100	15.147	98.823	85.020	70.393	78.389	33.266	-9.437
5200	15.168	99.117	85.289	71.908	80.653	32.741	-9.837
5300	15.189	99.406	85.552	73.426	83.000	32.206	-10.237
5400	15.211	99.688	85.811	74.946	85.437	31.661	-10.637
5500	15.233	99.970	86.066	76.468	87.966	31.106	-11.037
5600	15.255	100.245	86.317	77.993	90.589	30.541	-11.437
5700	15.278	100.515	86.564	79.520	93.300	29.966	-11.837
5800	15.300	100.781	86.807	81.048	96.100	29.381	-12.237
5900	15.323	101.042	87.046	82.570	98.983	28.786	-12.637
6000	15.346	101.300	87.281	84.113	101.950	28.181	-13.037

June 30, 1968; Dec. 31, 1968

ALUMINUM DIOXIDE UNINEGATIVE ION (AlO₂⁻) (IDEAL GAS) GFW = 58.9809

ΔH_f⁰ = [-144.5 ± 15] kcal/mol

ΔH_f⁰_{298.15} = [-145 ± 15] kcal/mol

Point Group D_{3h}

S_{298.15}⁰ = [55.5 ± 2] gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

Wavenumber, cm ⁻¹	Degeneracy
[800] (1)	
[320] (2)	
[1200] (1)	

Bond Distance: Al-O = [1.66] Å
Bond Angle: O-Al-O = [180°]
Rotational Constant: B₀ = [0.1912] cm⁻¹

σ = 2

Heat of Formation

The heat of formation of AlO₂⁻ is estimated from the following considerations. The heats of the following reactions are calculated from the tables:

BO₂ → B⁺ + 2O ΔH = 411 kcal
CO₂ → C + 2O ΔH = 384 kcal
BO₂ → B + O + O⁻ ΔH = 382 kcal
BOF → B + O + F ΔH = 355 kcal

It is apparent that the heat of dissociation of BO₂⁻ is closely predicted by use of the corresponding isoelectronic decomposition. Thus using

SiO₂ + Si + 2O ΔH = 299
we predict AlO₂⁻ + Al⁺ + 2O ΔH = [320]
and using AlOF → Al + O + F ΔH = 297
we predict AlO₂⁻ + Al + O + O⁻ ΔH = [320]

From these two reactions we estimate ΔHf(AlO₂⁻, g) = -158 and -135 kcal/mol and we adopt the value -145 ± 15 kcal/mol. From the value adopted for AlO₂(g) we obtain an electron affinity of 4.38 eV (101 kcal) which is comparable to that for BO₂(g).

Heat Capacity and Entropy

The configuration of the molecule is assumed to be linear using the correlations of Walsh, (1) for 16 electron XY₂ molecules; the ground state is assumed to be ¹Σ_g from the same correlation diagrams. The bond length is taken to be that in Al₂O₃ and the vibrational frequencies are estimated between those for AlO₂ and SiO₂.

The enthalpy at 0°K is -2.630 kcal/mol.

Reference

1. A. D. Walsh, J. Chem. Soc. 1953, 2766 (1953).

Aluminum Dioxide Uninegative Ion (AlO₂⁻)

(Ideal Gas) GFW = 58.9809

T, °K	C _p ⁰	S ⁰ - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔG _f ⁰	Log K _p
0						
100						
200						
298	11.081	55.509	+0.00	-145.000	-143.434	105.140
300	11.102	55.576	+0.21	-145.012	-143.424	104.485
400	12.066	58.910	+1.81	-145.659	-142.796	78.020
500	12.761	61.682	+2.425	-146.274	-142.009	62.072
600	13.255	64.055	+2.727	-146.483	-141.099	51.395
700	13.609	66.126	+2.882	-146.498	-140.045	43.736
800	13.866	67.961	+2.904	-146.136	-138.984	37.969
900	14.056	69.606	+2.892	-145.412	-137.800	33.462
1000	14.201	71.094	+2.839	-152.056	-136.354	29.600
1100	14.312	72.453	+2.743	-152.725	-134.753	26.773
1200	14.400	73.702	+2.615	-153.393	-133.091	24.239
1300	14.470	74.858	+2.467	-154.061	-131.370	22.065
1400	14.526	75.932	+2.311	-154.731	-129.600	20.231
1500	14.572	76.936	+2.155	-155.403	-127.782	18.616
1600	14.611	77.878	+2.000	-156.077	-125.918	17.200
1700	14.643	78.765	+1.847	-156.752	-124.013	15.943
1800	14.670	79.602	+1.693	-157.429	-122.065	14.821
1900	14.693	80.396	+1.540	-158.112	-120.084	13.813
2000	14.713	81.150	+1.387	-158.798	-118.066	12.902
2100	14.731	81.869	+1.234	-159.486	-116.012	12.073
2200	14.746	82.554	+1.081	-160.181	-113.926	11.318
2300	14.759	83.210	+0.928	-160.875	-111.805	10.624
2400	14.770	83.839	+0.775	-161.577	-109.656	9.986
2500	14.781	84.442	+0.622	-162.283	-107.482	9.396
2600	14.790	85.022	+0.469	-162.993	-105.274	8.849
2700	14.798	85.580	+0.316	-163.707	-103.043	8.341
2800	14.805	86.118	+0.163	-164.425	-100.782	7.862
2900	14.812	86.638	+0.010	-165.146	-98.496	7.417
3000	14.818	87.140	-0.143	-165.867	-96.184	6.992
3100	14.823	87.626	-0.296	-166.589	-93.847	6.582
3200	14.828	88.097	-0.449	-167.312	-91.486	6.180
3300	14.833	88.553	-0.602	-168.036	-89.106	5.786
3400	14.837	88.996	-0.755	-168.761	-86.712	5.400
3500	14.840	89.426	-0.908	-169.486	-84.302	5.022
3600	14.843	89.842	-1.061	-170.211	-81.877	4.650
3700	14.846	90.251	-1.214	-170.936	-79.437	4.282
3800	14.849	90.647	-1.367	-171.661	-76.982	3.920
3900	14.853	91.033	-1.520	-172.386	-74.512	3.562
4000	14.855	91.409	-1.673	-173.111	-72.027	3.209
4100	14.857	91.776	-1.826	-173.836	-69.527	2.862
4200	14.860	92.134	-1.979	-174.561	-67.012	2.520
4300	14.862	92.483	-2.132	-175.286	-64.472	2.182
4400	14.864	92.825	-2.285	-176.011	-61.917	1.849
4500	14.865	93.159	-2.438	-176.736	-59.347	1.520
4600	14.867	93.486	-2.591	-177.461	-56.762	1.196
4700	14.868	93.806	-2.744	-178.186	-54.162	0.877
4800	14.870	94.119	-2.897	-178.911	-51.547	0.562
4900	14.871	94.425	-3.050	-179.636	-48.917	0.250
5000	14.873	94.726	-3.203	-180.361	-46.272	-0.059
5100	14.874	95.020	-3.356	-181.086	-43.617	-0.372
5200	14.875	95.309	-3.509	-181.811	-40.952	-0.687
5300	14.876	95.592	-3.662	-182.536	-38.277	-1.002
5400	14.877	95.870	-3.815	-183.261	-35.592	-1.317
5500	14.878	96.143	-3.968	-183.986	-32.897	-1.632
5600	14.879	96.412	-4.121	-184.711	-30.192	-1.947
5700	14.880	96.675	-4.274	-185.436	-27.477	-2.262
5800	14.881	96.934	-4.427	-186.161	-24.752	-2.577
5900	14.881	97.188	-4.580	-186.886	-22.017	-2.892
6000	14.882	97.438	-4.733	-187.611	-19.272	-3.207

June 30, 1968; Dec. 31, 1968

T, °K	C _p	cal. mole ⁻¹ deg ⁻¹	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	6.981	47.055	61.819	2.172	47.975	47.975	INFINITE
200	7.449	55.010	55.804	1.476	48.401	44.157	- 96.500
298	7.982	55.090	55.804	.759	48.283	39.920	- 43.520
300	7.991	55.139	55.090	.015	48.000	35.868	- 26.591
400	8.334	57.489	55.408	.832	47.994	35.793	- 26.074
500	8.542	59.373	56.019	1.677	47.115	31.768	- 17.373
600	8.674	60.943	56.713	2.538	45.743	24.446	- 8.904
700	8.727	62.161	57.099	3.420	44.567	19.290	- 4.450
800	8.774	63.099	57.350	4.290	43.667	14.290	- 2.499
900	8.814	63.754	57.515	5.175	43.017	10.412	- 3.499
1000	8.852	64.242	57.577	6.065	42.544	12.752	- 2.787
1100	8.882	64.593	57.568	6.957	42.293	11.204	- 2.226
1200	8.906	64.819	57.481	7.851	42.148	9.817	- 1.773
1300	8.925	64.970	57.350	8.751	42.098	8.577	- 1.405
1400	8.940	65.058	57.184	9.651	42.125	7.469	- 1.095
1500	8.952	65.080	56.980	10.553	42.223	6.489	- .816
1600	8.963	65.063	56.733	11.456	42.374	5.629	- .556
1700	8.973	65.000	56.444	12.361	42.574	4.889	- .316
1800	8.980	64.891	56.114	13.268	42.819	4.269	- .096
1900	8.986	71.221	63.754	14.176	43.109	3.669	.130
2000	9.009	71.687	64.144	15.085	43.439	3.089	.236
2100	9.112	72.131	64.514	15.996	43.809	2.529	.340
2200	9.135	72.566	64.881	16.907	44.219	2.009	.450
2300	9.158	73.000	65.244	17.820	44.669	1.529	.570
2400	9.177	73.435	65.604	18.735	45.149	1.089	.699
2500	9.198	73.872	65.964	19.650	45.649	.689	.839
2600	9.219	74.309	66.323	20.566	46.169	.269	.989
2700	9.240	74.746	66.683	21.482	46.709	-.169	1.149
2800	9.261	75.183	67.043	22.402	47.269	-.589	1.319
2900	9.282	75.620	67.403	23.322	47.849	-.989	1.499
3000	9.303	76.057	67.763	24.242	48.449	-1.369	1.679
3100	9.324	76.494	68.123	25.164	49.069	-1.749	1.859
3200	9.345	76.931	68.483	26.086	49.709	-2.129	2.039
3300	9.366	77.368	68.843	27.010	50.369	-2.509	2.219
3400	9.387	77.805	69.203	27.935	51.049	-2.889	2.399
3500	9.408	78.242	69.563	28.861	51.739	-3.269	2.579
3600	9.429	78.679	69.923	29.787	52.439	-3.649	2.759
3700	9.450	79.116	70.283	30.713	53.149	-4.029	2.939
3800	9.471	79.553	70.643	31.644	53.869	-4.409	3.119
3900	9.492	79.990	71.003	32.574	54.599	-4.789	3.299
4000	9.513	80.427	71.363	33.504	55.339	-5.169	3.479
4100	9.534	80.864	71.723	34.436	56.089	-5.549	3.659
4200	9.555	81.301	72.083	35.366	56.849	-5.929	3.839
4300	9.576	81.738	72.443	36.296	57.609	-6.309	4.019
4400	9.597	82.175	72.803	37.226	58.369	-6.689	4.199
4500	9.618	82.612	73.163	38.156	59.129	-7.069	4.379
4600	9.639	83.049	73.523	39.086	59.889	-7.449	4.559
4700	9.660	83.486	73.883	40.016	60.649	-7.829	4.739
4800	9.681	83.923	74.243	40.946	61.409	-8.209	4.919
4900	9.702	84.360	74.603	41.876	62.169	-8.589	5.099
5000	9.723	84.797	74.963	42.806	62.929	-8.969	5.279
5100	9.744	85.234	75.323	43.736	63.689	-9.349	5.459
5200	9.765	85.671	75.683	44.666	64.449	-9.729	5.639
5300	9.786	86.108	76.043	45.596	65.209	-10.109	5.819
5400	9.807	86.545	76.403	46.526	65.969	-10.489	6.000
5500	9.828	86.982	76.763	47.456	66.729	-10.869	6.180
5600	9.849	87.419	77.123	48.386	67.489	-11.249	6.360
5700	9.870	87.856	77.483	49.316	68.249	-11.629	6.540
5800	9.891	88.293	77.843	50.246	69.009	-12.009	6.720
5900	9.912	88.730	78.203	51.176	69.769	-12.389	6.900
6000	9.933	89.167	78.563	52.106	70.529	-12.769	7.080

Dec. 31, 1960; Mar. 31, 1964

ALUMINUM SULFIDE (AIS)

(IDEAL GAS)

MOL. WT. = 59.046

Ground State Configuration $\sum^+$
 $\Delta H_f^0 = 48 \pm 20$ kcal. mole⁻¹
 $\Delta H_f^0 = 55.09$ cal. deg. mole⁻¹
 $\Delta H_f^0 = 298.15 = 48 \pm 20$ kcal. mole⁻¹

Electronic Levels and Quantum Weights

$$\frac{E_i, \text{ cm.}^{-1}}{0} \quad \frac{g_i}{2}$$

$$\omega_e x_e = 3.33 \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$\omega_e = 617.12 \text{ cm.}^{-1}$$

$$r_e = 2.03 \text{ \AA}$$

$$\alpha_e = 0.0018 \text{ cm.}^{-1}$$

$$B_e = 0.2799 \text{ cm.}^{-1}$$

Heat of Formation.

The dissociation energy of 4.1 e.v. was calculated by adding 1.7% to the dissociation energy obtained from a linear extrapolation of the vibrational levels, 3.5 e.v. This was done by analogy with the molecule AlO(g) whose observed D_0 is 1.7% larger than the linear extrapolation. The adopted value of 4.1 e.v. corresponds to a heat of formation of 48 kcal. mole⁻¹.

Heat Capacity and Entropy.

The vibrational and rotational constants were reported by C. N. McKinney and K. K. Innes, J. Mol. Spect. 3, 235 (1959) from an analysis of 6 bands of the $A^2\Sigma^+ - X^2\Sigma^+$ system.

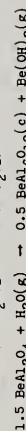
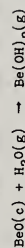
Beryllium Aluminate (BeAl₂O₄)
(Crystal) Mol. Wt. = 126.973BERYLLIUM ALUMINATE (BeAl₂O₄) (CRYSTAL)

MOL. WT. = 126.973

T, °K.	C _p	S° - (F° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _P
0	∞	∞	∞	∞	∞	∞
100	3.911	1.320	3.028	-541.322	-541.322	INFINITE
200	15.876	7.643	17.873	-542.870	-534.355	1167.775
298	25.177	15.843	30.000	-544.270	-525.275	573.966
300	25.316	15.909	30.000	-545.000	-515.786	378.063
400	31.340	24.174	16.917	-545.008	-515.606	375.600
500	34.589	31.545	19.120	-545.207	-505.762	276.332
600	36.721	38.050	21.744	-544.910	-495.907	216.750
700	38.234	43.835	24.494	-544.658	-486.083	177.047
800	39.478	48.983	26.848	-544.440	-476.299	149.700
900	40.799	53.777	29.632	-544.261	-466.568	120.931
1000	41.853	58.131	32.537	-544.118	-456.840	110.461
1100	42.840	62.167	35.069	-543.909	-446.790	97.641
1200	43.782	65.935	37.468	-543.614	-436.614	86.743
1300	44.693	69.483	39.641	-543.276	-426.483	77.669
1400	45.578	72.821	41.698	-542.905	-416.315	69.434
1500	46.447	75.995	43.657	-542.515	-406.168	62.096
1600	47.304	79.020	45.428	-542.107	-396.031	55.750
1700	48.150	81.913	47.020	-541.682	-386.363	52.772
1800	48.989	84.683	48.453	-541.240	-376.300	48.374
1900	49.829	87.360	50.000	-540.781	-366.340	44.096
2000	50.667	89.936	51.667	-540.307	-356.447	40.986
2100	51.470	92.427	53.466	-539.819	-346.647	37.856
2200	52.254	94.840	55.279	-539.318	-336.910	35.030
2300	53.022	97.183	57.119	-538.804	-327.233	32.466
2400	53.822	99.455	59.000	-538.277	-317.611	30.143
2500	54.567	101.667	60.753	-537.736	-307.443	27.995
2600	55.293	103.821	62.466	-537.181	-297.842	26.036
2700	56.005	105.921	64.133	-536.614	-288.294	24.232
2800	56.698	107.971	65.766	-536.033	-278.806	22.560
2900	57.332	109.971	67.366	-535.439	-269.372	21.000
3000	58.000	111.926	68.931	-534.831	-260.000	19.543
			70.467	-534.200	-250.683	18.179
			72.000	-533.557	-241.426	16.817

ΔH_f[°] 0 = -541 ± 5 kcal. mole⁻¹
 ΔH_f[°] 298.15 = -545 ± 5 kcal. mole⁻¹
 ΔH_m[°] = [42] kcal. mole⁻¹
 S_{298.15} = 15.84 cal. deg.⁻¹ mole⁻¹
 T_m[°] = 2143°K.

Heat of Formation.

W. A. Young, J. Phys. Chem. **64**, 1003 (1960) studied the equilibria

from his results one obtains ΔH_f[°] 1673 = -379 kcal. mole⁻¹, which corresponds to ΔH_f[°] 298 = -545 kcal. mole⁻¹.

Heat Capacity and Entropy.

G. T. Furawaka and W. O. Saba, and T. B. Douglas and W. H. Payne, National Bureau of Standards Report 6186, Jan. 1964 have measured the low temperature heat capacities and the high temperature enthalpy in the range 15 - 1173°K.

Melting Data.

The temperature of melting was taken from National Bureau of Standards Circular 500, Washington (1952).

The heat of melting was estimated as the sum of the ΔH_f[°] of the constituent oxides at 2100°K.

Point Group D_{2h} $\Delta H_f^\circ = -221.0 \pm 7 \text{ kcal/mol}$ $S_{298}^\circ = 130.8 \text{ gibbs/mol}$ $\Delta H_f^\circ = -231.5 \pm 7 \text{ kcal/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Heat Capacities

$\omega_{cm^{-1}}$	$\omega_{cm^{-1}}$	$\omega_{cm^{-1}}$	$\omega_{cm^{-1}}$
407 (1)	56 (1)	[110] (1)	342 (1)
192 (1)	(33)(1)	504 (1)	63 (1)
122 (1)	162 (1)	93 (1)	[116] (1)
			68 (1)

Bond Distances: Al-Br = $2.21 \pm 0.4 \text{ \AA}$ Al-Br₂ bridge = $2.33 \pm 0.4 \text{ \AA}$ Bond Angles: Br-Al-Br = $114^\circ 38'$ Br-bridge-Al-Br bridge = $86^\circ 44'$ Product of the Moments of Inertia: $I_A I_B I_C = 8.80123 \times 10^{-110} \text{ g}^3 \text{ cm}^6$

Heat of Formation

The vapor pressures of AlBr₃(c) and AlBr₃(l) have been measured by Dunne and Gregory (1) and Fischer et al. (2), respectively. Using these data, the heats of vaporization were calculated by both second and third law methods. The adopted value of ΔH_f° for AlBr₃(g) is $-231.5 \pm 7 \text{ kcal/mol}$. The results of these calculations are as follows with reaction (A) corresponding to 2AlBr₃(c) = Al₂Br₆(c) and reaction (B) corresponding to 2AlBr₃(l) = Al₂Br₆(g):

Source	Reac.	Method	No. Pts.	Range T ^o K	ΔH_f° , kcal/mol 2nd Law 3rd Law	Drift, au	ΔH_f° , kcal/mol 2nd Law 3rd Law
1	A	Effusion	3	273-310	19.7±0.7 20.25	2.2±2.4	-231.7
2	B	Weight Loss	18**	413-523	15.6±0.1 15.61	0.1±0.1	-231.5
2	B	Transport	4	396-471	16.1±0.2 15.80	-1.0±0.3	-231.5

*Calculation based on third law ΔH_f°

**One point rejected due to failure of a statistical test.

Heat Capacity and Entropy

The molecular structure, bond distances and angles were obtained from the electron diffraction work of Palmer and Elliott (3). The bond distances and angles have also been reported by Akishin et al. (4), and these values are in good agreement with those given by Palmer and Elliott (3). The principal moments of inertia are $I_A = 6.38492 \times 10^{-37}$, $I_B = 2.51547 \times 10^{-37}$, and $I_C = 6.52171 \times 10^{-37} \text{ g cm}^2$. It has been established that the condensed phases of AlBr₃ are dimeric (5), (6), thus spectroscopic studies of the crystal and liquid pertain to the structure of Al₂Br₆(g). Gerding and Smit (7) have studied the Raman spectra of Al₂Br₆(l). The eighteen fundamental vibrational frequencies of Al₂Br₆(g) have been predicted by Miller (8) based on seven of the frequencies reported by Gerding and Smit (7). Webb (9) has measured the infrared spectra of AlBr₃(c) in the 40-800 cm⁻¹ region, the results being in general accord with the predictions of Miller (8). The vibrational frequencies used are adjusted so that the values of ΔH_f° obtained by the third law method are in agreement with the corresponding second law values. These adjustments are based on the assumption that vibrations with a wave number below 300 cm⁻¹ have a lower wave number in the gas phase than they have in the condensed phase.

References

1. T. G. Dunne and N. W. Gregory, J. Am. Chem. Soc. **80**, 1526 (1958).
2. W. Fischer, O. Rahlfe, and B. Benze, Z. Anorg. Chem. **203**, 1 (1932).
3. K. J. Palmer and N. Elliott, J. Am. Chem. Soc. **80**, 1852 (1958).
4. P. A. Akishin, N. G. Rambidi, and E. Z. Zosorin, Kristallografiya **1**, 167 (1959).
5. R. A. Rense and C. H. MacGillivray, Rec. Trav. Chim. **84**, 275 (1945).
6. K. N. Snenenko and T. N. Naumova, Russ. J. Inorg. Chem. (English Transl.) **9**, 718 (1964).
7. H. Gerding and E. Smit, Z. Physik. Chem. **51B**, 217 (1942).
8. R. H. Miller, Jr., Ph.D. Dissertation, Ohio University, 1965.
9. D. U. Webb, The Dow Chemical Co., Midland, Michigan, 2nd Quarterly Report, April 1 - June 30, 1967, Contract F04611-67-C-0009.

Dec. 31, 1961; June 30, 1964; June 30, 1967

(IDEAL GAS)

ALUMINUM TRICHLORIDE, DIMER (Al₂Cl₆)

Point Group D_{2h}
 $S_{298.15}^{\circ} = 113.647 \pm 1.0$ gibbs/mol
 Ground State Quantum Weight = [1]

GTW = 266.681
 $\Delta H_f^{\circ} = -308.95 \pm 0.8$ kcal/mol
 $\Delta H_{298.15}^{\circ} = -309.64 \pm 0.8$ kcal/mol

Aluminum Trichloride, Dimer (Al₂Cl₆)

(Ideal Gas)

GTW = 266.681

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	Log K ^p
0	-0.000	INFINITE	INFINITE	- 8.0A3	- 308.953	INFINITE
100	24.478	79.445	163.485	- 6.4A0	- 309.610	663.700
200	33.306	86.420	116.979	- 3.512	- 309.748	395.317
298	37.737	91.420	113.647	- 3.000	- 309.840	213.512
300	37.749	113.481	113.648	- 0.070	- 309.637	212.513
400	40.019	125.083	115.182	- 3.972	- 308.423	156.137
500	41.225	134.165	118.084	- 8.020	- 308.176	122.336
600	41.935	141.760	121.814	- 12.001	- 308.040	90.891
700	42.465	148.030	125.084	- 15.974	- 308.026	68.751
800	42.845	153.610	128.079	- 19.947	- 308.126	51.704
900	43.115	158.670	131.245	- 23.920	- 308.478	38.341
1000	43.307	163.408	134.288	- 28.250	- 313.429	24.771
1100	43.461	167.807	137.097	- 32.561	- 313.427	18.558
1200	43.587	171.904	139.794	- 36.847	- 313.425	13.363
1300	43.691	175.631	142.381	- 41.109	- 313.218	8.945
1400	43.771	179.037	144.797	- 45.344	- 313.114	5.204
1500	43.841	182.037	147.114	- 49.544	- 313.010	2.197
1600	43.895	184.680	149.323	- 53.727	- 312.909	0.007
1700	43.935	186.925	151.574	- 57.874	- 312.807	24.589
1800	43.965	188.861	153.868	- 61.993	- 312.707	26.369
1900	43.988	191.314	156.380	- 66.076	- 312.609	22.350
2000	43.997	193.587	158.723	- 70.129	- 312.518	20.553
2100	43.993	195.672	160.913	- 74.188	- 312.426	18.928
2200	43.979	197.569	162.976	- 78.261	- 312.341	17.450
2300	43.958	199.436	164.976	- 82.340	- 312.255	16.100
2400	43.929	201.482	166.967	- 86.429	- 312.177	14.864
2500	43.894	203.272	168.504	- 90.419	- 312.107	13.724
2600	43.854	204.982	169.900	- 94.381	- 312.038	12.678
2700	43.810	206.626	171.257	- 98.315	- 311.978	11.705
2800	43.763	208.215	172.582	- 102.220	- 311.924	10.807
2900	43.714	209.746	173.881	- 106.095	- 311.876	9.963
3000	43.661	211.225	175.151	- 110.000	- 311.837	9.168
3100	43.604	212.657	176.394	- 113.927	- 311.802	8.422
3200	43.544	214.042	177.613	- 117.874	- 311.771	7.727
3300	43.481	215.386	178.807	- 121.840	- 311.742	7.077
3400	43.415	216.689	179.976	- 125.815	- 311.716	6.468
3500	43.346	217.954	181.121	- 129.800	- 311.692	5.898
3600	43.274	219.185	182.242	- 133.795	- 311.669	5.368
3700	43.200	220.381	183.337	- 137.800	- 311.647	4.878
3800	43.125	221.545	184.404	- 141.815	- 311.626	4.428
3900	43.049	222.680	185.446	- 145.840	- 311.606	4.008
4000	42.972	223.786	186.464	- 149.874	- 311.587	3.618
4100	42.894	224.864	187.458	- 153.918	- 311.569	3.258
4200	42.815	225.917	188.428	- 157.972	- 311.552	2.928
4300	42.735	226.944	189.373	- 162.036	- 311.536	2.628
4400	42.654	227.949	190.294	- 166.109	- 311.521	2.358
4500	42.572	228.930	191.191	- 170.191	- 311.506	2.118
4600	42.489	229.890	192.064	- 174.282	- 311.492	1.908
4700	42.405	230.830	192.914	- 178.382	- 311.478	1.728
4800	42.320	231.750	193.741	- 182.491	- 311.465	1.568
4900	42.235	232.651	194.546	- 186.609	- 311.452	1.428
5000	42.150	233.533	195.328	- 190.736	- 311.440	1.308
5100	42.064	234.398	196.088	- 194.872	- 311.428	1.208
5200	41.978	235.247	196.825	- 199.018	- 311.416	1.128
5300	41.891	236.079	197.539	- 203.174	- 311.405	1.058
5400	41.804	236.896	198.230	- 207.339	- 311.394	0.998
5500	41.717	237.698	198.900	- 211.514	- 311.383	0.948
5600	41.630	238.485	199.549	- 215.699	- 311.372	0.908
5700	41.543	239.258	200.178	- 219.894	- 311.361	0.878
5800	41.456	240.018	200.787	- 224.099	- 311.350	0.848
5900	41.369	240.765	201.376	- 228.314	- 311.340	0.818
6000	41.282	241.500	201.944	- 232.539	- 311.330	0.788

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

Bond Lengths: Al-Cl = 2.05 Å, Al-Cl-bridge = 2.23 Å
 Bond Angles: Cl-Al-Cl = 120°, Cl-bridge-Al-Cl-bridge = 83°
 Product of the Moments of Inertia: $I_A I_B I_C = 5.988 \times 10^{-111}$ g cm⁶
 $\sigma = 4$

Heat of Formation

The heat of formation is calculated from the value adopted for AlCl₃(g) and the heat of sublimation as derived from vapor pressure data. Vapor pressures were corrected for vapor non-ideality by means of the equation $\log^* P = -R \ln P - BP/T$. The Berthelot equation of state and critical constants $T_c = 625.7^\circ K$ and $P_c = 26.1$ atm reported by Denisova and Baskova (1) were used to calculate B. Boston et al. (2) and Nisels' son and Sokolova (3) confirm T_c within $\pm 2^\circ K$. The corrected vapor pressures were used to derive $\Delta H_{298.15}^{\circ}$ by both second law and third law methods.

Investigator(s)	Temp. Range °K	Number of Data Points	$\Delta H_{298.15}^{\circ}$ (kcal/mol Al ₂ Cl ₆)	Drift eu
Smits and Meijering (4)	444.7-484.6	7 ^a	27.53	0.2±0.2
Smits and Meijering (4)	462.4-481.8	10	27.25	0.8±0.5
Treadwell and Terbesi (5)	388.7-476.2	11	28.33	-1.7±0.3
Treadwell and Terbesi (5)	466.5-476.2	3	27.43	27.65
Fischer et al. (6)	392.8-428.3	9	27.67	0.0±1.1
Fischer et al. (6)	403.8-450.4	12 ^b	27.74	27.65
Nisels' son et al. (7)	471.2-506.5	18 ^c	27.31	0.7±0.1
Friedel and Crafts (8)	441.0-455.9	5	29.81	27.86
Friedel and Crafts (8)	477.4-486.2	3	30.00	27.82
Maier (9)	392.8-454.5	8 ^d	25.87	3.6±1.7
Dunne and Gregory (10)	294.2-322.2	12 ^e	29.96	-6.9
Denisova and Baskova (1)	467.8-511.6	8	26.34	2.5±0.3

^aNine points reported, points at 420.8° and 433.5°K rejected by statistical test.

^bFourteen points reported, points at 385.2° and 441.3°K rejected by statistical test.

^cThirteen points reported, point at 472.2°K rejected by statistical test.

^dFive points reported, point at 342.0°K rejected by statistical test.

^eEight points not reported; their vapor pressure equation was used to calculate 2 points at extremes of temperature range covered.

The first seven data sets show good agreement between second and third law values and an average of $\Delta H_{298.15}^{\circ} = 27.66 \pm 0.55$ kcal/mol Al₂Cl₆ is adopted. The remaining data sets show serious discrepancies between second and third law values, indicating temperature dependent errors in measurement, and are given no weight.

Heat Capacity and Entropy

Electron diffraction data by Palmer and Elliott (11) and by Akishin et al. (12) are in agreement within experimental error and average values for bond angles and distances as given above are selected. The principal moments of inertia are: $I_A = 2.2172 \times 10^{-37}$, $I_B = 9.991 \times 10^{-38}$, and $I_C = 2.7023 \times 10^{-37}$ g cm². Klemperer (13) observed three frequencies in the infrared spectrum of Al₂Cl₆ vapor, Beattie and Horder (14) and Maroni et al. (15) reported gas phase Raman spectra, and Gerding and Sait (16) and Pershina and Raskin (17) measured liquid phase Raman frequencies. With previous vibrational assignments and normal coordinate calculations by Onishi and Shimizu (18), Miller (19), and Maroni et al. (15) as a starting point, a new assignment was made (see above) which incorporates additional frequencies observed by Beattie and Horder (14) and Pershina and Raskin (17).

Raman and infrared spectra of Al₂Br₆ and Al₂I₆ determined by Beattie, et al. (20) were very helpful. The new assignment differs with earlier calculations primarily in the assumption that the frequencies at 36 cm⁻¹ and 19 cm⁻¹ observed by Pershina and Raskin in the liquid can be assigned to modes not ordinarily Raman active. This assumption is supported by the compatibility of thermodynamic functions based on the new assignment with vapor pressure data as listed above. Use of the frequencies 89 cm⁻¹ and 56 cm⁻¹ of Miller (19) gives 3rd law heats of sublimation nearly 2 kcal/mol Al₂Cl₆ higher than the average of 2nd law values.

References

1. N. D. Denisova and A. P. Baskova, Zh. Fiz. Khim. 43, 2353 (1969).
2. C. R. Boston, S. J. Yosin, and L. F. Grantham, J. Chem. Phys. 51, 1669 (1969).
3. L. A. Nisels' son and T. D. Sokolova, Zh. Neorg. Khim. 10, 1516 (1965).
4. A. Smits and J. L. Meijering, Z. Phys. Chem. B, 98 (1938).
5. W. F. Treadwell and L. Terbesi, Helv. Chim. Acta 15, 1053 (1932).
6. W. F. Treadwell and L. Terbesi, Helv. Chim. Acta 16, 201 (1933).
7. L. A. Nisels' son, A. J. Pustil'nikov, O. R. Govrilov, and V. A. Rodin, Zh. Neorg. Khim. 10, 1764 (1965).
8. C. Friedel and J. M. Crafts, Compt. Rend. 108, 1764 (1888).
9. C. G. Maier, U. S. Bur. Mines Tech. Paper 350, (1929).
10. C. G. Maier and N. W. Gregory, J. Amer. Chem. Soc. 60, 1530 (1938).
11. J. A. Palmer and N. Elliott, J. Amer. Chem. Soc. 60, 1852 (1938).
12. V. A. Akishin, Zh. Neorg. Khim. 10, 1516 (1965).
13. W. Klemperer, J. Chem. Phys. 24, 353 (1956).
14. I. R. Beattie and J. R. Horder, J. Chem. Soc. 1939A, 2655.
15. V. A. Maroni, D. M. Gruen, R. L. McBeth, and E. J. Cairns, Spectrochim. Acta 28A, 418 (1970).
16. H. Gerding and E. Sait, Z. Phys. Chem. B50, 171 (1941).
17. V. Pershina and Sh. Sh. Raskin, Opt. Spectr. 13, 272 (1962).
18. T. Onishi and T. Shimizu, Spectrochim. Acta 20, 323 (1964).
19. E. H. Miller, Ph.D. Thesis, Ohio State University, 1964.
20. I. R. Beattie, T. Gilson, and G. A. Ozin, J. Chem. Soc. 1958A, 1694.

Tripotassium Nonachloroaluminate (K₃Al₂Cl₉)
(Crystal) Mol. Wt. = 490.373

T, °K.	C _p	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$\frac{H^* - H_{298}^0}{T}$ kcal. mole ⁻¹	ΔH_f^0	ΔF_f^0	Log K _f
0						
100						
200						
298	80.600	112.000	112.000	.000	- 627.634	460.046
300	80.750	112.499	112.002	.149	- 627.287	456.657
400	84.400	136.236	115.213	8.400	- 608.566	332.380
500	87.780	155.440	121.397	17.021	- 589.555	237.681
600	90.760	171.712	128.461	25.951	- 571.022	207.984
700	93.405	185.005	135.674	35.162	- 552.766	172.573
800	95.760	198.534	142.757	44.622	- 534.775	146.087
900	97.500	209.010	149.596	54.282	- 517.021	125.544
1000	98.600	220.288	156.154	64.134	- 499.159	109.081
1100	102.060	229.893	162.426	74.214	- 478.238	95.013
1200	104.880	238.892	168.426	84.558	- 455.239	82.006
1300	108.060	247.410	174.177	95.202	- 432.540	72.713
1400	111.600	255.345	179.701	106.182	- 410.130	64.021
1500	115.500	263.376	185.019	117.534	- 388.024	56.552

June 30, 1962; Sept. 30, 1964

TRIPOTASSIUM NONACHLOROALUMINATE (K₃Al₂Cl₉) (CRYSTAL)

MOL. WT. = 490.373

Al₂Cl₉K₃

$\Delta H_f^0 =$ Unknown

$\Delta H_f^0 298.15 = -683.6 \pm 3$ kcal. mole⁻¹

$\Delta H_m^0 =$ Unknown

$S_{298.15}^0 = [112]$ cal. deg.⁻¹ mole⁻¹

$T_m =$ Unknown

Heat of Formation.

The value of $\Delta H_f^0 298.15$ for K₃Al₂Cl₉(c) was calculated from the heat of solution, $\Delta H_r^0 = -112.07$ kcal. mole⁻¹, of K₃Al₂Cl₉(c) in water (one mole of solute in 36 l. of water) determined by E. Baud, Ann. chim. phys. 1, 8 (1904).

Heat Capacity and Entropy.

Heat capacities and $S_{298.15}^0$ were estimated based on an assumption that the property of the mixed chloride (2AlCl₃ · 3KCl) is the sum of the corresponding values for its component chlorides, i.e. AlCl₃(c) and KCl(c).

Al₂Cl₉K₃

Point Group {D_{2h}}

$$S_{298.15}^0 = 92.5 \pm 3 \text{ gibbs/mol}$$

$$\Delta H_f^0 = -627.3 \pm 4 \text{ kcal/mol}$$

$$\Delta H_f^{298.15} = -629.45 \pm 4 \text{ kcal/mol}$$

Ground State Quantum Weight = [1]

Aluminum Trifluoride, Dimer (Al₂F₆)
(Ideal Gas)

$$GFW = 167.9534$$

T, °K	Cp°	S°	-G°-H°/300	H°-H° ₃₀₀	ΔH°	Log Kp
0	0.000	INFINITE		6.326	-627.254	INFINITE
100	17.347	65.000	18.000	6.326	-627.254	6.326
200	27.347	60.628	15.235	2.489	-629.095	6.326
298	31.044	62.476	12.476	1.000	-629.450	6.326
300	32.048	62.476	12.476	1.059	-629.455	6.326
400	37.690	102.431	93.782	3.460	-629.562	6.326
500	42.826	140.660	126.537	7.152	-629.553	6.326
600	47.466	172.669	152.419	11.029	-629.490	6.326
700	51.653	200.547	171.070	15.111	-629.413	6.326
800	55.429	224.380	186.426	19.253	-629.373	6.326
900	58.800	245.106	200.000	23.438	-629.309	6.326
1000	61.800	263.626	211.866	27.655	-629.217	6.326
1100	64.450	280.000	221.000	31.900	-629.100	6.326
1200	66.750	294.500	228.500	36.175	-628.963	6.326
1300	68.750	307.500	234.500	40.488	-628.800	6.326
1400	70.500	319.000	239.000	44.738	-628.613	6.326
1500	72.000	329.000	242.000	48.925	-628.400	6.326
1600	73.300	337.500	244.500	53.059	-628.163	6.326
1700	74.450	345.000	246.500	57.126	-627.900	6.326
1800	75.500	351.500	248.000	61.126	-627.613	6.326
1900	76.450	357.000	249.000	65.059	-627.300	6.326
2000	77.300	361.500	249.500	68.925	-626.963	6.326
2100	78.000	365.000	249.500	72.725	-626.600	6.326
2200	78.500	367.500	249.000	76.450	-626.217	6.326
2300	78.800	369.000	248.500	80.100	-625.800	6.326
2400	78.900	369.500	248.000	83.675	-625.350	6.326
2500	78.800	369.000	247.500	87.175	-624.863	6.326
2600	78.500	367.500	246.500	90.600	-624.338	6.326
2700	78.000	365.000	245.000	93.975	-623.763	6.326
2800	77.300	361.500	243.500	97.300	-623.138	6.326
2900	76.450	357.000	241.000	100.475	-622.463	6.326
3000	75.500	351.500	237.500	103.500	-621.738	6.326
3100	74.450	345.000	233.000	106.375	-620.963	6.326
3200	73.300	337.500	227.500	109.000	-620.138	6.326
3300	72.000	329.000	221.000	111.375	-619.263	6.326
3400	70.500	319.000	213.500	113.500	-618.338	6.326
3500	68.925	307.500	205.000	115.375	-617.363	6.326
3600	67.250	294.500	195.500	116.925	-616.338	6.326
3700	65.500	280.000	185.000	118.125	-615.263	6.326
3800	63.625	263.626	173.626	118.975	-614.138	6.326
3900	61.625	245.106	161.626	119.375	-612.963	6.326
4000	59.500	224.380	149.500	119.325	-611.738	6.326
4100	57.250	200.547	137.250	118.825	-610.463	6.326
4200	54.925	171.070	125.070	117.875	-609.138	6.326
4300	52.500	140.660	112.660	116.475	-607.763	6.326
4400	50.000	102.431	99.569	114.625	-606.338	6.326
4500	47.425	65.000	86.000	112.325	-604.863	6.326
4600	44.775	27.347	72.347	109.575	-603.338	6.326
4700	42.075	0.000	58.000	106.275	-601.763	6.326
4800	39.325	INFINITE	43.000	102.525	-599.138	6.326
4900	36.525	INFINITE	27.347	98.325	-596.463	6.326
5000	33.675	INFINITE	11.000	93.675	-593.738	6.326

June 30, 1970

Heat of Formation
The existence of small amounts of dimer in the saturated vapor was inferred from the intensities of AlF₃⁺, AlF₂⁺, and AlF₂⁺ observed by mass spectrometry (1, 2, 3). Büchler et al. (1) concluded that the precursor of the first two ions was mainly AlF₃⁺, while the dimer was the precursor of AlF₂⁺. Intensities of AlF₂⁺ relative to those of AlF₃⁺ were observed as 0.0057 (1), 0.007 (2) and 0.025 (3) at ionizing energies of 60, 90 and 100 V for vapor at 1025, 1100 and 1025°K, respectively.

The temperature dependence of ion intensities was used to derive 2nd-law values of ΔH_f⁰ for monomer and dimer (1, 2) and a value of ΔH(dimerization) based on an estimate for the entropy of dimerization (3). The absolute pressure of the monomer was obtained (2) from integration of the intensity of AlF₂⁺ during total sublimation at 1100°K, then the pressure of dimer was estimated from the relative ion intensity assuming a relative ionization cross section equal to two and neglecting other effects. Krause and Douglas (4) reported ΔH_f⁰(monomer) plus ΔH⁰ and ΔS⁰ for dimerization; these were derived by combination of ΔH_f⁰(dimer) (1) with precise sublimation pressures from entrainment data near 1200°K, where the dimer is more abundant. After reduction to 1000 K with JANAF functions, these results may be summarized as follows:

Source	Method	ΔH _f ⁰ , kcal/mol*	ΔS _f ⁰ , gibbs/mol*
Krause (4)	Entrainment	c + m	c + m
Büchler (1)	Ion Intensities	68.1 ± 0.4	2c + d
Erkolin (2)	Ion Intensities	67.3 ± 3	2c + d
Porter (3)	Ion Intensities	70.5	2c + d
JANAF	Adopted	68.4	2c + d
		87.8	2c + d
		[-49]	2c + d
		[52.83]	2c + d
		[-35.9]	2c + d

* Reactions are abbreviated by c = crystal, d = dimer gas and m = monomer gas. Brackets enclose those values assumed in deriving the other values.

JANAF values are given in the last line. These are based on JANAF entropies, on ΔH⁰(dimerization) = -49 kcal/mol for which there is close agreement, and on the entrainment pressures of Krause and Douglas (4). Reduction of the dimer value to 298.15°K gives ΔH_f⁰ = 92.55 ± 4 and ΔH_f⁰ = -629.45 ± 4 kcal/mol. The table for AlF₃(g) gives a detailed comparison of observed and predicted total pressures along with predictions of the mole fraction of dimer in the saturated vapor. The latter are reasonably consistent with the relative ion intensities.

Heat Capacity and Entropy

The molecular structure is assumed to be similar to that of Al₂Cl₆. Bond distances and bond angles are estimated by comparison with AlF₃(g), AlCl₃(g) and Al₂Cl₆(g). Principal moments of inertia are I_A = 35.36 × 10⁻³⁹, I_B = 79.74 × 10⁻³⁹ and I_C = 94.66 × 10⁻³⁹ g cm².

Six observed vibrational frequencies are from infrared spectra of the dimer isolated in rare-gas matrices (2). Unobserved fundamentals (2) in infrared, 9 in Raman and 1 inactive) are estimated such that the entropy is consistent with the result of Krause and Douglas (4) as given above. The estimated fundamentals are based on comparisons with Al₂Cl₆, Al₂Br₆ and Al₂I₆ which have been restudied extensively (9-11) since the calculations of Miller (12). Assignments used in the comparisons are minor modifications of those given by Beattie et al. (3).

References

1. A. Büchler, E. P. Marram and J. L. Stauffer, *J. Phys. Chem.*, **71**, 4139 (1967).
2. E. V. Erokhin, N. A. Zhigul'skaya, L. N. Sidorov and P. A. Akishin, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **3** (5), 873 (1967).
3. R. F. Porter and T. E. Zeller, *J. Chem. Phys.*, **33**, 859 (1960).
4. R. F. Porter and T. E. Zeller, *J. Chem. Phys.*, **33**, 859 (1960).
5. E. V. Erokhin and E. P. Zaslavskiy, *J. Phys. Chem.*, **72**, 475 (1968).
6. E. V. Erokhin and E. P. Zaslavskiy, *J. Phys. Chem.*, **72**, 475 (1968).
7. A. Snelson, *J. Phys. Chem.*, **71**, 302 (1967).
8. I. R. Beattie and J. R. Horder, *J. Chem. Soc. A*, 1565 (1967).
9. I. R. Beattie and Sh. Sh. Raskin, *Optics and Spectroscopy* (English translation), **13**, 272 (1962).
10. E. U. Webb, B. H. Justice and H. Prophet, *J. Chem. Thermodynamics*, **1**, 227 (1969).
11. V. V. Korolov, B. H. Justice and H. Prophet, *J. Chem. Thermodynamics*, **1**, 227 (1969).
12. R. H. Miller, Ph.D. Thesis, Ohio University, Aug. 21, 1965.

Aluminum Triiodide, Dimeric (AlI₃)₂
(Ideal Gas) Mol. Wt. = 815.42

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	Log K _p
100	31.382	99.000	INFINITE	119.029	INFINITE
200	38.295	123.756	173.842	119.029	271.646
300	40.892	139.608	281.262	119.029	181.370
400	42.054	151.809	411.230	119.029	96.044
500	42.654	161.261	544.468	119.029	133.639
600	43.092	169.061	678.076	119.029	97.497
700	43.417	175.499	812.174	119.029	75.154
800	43.678	181.670	946.851	119.029	59.246
900	43.870	186.573	1080.009	119.029	46.582
1000	44.035	191.146	1211.098	119.029	36.654
1100	44.184	195.488	1340.001	119.029	29.227
1200	44.321	199.574	1466.786	119.029	23.632
1300	44.451	203.458	1591.466	119.029	19.667
1400	44.574	207.187	1714.951	119.029	16.837
1500	44.692	210.804	1837.261	119.029	14.683
1600	44.805	214.353	1958.409	119.029	12.878
1700	44.913	217.862	2078.409	119.029	11.396
1800	45.016	221.254	2197.261	119.029	10.182
1900	45.114	224.551	2315.001	119.029	9.182
2000	45.208	227.779	2431.633	119.029	8.353
2100	45.298	230.951	2547.166	119.029	7.653
2200	45.384	234.082	2661.700	119.029	7.053
2300	45.466	237.184	2775.233	119.029	6.533
2400	45.544	240.262	2887.766	119.029	6.083
2500	45.618	243.320	2999.300	119.029	5.693
2600	45.688	246.362	3109.833	119.029	5.353
2700	45.754	249.390	3219.366	119.029	5.053
2800	45.816	252.404	3327.900	119.029	4.793
2900	45.874	255.404	3435.433	119.029	4.573
3000	45.928	258.390	3542.000	119.029	4.383
3100	45.978	261.362	3647.633	119.029	4.223
3200	46.024	264.320	3752.266	119.029	4.083
3300	46.066	267.262	3855.900	119.029	3.953
3400	46.104	270.184	3958.533	119.029	3.833
3500	46.138	273.090	4060.166	119.029	3.723
3600	46.168	275.982	4160.800	119.029	3.623
3700	46.194	278.862	4260.433	119.029	3.533
3800	46.216	281.730	4359.066	119.029	3.453
3900	46.234	284.582	4456.700	119.029	3.383
4000	46.248	287.420	4553.333	119.029	3.323
4100	46.258	290.242	4649.000	119.029	3.273
4200	46.264	293.050	4743.633	119.029	3.233
4300	46.266	295.842	4837.266	119.029	3.193
4400	46.264	298.618	4929.900	119.029	3.163
4500	46.258	301.380	5021.533	119.029	3.133
4600	46.248	304.128	5112.166	119.029	3.103
4700	46.234	306.862	5201.800	119.029	3.073
4800	46.216	309.582	5290.433	119.029	3.043
4900	46.194	312.290	5378.066	119.029	3.013
5000	46.168	314.982	5464.700	119.029	2.983
5100	46.138	317.662	5550.333	119.029	2.953
5200	46.104	320.330	5635.000	119.029	2.923
5300	46.066	322.982	5718.633	119.029	2.893
5400	46.024	325.618	5801.266	119.029	2.863
5500	45.978	328.240	5882.900	119.029	2.833
5600	45.928	330.848	5963.533	119.029	2.803
5700	45.874	333.442	6043.166	119.029	2.773
5800	45.816	336.022	6121.800	119.029	2.743
5900	45.754	338.588	6199.433	119.029	2.713
6000	45.688	341.140	6276.066	119.029	2.683

Dec. 31, 1961; June 30, 1964

ALUMINUM TRIIODIDE, DIMERIC ((AlI₃)₂) (IDEAL GAS) MOL. WT. = 815.42

Point Group D_{2h}
ΔH_f^o 0 = -119.0 ± 3.0 kcal. mole⁻¹
ΔH_f^o 298.15 = -121.0 ± 3.0 kcal. mole⁻¹
S_{298.15}^o = [139.608] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies
(ω, cm.⁻¹) (ω, cm.⁻¹) (ω, cm.⁻¹)

344 (1)	[53] (1)	[290] (1)
146 (1)	[430] (1)	[53] (1)
94 (1)	[130] (1)	[50] (1)
53 (1)	[20] (1)	[330] (1)
[30] (1)	410 (1)	[140] (1)
[300] (1)	[65] (1)	[55] (1)

Bond Distance: Al-I = 2.53 Å Al-I-bridge = 2.58 Å

Bond Angle: I-Al-I = 112 ± 1° I-bridge-Al-I-bridge = 68 ± 1°

Product of the Moments of Inertia: I_AI_BI_C = 5.2175 X 10⁻¹⁰⁹ g.³ cm.⁶

Heat of Formation.

W. Fischer, O. Rahlfs and B. Benze, Z. anorg. allgem. Chem. 205, 1 (1932) measured the vapor pressure of AlI₃(l). The vapor consists of both Al₂I₆(g) and AlI₃(g) species. The partial pressures of Al₂I₆(g) and AlI₃(g) at different temperatures for the equilibrium Al₂I₆(g) → 2AlI₃(g) were determined by W. Fischer, O. Rahlfs and B. Benze, loc. cit. From these partial pressures the mole ratios of Al₂I₆(g) and AlI₃(g) at other temperatures were estimated. The partial pressures of Al₂I₆(g) over AlI₃(l) were calculated from the total pressure using the estimated mole ratio values. The heat of vaporization, ΔH_v 298.15 = 20.5 ± 1.0 kcal. mole⁻¹, was evaluated employing the vapor pressures obtained by second law method. The corresponding third law value is 22.4 kcal. mole⁻¹. It was not used due to the uncertainties involved in the estimation of the vibrational frequencies. The heat of formation for Al₂I₆(g) was calculated from ΔH_f^o(l) and ΔH_v^o obtained.

Heat Capacity and Entropy.

Molecular structure, bond distances and angles were reported by K. J. Palmer and N. Elliott, J. Am. Chem. Soc. 60, 1852 (1938). Five vibrational frequencies (344, 146, 94, 53 and 410 cm.⁻¹) were adopted from the Raman spectrum of Al₂I₆(l) measured by H. Gerding and E. Smit, Z. physik. Chem. 50B, 171 (1941). The remaining ones were estimated by comparison with those for Al₂O₆(g) and Al₂Br₆(g) and adjusted so that the value of ΔH_f^o 298.15 obtained by the third law method is in reasonable agreement with the corresponding second law value. The three principal moments of inertia are: I_A = 9.32506 X 10⁻³⁷, I_B = 4.60285 X 10⁻³⁷, and I_C = 1.21558 X 10⁻³⁶ g. cm.².

Magnesium Aluminate (MgAl_2O_4)
(Crystal) Mol. Wt. = 142.28

T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _f
0	.000	INFINITE	3.883	-547.349	-547.349	-547.349	INFINITE
100	5.418	2.075	3.531	-548.989	-548.989	-548.989	1150.844
200	19.539	9.977	2.314	-550.578	-550.578	-550.578	302.360
298	27.771	19.286	.000	-551.200	-551.200	-551.200	302.167
300	27.905	19.440	.052	-551.208	-551.208	-551.208	379.658
400	33.247	26.289	3.140	-551.349	-551.349	-551.349	279.254
500	36.088	36.040	22.802	-551.228	-551.228	-551.228	219.013
600	37.923	42.789	25.583	-551.014	-551.014	-551.014	178.885
700	39.284	48.753	28.475	-550.773	-550.773	-550.773	150.200
800	40.392	54.063	31.347	-550.541	-550.541	-550.541	128.711
900	41.353	58.877	34.142	-550.335	-550.335	-550.335	112.003
1000	42.222	63.280	36.839	-550.273	-550.273	-550.273	98.522
1100	43.038	67.333	39.430	-550.204	-550.204	-550.204	87.454
1200	43.801	71.121	41.935	-550.127	-550.127	-550.127	78.458
1300	44.519	74.658	44.299	-550.040	-550.040	-550.040	70.445
1400	45.281	77.983	46.587	-549.945	-549.945	-549.945	63.697
1500	45.987	81.130	48.788	-549.845	-549.845	-549.845	57.804
1600	46.658	84.119	50.902	-549.741	-549.741	-549.741	52.592
1700	47.321	86.968	52.940	-549.637	-549.637	-549.637	47.593
1800	48.018	89.693	54.907	-549.534	-549.534	-549.534	43.134
1900	48.690	92.307	56.807	-549.430	-549.430	-549.430	39.719
2000	49.346	94.822	58.645	-549.325	-549.325	-549.325	36.363
2100	49.932	97.254	60.428	-549.217	-549.217	-549.217	33.371
2200	50.475	99.579	62.153	-549.105	-549.105	-549.105	30.818
2300	50.984	101.834	63.829	-548.991	-548.991	-548.991	28.150
2400	51.459	104.014	65.459	-548.873	-548.873	-548.873	25.873
2500	51.900	106.124	67.043	-548.751	-548.751	-548.751	23.785
2600	52.308	108.157	68.588	-548.625	-548.625	-548.625	21.881
2700	52.681	110.169	70.099	-548.495	-548.495	-548.495	20.182
2800	53.021	112.071	71.554	-548.361	-548.361	-548.361	18.191
2900	53.328	113.937	72.963	-548.223	-548.223	-548.223	16.258
3000	53.600	115.749	74.379	-548.082	-548.082	-548.082	14.499

Al_2MgO_4

MOL. WT. = 142.28

(CRYSTAL)

MAGNESIUM ALUMINATE (MgAl_2O_4)

$\Delta H_f^\circ \text{ O} = -547.3 \pm 1.9 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ \text{ 298.15} = -551.2 \pm 1.9 \text{ kcal. mole}^{-1}$
 $\Delta H_m^\circ = \text{Unknown}$

$S_{298.15}^\circ = 19.27 \pm 0.10 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 2408^\circ\text{K.}$

Heat of Formation.

The value of $\Delta H_f^\circ \text{ 298.15}$ was calculated from $\Delta H_f^\circ \text{ 298.15} = 124.6 \pm 1.5 \text{ kcal. mole}^{-1}$ for the reaction:
 $4\text{MgO(c)} + 2\text{Al(l)} = \text{MgAl}_2\text{O}_4\text{(c)} + 3\text{Mg(g)}$. The value of $\Delta H_f^\circ \text{ 298.15}$ was obtained by the third-law method, using
vapor pressure data reported by K. Grjotheim, O. Horstad, and J. M. Toguri, Can. J. Chem. **39**, 443 (1961). From
the Knudsen experiments with $\text{MgAl}_2\text{O}_4\text{(c)}$, R. L. Altman, J. Phys. Chem., **57**, 366 (1963) calculated the value of
 $\Delta H_f^\circ \text{ 298.15}$ as $-552 \text{ kcal. mole}^{-1}$ which agrees with the value used.

Heat Capacity and Entropy.

The low temperature heat capacity, $53\text{--}296^\circ\text{K.}$, was measured by E. G. King, J. Phys. Chem. **59**, 218 (1955).
The high temperature heat capacity, $400\text{--}1800^\circ\text{K.}$, was reported by K. R. Bórnicksen, J. Phys. Chem. **59**, 220 (1955).
These two sets of data were joined smoothly and extrapolated to 3000°K. $S_{298.15}^\circ$ was reported by E. G. King, loc.
cit., based on S_{21}° (extrap.) = $0.32 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Temperature of Melting.

T_m was taken from "Data on Chemicals for Ceramic Use," U. S. National Research Council Bulletin 118, 1949.

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	0.000	0.000	INFINITE	2.777	30.951	30.951	INFINITE	
100	6.767	51.375	70.763	1.959	30.702	33.433	73.065	
200	9.805	57.616	62.932	1.023	30.970	36.101	79.486	
298	10.716	61.966	61.966	0.000	31.400	38.539	81.246	
300	10.934	62.033	61.966	0.020	31.408	38.578	81.246	
400	11.749	65.297	62.405	1.157	31.821	40.924	82.388	
500	12.321	67.984	63.260	2.362	32.236	43.128	83.650	
600	12.711	70.267	64.242	3.615	32.672	45.266	84.967	
700	12.982	72.248	65.248	4.900	33.150	47.329	86.339	
800	13.174	73.994	66.234	6.208	33.673	49.319	87.765	
900	13.314	75.555	67.184	7.533	34.249	51.240	89.242	
1000	13.418	76.963	68.093	8.870	34.870	53.075	90.765	
1100	13.498	78.246	68.959	10.216	40.343	53.988	92.338	
1200	13.561	79.423	69.782	11.569	40.814	55.207	93.965	
1300	13.610	80.511	70.566	12.928	41.284	56.389	95.639	
1400	13.650	81.521	71.313	14.291	41.753	57.533	97.361	
1500	13.682	82.464	72.025	15.657	42.222	58.644	99.131	
1600	13.709	83.347	72.706	17.027	42.691	59.722	100.947	
1700	13.731	84.179	73.356	18.399	43.159	60.778	102.807	
1800	13.750	84.965	73.980	19.773	43.630	61.796	104.710	
1900	13.766	85.709	74.578	21.149	44.102	62.781	106.655	
2000	13.780	86.415	75.152	22.526	44.574	63.742	108.635	
2100	13.792	87.088	75.704	23.905	45.048	64.712	110.648	
2200	13.802	87.730	76.236	25.285	45.524	65.637	112.692	
2300	13.812	88.343	76.750	26.665	46.002	66.539	114.765	
2400	13.820	88.931	77.245	28.047	46.481	67.421	116.865	
2500	13.827	89.496	77.724	29.429	46.963	68.285	118.990	
2600	13.833	90.038	78.187	30.812	47.446	69.130	121.140	
2700	13.838	90.560	78.630	32.196	47.931	69.955	123.314	
2800	13.843	91.063	79.071	33.580	48.416	70.765	125.512	
2900	13.848	91.549	79.493	34.965	48.901	71.559	127.733	
3000	13.852	92.019	79.902	36.350	49.386	72.337	129.985	
3100	13.856	92.473	80.301	37.735	49.873	73.111	132.267	
3200	13.859	92.913	80.688	39.121	50.360	73.875	134.579	
3300	13.862	93.340	81.065	40.507	50.848	74.619	136.921	
3400	13.865	93.754	81.432	41.893	51.336	75.343	139.293	
3500	13.868	94.155	81.790	43.280	51.824	76.057	141.695	
3600	13.870	94.546	82.139	44.667	52.312	76.761	144.126	
3700	13.872	94.926	82.479	46.054	52.800	77.455	146.585	
3800	13.874	95.296	82.812	47.441	53.288	78.139	149.071	
3900	13.876	95.657	83.136	48.829	53.776	78.813	151.584	
4000	13.878	96.008	83.454	50.216	54.264	79.477	154.125	
4100	13.879	96.351	83.768	51.604	54.752	80.131	156.694	
4200	13.881	96.685	84.068	52.992	55.240	80.775	159.289	
4300	13.882	97.012	84.365	54.380	55.728	81.409	161.910	
4400	13.883	97.331	84.656	55.768	56.216	82.033	164.556	
4500	13.885	97.643	84.941	57.157	56.704	82.647	167.227	
4600	13.886	97.948	85.221	58.545	57.192	83.251	169.922	
4700	13.887	98.247	85.495	59.934	57.680	83.845	172.641	
4800	13.888	98.539	85.764	61.323	58.168	84.429	175.384	
4900	13.889	98.825	86.027	62.712	58.704	85.003	178.151	
5000	13.890	99.106	86.286	64.100	59.240	85.567	180.942	
5100	13.890	99.381	86.540	65.489	59.776	86.121	183.757	
5200	13.891	99.651	86.790	66.879	60.312	86.665	186.596	
5300	13.892	99.915	87.035	68.268	60.848	87.199	189.459	
5400	13.893	100.175	87.274	69.657	61.384	87.723	192.345	
5500	13.893	100.430	87.513	71.046	61.919	88.237	195.254	
5600	13.894	100.680	87.745	72.436	62.454	88.741	198.186	
5700	13.894	100.926	87.975	73.826	62.990	89.235	201.141	
5800	13.895	101.168	88.200	75.214	63.526	89.719	204.119	
5900	13.896	101.405	88.422	76.604	64.062	90.193	207.120	
6000	13.896	101.639	88.640	77.994	64.598	90.657	210.144	

Dec. 31, 1960; Sept. 30, 1961; Sept. 30, 1965

Point Group C_{2v}S°_{298.15} = 62.0 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹
715 (1)
[238] (1)
994 (1)

Bond Distance: Al-O = 1.66 Å

Bond Angle: Al-O-Al = 145°

Product of the Moments of Inertia: I_AI_BI_C = 263.2477 X 10⁻¹¹⁷ g.³ cm.⁶

Heat of Formation.

The value of ΔH°_f 298 = -31.4 ± 7 kcal. mole⁻¹ for Al₂O(g) was calculated from ΔH°_f 298 = 247 ± 7 kcal. mole⁻¹ for the reaction Al₂O(g) = 2Al(g) + O(g); and ΔH°_f 298 = 131 ± 7 kcal. mole⁻¹ for the reaction Al₂O(g) = AlO(g) + Al(g). The value of ΔH°_f 298 were obtained by the third law method, using the partial pressure data reported by J. Drowart, G. Delmaris, R. Burns and M. Ingraham, *J. Chem. Phys.* **32**, 1368 (1960). (The second law values which are in poor agreement with the third law values, are ΔH°_f 298 = 271 ± 10 kcal. mole⁻¹ and ΔH°_f = 154 ± 10 kcal. mole⁻¹, respectively.) L. Brewer and A. Searcy, *J. Am. Chem. Soc.*, **73**, 5308 (1951), reported that under reducing condition, Al₂O₃ vaporizes mostly to Al₂O(g), but under neutral condition AlO(g) and O(g) are the major products. Brewer and Searcy also measured the vapor pressures of the Al-Al₂O₃ system by Knudsen effusion method, and obtained the heat of formation of Al₂O(g) from gaseous atoms as ΔH°_f 298 = -248 kcal. mole⁻¹. This value leads the heat of formation for Al₂O(g), ΔH°_f 298 = -32.4 ± 7, which agrees with the value selected.

Other references appearing in the recent literature were:

1. Lao Brewer, AEC Report UCR-8356 (1958).
2. G. Delmaris, J. Drowart, M. Ingraham, *J. Chem. Phys.*, **30**, 318 (1959).
3. R. Porter, P. Shisael and M. Ingraham, *J. Chem. Phys.*, **23**, 339 (1955).
4. R. J. Ackerman and R. J. Thorn, *J. Am. Chem. Soc.*, **78**, 4169 (1956).
5. C. N. Cochran, *J. Am. Chem. Soc.*, **77**, 2190 (1955).
6. M. Cook, A. Faller, R. Keyes, W. Partridge and W. Ursenbach, *J. Phys. Chem.*, **61**, 189 (1957).

Heat Capacity and Entropy.

The matrix isolation of high temperature vapors for the investigation of the infrared spectrum of Al₂O has been used to determine the bond distance, angle and vibrational frequencies by M. Linevsky, D. White and D. Mann, *J. Chem. Phys.*, **41**, 542 (1964). These reported data have been adopted in this table. The symmetric structure Al-O-Al instead of Al-Al-O for Al₂O(g) was chosen for two reasons: (1) The dissociation energy of Al₂O(g), D°₂₉₈ = 247 ± 7 kcal/mole, is approximately twice the dissociation energy of AlO(g), D°₂₉₈ = 115 ± 5 kcal. mole⁻¹, which implies that the symmetric structure is more reasonable. (2) The dissociation energy of Al₂O(g) has been estimated to be only 39 kcal. mole⁻¹ by J. Drowart and R. Honig, *J. Phys. Chem.*, **61**, 980 (1957). This implies that the Al-O bond energy in "Al-Al-O" structure would be as large as 208 kcal. mole⁻¹ if D°Al-Al = 39 kcal. mole⁻¹. Therefore Al₂O(g) must have a symmetric structure. Linevsky et al., loc. cit., have also concluded the bent symmetric structure (instead of a linear one) and the calculated ω₂ from the observed infrared spectra and the re-analysis of the ultraviolet spectra. The three principal moments of inertia are I_A = 0.5105 X 10⁻³⁹ g.², I_B = 22.4539 X 10⁻³⁹ and I_C = 22.9644 X 10⁻³⁹ g.²

Drowart, et al. (loc. cit.), also postulated a bent asymmetric molecule for Al₂O(g), and estimated the bond distance Al-O = [1.0176] Å and angle Al-O-Al = [110]° and the vibrational frequencies as [1079] cm.⁻¹, [351] cm.⁻¹ and [921] cm.⁻¹

The National Bureau of Standards Report No. 6494 "Preliminary Report on the Thermodynamic Properties of Li, Be, Mg, Al and Their Compounds with Hydrogen, Oxygen, Nitrogen, Fluorine and Chlorine" July, 1959, has proposed a trigonal structure for Al₂O(g) with bond distance Al-O = [1.87] Å, and Al-Al = [2.0] Å. Its vibration frequencies were estimated as [450] cm.⁻¹, [1000] cm.⁻¹ and [1000] cm.⁻¹.

Dialuminum Monoxide Unipositive Ion (Al₂O⁺)

(Ideal Gas) GFW = 69.9618

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	kcal/mol ΔH°	ΔG°	Log Kp
100						
200						
250	10.918	62.697	62.697	146.000	137.161	100.542
300	10.935	62.765	62.698	146.001	137.106	99.881
350	10.952	62.833	62.712	146.002	137.051	99.220
400	10.969	62.900	62.780	146.003	136.996	98.559
450	10.986	62.967	62.848	146.004	136.941	97.898
500	10.999	63.034	62.916	146.005	136.886	97.237
600	11.016	63.136	63.044	146.006	136.776	96.216
700	11.033	63.238	63.172	146.007	136.666	95.195
800	11.050	63.340	63.300	146.008	136.556	94.174
900	11.067	63.442	63.428	146.009	136.446	93.153
1000	11.084	63.544	63.556	146.010	136.336	92.132
1100	11.101	63.646	63.684	146.011	136.226	91.111
1200	11.118	63.748	63.812	146.012	136.116	90.090
1300	11.135	63.850	63.940	146.013	136.006	89.069
1400	11.152	63.952	64.068	146.014	135.896	88.048
1500	11.169	64.054	64.196	146.015	135.786	87.027
1600	11.186	64.156	64.324	146.016	135.676	86.006
1700	11.203	64.258	64.452	146.017	135.566	84.985
1800	11.220	64.360	64.580	146.018	135.456	83.964
1900	11.237	64.462	64.708	146.019	135.346	82.943
2000	11.254	64.564	64.836	146.020	135.236	81.922
2100	11.271	64.666	64.964	146.021	135.126	80.901
2200	11.288	64.768	65.092	146.022	135.016	79.880
2300	11.305	64.870	65.220	146.023	134.906	78.859
2400	11.322	64.972	65.348	146.024	134.796	77.838
2500	11.339	65.074	65.476	146.025	134.686	76.817
2600	11.356	65.176	65.604	146.026	134.576	75.796
2700	11.373	65.278	65.732	146.027	134.466	74.775
2800	11.390	65.380	65.860	146.028	134.356	73.754
2900	11.407	65.482	65.988	146.029	134.246	72.733
3000	11.424	65.584	66.116	146.030	134.136	71.712
3100	11.441	65.686	66.244	146.031	134.026	70.691
3200	11.458	65.788	66.372	146.032	133.916	69.670
3300	11.475	65.890	66.500	146.033	133.806	68.649
3400	11.492	65.992	66.628	146.034	133.696	67.628
3500	11.509	66.094	66.756	146.035	133.586	66.607
3600	11.526	66.196	66.884	146.036	133.476	65.586
3700	11.543	66.298	67.012	146.037	133.366	64.565
3800	11.560	66.400	67.140	146.038	133.256	63.544
3900	11.577	66.502	67.268	146.039	133.146	62.523
4000	11.594	66.604	67.396	146.040	133.036	61.502
4100	11.611	66.706	67.524	146.041	132.926	60.481
4200	11.628	66.808	67.652	146.042	132.816	59.460
4300	11.645	66.910	67.780	146.043	132.706	58.439
4400	11.662	67.012	67.908	146.044	132.596	57.418
4500	11.679	67.114	68.036	146.045	132.486	56.397
4600	11.696	67.216	68.164	146.046	132.376	55.376
4700	11.713	67.318	68.292	146.047	132.266	54.355
4800	11.730	67.420	68.420	146.048	132.156	53.334
4900	11.747	67.522	68.548	146.049	132.046	52.313
5000	11.764	67.624	68.676	146.050	131.936	51.292
5100	11.781	67.726	68.804	146.051	131.826	50.271
5200	11.798	67.828	68.932	146.052	131.716	49.250
5300	11.815	67.930	69.060	146.053	131.606	48.229
5400	11.832	68.032	69.188	146.054	131.496	47.208
5500	11.849	68.134	69.316	146.055	131.386	46.187
5600	11.866	68.236	69.444	146.056	131.276	45.166
5700	11.883	68.338	69.572	146.057	131.166	44.145
5800	11.900	68.440	69.700	146.058	131.056	43.124
5900	11.917	68.542	69.828	146.059	130.946	42.103
6000	11.934	68.644	69.956	146.060	130.836	41.082

June 30, 1968



GFW = 69.9618

ΔH°₀ = 146.5 ± 10 kcal/mol

ΔH°_{298.15} = 146 ± 10 kcal/mol

Point Group [C_{2v}]

S°_{298.15} = [62.7 ± 2] gibbs/mol

Ground State Quantum Weight = [2]

(IDEAL GAS)

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	
[700] (1)	
[250] (1)	
[1000] (1)	

Bond Distance: Al-O = [1.86] Å

Bond Angle: Al-O-Al = [155°]

Product of the Moments of Inertia: I_AI_BI_C = [1.481 x 10⁻¹¹⁵] g³ cm⁶

Heat of Formation

The ionization potential of Al₂O has been reported as 7.7 ± 0.2eV (177.6 kcal) by R. F. Porter, P. Schissel, and M. G. Inghram, J. Chem. Phys. 23, 339 (1955), and has been confirmed as 7.7 ± 0.5eV by G. DeMaria, J. Drowart, M. G. Inghram, J. Chem. Phys. 30, 318 (1959). Using this value with ΔH°₂₉₈(Al₂O, g) = -31.4 kcal/mol, we obtain ΔH°₂₉₈(Al₂O⁺, g) = 146 ± 10 kcal/mol.

Heat Capacity and Entropy

The molecule is assumed to be bent by analogy with Al₂O, although both these molecules are predicted to be linear according to A. D. Walsh, J. Chem. Soc. 2266 (1953). The electronic ground state is doublet, since there is an odd number of electrons. The bond length is estimated to be the same as that in Al₂O and the vibrational frequencies are also assumed to be close to those for Al₂O. Since normally the molecule Al₂O ought to be linear, the bending must occur due to the occupancy of an outermost orbital with strong angular variation. Presumably this orbital is occupied by a pair of electrons, one of which will be removed in Al₂O⁺, thus causing an opening of the bond angle. On this basis the angle is estimated to be greater than that in Al₂O. The individual moments of inertia are: I_A = 2.645 x 10⁻⁴⁰ g cm², I_B = 2.353 x 10⁻³⁸ g cm² and I_C = 2.380 x 10⁻³⁸ g cm². The enthalpy at 0°K is -2.769 kcal/mol.



Point Group [V_h]
S_{298.15} = [83.7] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

ΔH_f⁰ = -95.7 ± 7 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -97.0 ± 7 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω _e , cm. ⁻¹	ω _e , cm. ⁻¹
[200] (1)	[930] (1)
[800] (1)	[1000] (1)
[930] (1)	[1000] (1)

Bond Distance: Al-O = [1.60] Å
Bond Angles: Al-O-Al = [90]°, O-Al-O = [90]°
Products of the Moments of Inertia: I_AI_BI_C = [1.4246 X 10⁻¹¹⁴] g.³ cm.⁶
σ = [4]

Heat of Formation.

The value of ΔH_f⁰ 298 = -97 ± 7 kcal. mole⁻¹ for Al₂O₂(g) was calculated from ΔH_f⁰ 298 = 372 ± 7 kcal. mole⁻¹ for the reaction Al₂O₂(g) = 2Al(g) + 2O(g). The value of ΔH_f⁰ 298 was obtained by the third law method, using the partial pressure data reported by J. Drowart, G. Defaria, R. Burna and M. Inghram, J. Chem. Phys. 32, 1386 (1960). (The second law value for ΔH_f⁰ which is in poor agreement with the third law value, is 451 ± 25 kcal. mole⁻¹.)

Heat Capacity and Entropy.

The molecular structure (plane cyclic model) and vibrational frequencies of Al₂O₂(g) were obtained from Drowart, et al., J. Chem. Phys., 32, 1386 (1960). The bond distance Al-O in Al₂O₂ was assumed to be the same as that in AlO (g.). The three principal moments of inertia are I_A = 6.8005 X 10⁻³⁵, I_B = 11.4874 X 10⁻³⁵ and I_C = 19.2879 X 10⁻³⁵ g. cm.²

The configuration was proposed by Drowart, et al., instead of the alternate linear structure OAl-AlO for the reason discussed below. The OB-BO bond 1.2 compares to the B₂ dissociation energy 3.4 in the same way as the NC-CN bond compares to the C-C single bond. However, for Al₂O₂(g), the relationship between OAl-AlO and Al₂ would be quite different.

- References (1) M. Inghram, R. Porter and W. Chupka, J. Chem. Phys., 25, 498 (1956).
(2) D. White, P. Walsh and D. Mann, J. Chem. Phys., 25, 508 (1956).
(3) T. L. Cottrell, "The Strength of Chemical Bonds", Butterworths Scientific Publications, London (1956).
(4) O. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., (1950).

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	h ⁰ -H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	9.017	52.453	2.920	-95.666	-95.666	-95.666	INFINITE
200	10.510	73.450	2.100	-96.525	-96.525	-96.525	210.945
298	12.496	83.695	1.127	-96.353	-96.353	-96.353	106.106
300	12.534	83.695	1.023	-97.012	-97.012	-97.012	70.913
400	14.394	86.421	1.373	-97.567	-97.567	-97.567	53.108
500	15.780	87.013	2.866	-98.039	-98.039	-98.039	42.513
600	16.758	87.982	4.516	-98.476	-98.476	-98.476	35.356
700	17.447	88.620	6.228	-98.916	-98.916	-98.916	30.221
800	17.941	89.085	7.968	-99.376	-99.376	-99.376	26.353
900	18.304	89.481	9.812	-99.870	-99.870	-99.870	23.329
1000	18.576	89.842	11.656	-100.397	-100.397	-100.397	20.817
1100	18.785	90.172	13.525	-100.957	-100.957	-100.957	18.719
1200	18.948	90.484	15.412	-101.548	-101.548	-101.548	16.965
1300	19.078	90.778	17.313	-102.168	-102.168	-102.168	15.476
1400	19.182	91.054	19.226	-102.815	-102.815	-102.815	14.196
1500	19.268	91.313	21.149	-103.488	-103.488	-103.488	13.082
1600	19.339	91.558	23.080	-104.186	-104.186	-104.186	12.104
1700	19.398	91.791	25.016	-104.908	-104.908	-104.908	11.239
1800	19.448	91.999	26.959	-105.654	-105.654	-105.654	10.468
1900	19.490	92.188	28.906	-106.424	-106.424	-106.424	9.775
2000	19.527	92.354	30.857	-107.218	-107.218	-107.218	9.150
2100	19.558	92.500	32.811	-108.036	-108.036	-108.036	8.582
2200	19.585	92.628	34.768	-108.878	-108.878	-108.878	8.064
2300	19.609	92.741	36.728	-109.744	-109.744	-109.744	7.500
2400	19.631	92.841	38.690	-110.634	-110.634	-110.634	7.134
2500	19.649	92.928	40.654	-111.548	-111.548	-111.548	6.751
2600	19.664	93.003	42.620	-112.486	-112.486	-112.486	6.379
2700	19.678	93.068	44.587	-113.448	-113.448	-113.448	6.032
2800	19.694	93.125	46.556	-114.434	-114.434	-114.434	5.702
2900	19.706	93.175	48.526	-115.444	-115.444	-115.444	5.382
3000	19.717	93.219	50.497	-116.478	-116.478	-116.478	5.071
3100	19.727	93.258	52.469	-117.536	-117.536	-117.536	4.771
3200	19.736	93.292	54.442	-118.618	-118.618	-118.618	4.486
3300	19.744	93.319	56.416	-119.724	-119.724	-119.724	4.214
3400	19.751	93.341	58.381	-120.854	-120.854	-120.854	3.951
3500	19.756	93.358	60.336	-122.008	-122.008	-122.008	3.694
3600	19.764	93.371	62.283	-123.186	-123.186	-123.186	3.442
3700	19.770	93.380	64.219	-124.388	-124.388	-124.388	3.194
3800	19.775	93.386	66.146	-125.614	-125.614	-125.614	2.950
3900	19.780	93.389	68.064	-126.864	-126.864	-126.864	2.711
4000	19.785	93.390	70.252	-128.138	-128.138	-128.138	2.476
4100	19.789	93.390	72.231	-129.436	-129.436	-129.436	2.246
4200	19.793	93.390	74.210	-130.758	-130.758	-130.758	2.021
4300	19.796	93.390	76.180	-132.104	-132.104	-132.104	1.800
4400	19.800	93.390	78.170	-133.474	-133.474	-133.474	1.582
4500	19.803	93.390	80.150	-134.868	-134.868	-134.868	1.368
4600	19.806	93.390	82.130	-136.286	-136.286	-136.286	1.158
4700	19.809	93.390	84.111	-137.728	-137.728	-137.728	0.952
4800	19.811	93.390	86.092	-139.194	-139.194	-139.194	0.750
4900	19.814	93.390	88.073	-140.684	-140.684	-140.684	0.551
5000	19.816	93.390	90.055	-142.198	-142.198	-142.198	0.356
5100	19.818	93.390	92.036	-143.736	-143.736	-143.736	0.165
5200	19.820	93.390	94.018	-145.298	-145.298	-145.298	-0.031
5300	19.822	93.390	96.000	-146.884	-146.884	-146.884	-0.232
5400	19.824	93.390	97.983	-148.494	-148.494	-148.494	-0.437
5500	19.826	93.390	99.965	-150.128	-150.128	-150.128	-0.646
5600	19.828	93.390	101.948	-151.786	-151.786	-151.786	-0.859
5700	19.829	93.390	103.931	-153.468	-153.468	-153.468	-1.076
5800	19.831	93.390	105.914	-155.174	-155.174	-155.174	-1.296
5900	19.832	93.390	107.897	-156.904	-156.904	-156.904	-1.519
6000	19.833	93.390	109.880	-158.658	-158.658	-158.658	-1.745

Aluminum Dioxide Unipositive Ion (Al₂O₂⁺)

GF_W = 85.9612

(Ideal Gas)

T, K	C _p ^a	S ^b - (C _p ^a - H ⁰ ₂₉₈)/T	H ⁰ - H ²⁹⁸	ΔH ⁰	ΔG ⁰	Log Kp
0						
100						
200						
298	13.059	66.387	66.387	.000	131.000	128.963 = 94.532
300	13.139	66.468	66.468	.024	130.998	128.949 = 93.939
400	15.211	68.519	68.519	1.437	130.999	128.271 = 70.084
500	16.319	72.018	66.003	3.007	131.073	127.581 = 55.765
600	17.205	75.077	67.266	4.686	131.176	126.872 = 46.213
700	17.814	77.182	68.186	6.283	131.346	125.408 = 34.260
800	18.214	78.578	68.983	7.781	131.508	124.125 = 24.260
900	18.556	82.358	71.148	10.084	131.346	124.665 = 30.273
1000	18.788	84.322	72.370	11.952	126.218	124.293 = 27.164
1100	18.965	86.121	73.539	13.840	126.246	124.099 = 24.656
1200	19.102	87.777	74.658	15.749	126.261	123.702 = 22.786
1300	19.209	89.299	75.748	17.678	126.269	123.202 = 20.766
1400	19.293	90.738	76.748	19.595	126.360	123.500 = 19.279
1500	19.370	92.072	77.726	21.519	126.402	123.292 = 17.964
1600	19.429	93.324	78.662	23.459	126.444	123.084 = 16.812
1700	19.479	94.503	79.560	25.404	126.487	122.873 = 15.805
1800	19.521	95.612	80.438	27.353	126.530	122.662 = 14.919
1900	19.555	96.678	81.298	29.308	126.565	122.445 = 14.083
2000	19.586	97.678	82.044	31.265	126.601	122.225 = 13.356
2100	19.612	98.634	82.813	33.225	126.635	122.004 = 12.697
2200	19.635	99.547	83.553	35.182	126.664	121.782 = 12.098
2300	19.655	100.425	84.268	37.138	126.691	121.557 = 11.550
2400	19.672	101.257	84.958	39.118	126.716	121.332 = 11.050
2500	19.687	102.061	85.626	41.086	126.735	121.111 = 10.588
2600	19.701	102.833	86.273	43.056	126.752	120.888 = 10.162
2700	19.713	103.569	86.900	45.008	126.769	120.667 = 9.770
2800	19.724	104.278	87.510	46.946	126.784	120.447 = 9.400
2900	19.734	104.964	88.100	48.871	11.522	126.797 = 9.050
3000	19.743	105.656	88.674	50.945	10.998	131.642 = 8.562
3100	19.751	106.303	89.232	52.920	10.477	136.388 = 8.045
3200	19.758	106.915	89.775	54.891	9.958	141.136 = 7.508
3300	19.765	107.495	90.300	56.848	9.443	145.883 = 6.958
3400	19.771	108.048	90.820	58.848	8.942	150.527 = 6.476
3500	19.777	108.572	91.323	60.826	8.435	155.209 = 6.092
3600	19.782	109.059	91.813	62.804	7.934	159.884 = 5.706
3700	19.787	109.520	92.282	64.781	7.436	164.556 = 5.310
3800	19.791	109.958	92.731	66.746	6.944	169.226 = 4.916
3900	19.795	110.383	93.177	68.700	6.452	173.897 = 4.524
4000	19.799	111.344	93.664	70.720	5.968	178.416 = 4.148
4100	19.803	111.833	94.101	72.700	5.486	183.016 = 3.756
4200	19.806	112.300	94.561	74.661	5.002	187.603 = 3.363
4300	19.809	112.748	95.048	76.601	4.517	192.197 = 2.970
4400	19.812	113.232	95.558	78.632	4.041	196.770 = 2.578
4500	19.814	113.677	95.961	80.624	3.596	201.325 = 2.186
4600	19.817	114.113	96.355	82.605	3.133	205.869 = 1.794
4700	19.821	114.556	96.721	84.559	2.696	210.406 = 1.402
4800	19.824	114.996	97.068	86.488	2.266	214.936 = 1.010
4900	19.828	115.365	97.293	88.551	1.778	219.464 = 0.618
5000	19.825	115.765	97.658	90.534	1.338	223.971 = 0.226
5100	19.827	116.158	98.017	92.516	.904	228.475 = -0.161
5200	19.830	116.521	98.310	94.482	.470	232.968 = -0.554
5300	19.832	116.861	98.591	96.432	.035	237.451 = -0.941
5400	19.832	117.251	98.857	98.465	.360	241.928 = -1.328
5500	19.833	117.655	99.392	100.448	.765	246.395 = -1.715
5600	19.835	118.013	99.721	102.432	1.161	250.856 = -2.102
5700	19.837	118.349	100.000	104.399	1.526	255.316 = -2.489
5800	19.839	118.709	100.268	106.346	1.881	259.776 = -2.876
5900	19.838	119.048	100.678	108.383	2.298	264.206 = -3.263
6000	19.839	119.381	100.987	110.367	2.656	268.647 = -3.650

June 30, 1968



GF_W = 85.9612

(IDEAL GAS)

ΔH_f⁰ = 132.3 ± 20 kcal/mol

ΔH_f⁰ = 131 ± 20 kcal/mol

Point Group [D_{2h}]

S_{298.15}⁰ = [64.4 ± 3] gibbs/mol

Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies	ω, cm ⁻¹
[180] (1)	[650] (1)
[550] (1)	[900] (1)
[850] (1)	[900] (1)

Bond Angle: Al-O = [1.66] Å

Bond Distance: Al-O = [1.66] Å

Product of the Moments of Inertia: I_AI_BI_C = [1.777 × 10⁻¹¹u³ cm⁶]

Heat of Formation

G. DeMaria, J. Drowart, and M. G. Inghram, J. Chem. Phys. 30, 118 (1959), have reported an ionization potential for Al₂O₂⁺ of 9.9 ± 0.5 eV (228 kcal). Using this value in conjunction with ΔH_f⁰ (Al₂O₂, g) = -97 kcal/mol, we obtain ΔH_f⁰ (Al₂O₂⁺, g) = 131 ± 20 kcal/mol.

Heat Capacity and Entropy

The molecular configuration is assumed to be the same as that used for Al₂O₂. The bond length is assumed to be longer than that in Al₂O₂ and is made equal to that reported for Al₂O. The bond angle is arbitrarily estimated to be the same as that in Al₂O₂. The vibrational frequencies are estimated to be slightly lower than those for Al₂O₂, since the Al₂O₂⁺ molecule should be less rigidly bound. The ground state is assumed to be doublet, since there is an odd number of electrons. The individual moments of inertia are I_A = 7.32 × 10⁻³⁹ g cm², I_B = 1.234 × 10⁻³⁸ g cm², and I_C = 1.965 × 10⁻³⁸ g cm². The enthalpy at 0°K is -3.010 kcal/mole.



Aluminum Oxide (alpha Al₂O₃)

(Crystal) Mol. Wt. = 101.960

ALUMINUM OXIDE (ALPHA Al₂O₃)

(CRYSTAL)

MOL. WT. = 101.960

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _f
0	+0.00	INFINITE	-	2.394	-397.494	-397.494	INFINITE
100	3.069	1.024	24.184	2.316	-398.697	-392.241	857.201
200	12.223	5.946	13.711	1.553	-399.838	-385.359	421.047
298	18.889	12.174	12.174	+0.00	-399.838	-378.078	277.125
300	18.979	12.201	12.174	+0.035	-400.406	-378.040	275.316
400	22.986	18.539	12.572	2.447	-400.555	-370.418	202.378
500	25.345	23.752	14.598	4.577	-400.475	-362.891	158.612
600	26.889	28.517	16.529	7.193	-400.304	-355.369	125.444
700	27.969	32.149	18.569	9.940	-400.098	-347.920	108.620
800	28.724	35.031	20.633	12.804	-399.767	-340.546	96.775
900	29.254	37.661	22.833	15.695	-399.407	-333.066	80.875
1000	29.614	40.078	24.634	18.644	-400.522	-325.301	71.091
1100	30.176	42.938	26.261	21.644	-404.181	-317.396	63.058
1200	30.994	45.234	28.012	24.774	-403.847	-309.250	56.369
1300	31.670	47.201	29.839	27.945	-403.460	-299.860	50.674
1400	31.290	55.539	31.597	30.859	-403.019	-293.868	45.673
1500	31.620	55.509	32.439	34.004	-402.581	-286.086	41.681
1600	31.920	57.559	34.321	37.161	-402.119	-278.334	38.017
1700	32.400	61.253	37.117	43.024	-401.633	-262.020	31.020
1800	32.760	63.116	38.439	46.886	-400.613	-255.254	26.359
2000	33.000	64.803	39.716	50.175	-400.075	-247.619	27.057
2100	33.220	66.419	40.949	53.486	-399.521	-240.011	24.877
2200	33.400	67.869	42.142	56.115	-398.956	-232.452	23.088
2300	33.770	70.889	44.718	63.553	-397.276	-217.330	14.306
2400	34.100	72.286	45.505	66.952	-397.172	-209.834	18.343
2600	34.310	73.627	46.561	70.372	-396.550	-202.354	17.009
2700	34.500	74.726	47.589	73.214	-395.915	-194.899	15.775
2800	34.670	75.686	48.586	75.960	-395.267	-187.467	14.611
2900	34.840	77.408	49.560	80.760	-395.307	-171.598	12.931
3000	35.140	78.596	50.508	84.264	-394.227	-150.072	11.588
3100	35.340	79.751	51.433	87.788	-393.132	-126.584	10.334
3200	35.720	80.876	52.335	91.332	-392.028	-104.153	9.161
3300	35.970	82.077	53.206	94.840	-390.907	-82.786	8.061
3400	35.906	83.042	54.078	98.476	-389.777	-61.398	7.028
3500	35.095	84.085	54.921	102.076	-388.634	-40.992	6.056

Dec. 31, 1960; Sept. 30, 1961; Mar. 31, 1964

$$\Delta H_f^0 = -397.5 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -400.4 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_m = 28.30 \pm 0.55 \text{ kcal. mole}^{-1}$$

$$T_m = 2315^\circ\text{K.}$$

$$S_{298.15}^0 = 12.174 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Heat of Formation.

The value of ΔH_f^0 derived from the direct combustion of pure aluminum in oxygen was taken from A. D. Mah, J. Phys. Chem. **61**, 1572 (1957). Other values for ΔH_f^0 obtained in the same way are: $-399.04 \pm .24$ kcal. mole⁻¹ reported by P. E. Snyder and H. Seitz, J. Am. Chem. Soc. **81**, 683 (1959); $-400.4 \pm .3$ kcal. mole⁻¹ reported by C. E. Holley, Jr., and E. J. Huber, Jr., J. Am. Chem. Soc. **72**, 5577 (1951); and -402 ± 2 kcal. mole⁻¹ reported by A. Schneider and O. Götow, Z. anorg. u. allgem. Chem. **277**, 41 (1954).

Heat Capacity and Entropy.

The heat capacity measurements reported by G. T. Furukawa, T. B. Douglas, R. E. McConkey, and D. C. Ginnings, (15° to 1200°K.), J. Research Natl. Bur. Standards **57**, 67 (1956), were employed in this table. Low temperature measurements were also made by P. Simon and R. C. Swain (30-280°K.), Z. Physik. Chem. **28B**, 189 (1935); E. C. Kerr, H. L. Johnston, and N. C. Hallett (20° to 295°K.), J. Am. Chem. Soc. **72**, 4740 (1950); J. W. Edwards and G. L. Kingdon (53-291°K.), Trans. Faraday Soc. **58**, 1313-22 (1962); E. N. Rodighina and K. Z. Gmel'akii, (100-900°K.), Zhur. Fiz. Khim. **32**, 1859-62 (1956); B. E. Walker, J. A. Grand, and R. R. Miller (300-900°K.), J. Phys. Chem. **60**, 231-3 (1956); R. Dawson, E. B. Brackett (700-1400°K.), J. Phys. Chem. **67**, 1689 (1963), and L. Terbasai (0-1300°K.), Helv. Chim. Acta. **47**, 804 (1934). All of the above low temperature data are in good agreement with Furukawa's work.

The heat capacities above 1200°K. (1200-2500°K.) were taken from the enthalpy measurements of P. B. Kantor, L. S. Lazareva, V. V. Kandyba, and E. M. Pomichov, Ukr. Fiz. Zh. **7**, 205-10 (1962). The heat capacity values above 2500°K. were extrapolated. High temperature measurements were also made by the following investigators: V. Ya. Chekhovskoi (500-2000°K.), Inzh. Fiz. Zh., Akad. Nauk. Belorussk SSR **5**, 62-5 (1962); A. Perrier and M. Olette (1100-2300°K.), Compt. Rend. **254**, 4293-95 (1962); C. H. Shomate and B. P. Naylor (500-1800°K.), J. Am. Chem. Soc. **81**, 72 (1945) and H. L. Johnston and M. Hoch (1000-2000°K.), J. Phys. Chem. **65**, 1184-5 (1961); and V. A. Kirillin, A. E. Sheidlin, and V. Ya. Chekhovskii (500-2000°K.), Doklady Akad. Nauk. SSSR **135**, 125-8 (1960). Numerical values were not available from Kirillin, et al., but graphical values were in close agreement with an extrapolation of Furukawa's data. The entropy at 298.15 was reported by T. Furukawa, et al., loc. cit., using $S_{15}^0 = 0.0105$ cal. deg.⁻¹ mole⁻¹.

Melting Data.

The melting data were obtained from the measurements of P. B. Kantor, L. S. Lazareva, V. V. Kandyba, and E. M. Pomichov, loc. cit. S. J. Schneider "Compilation of the Melting Points of the Metal Oxides," NBS Monograph **68**, p. 6, Oct. 10, 1963, gives a review of the melting points that range from 2287 to 2345°K.

Aluminum Oxide, Gamma (γ - Al_2O_3)
(Crystal) Mol. Wt. = 101.9612

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH_f°	ΔF_f°	Log K _p
0									
100	19.833	12.550	12.550		0.000	-396.000	-373.790	273.982	
200	19.928	12.673	12.550		0.037	-396.005	-373.652	272.193	
300	20.023	12.796	12.550		0.074	-396.010	-373.514	270.404	
400	20.118	12.919	12.550		0.111	-396.015	-373.376	268.615	
500	20.213	13.042	12.550		0.148	-396.020	-373.238	266.826	
600	20.308	13.165	12.550		0.185	-396.025	-373.100	265.037	
700	20.403	13.288	12.550		0.222	-396.030	-372.962	263.248	
800	20.498	13.411	12.550		0.259	-396.035	-372.824	261.459	
900	20.593	13.534	12.550		0.296	-396.040	-372.686	259.670	
1000	20.688	13.657	12.550		0.333	-396.045	-372.548	257.881	
1100	20.783	13.780	12.550		0.370	-396.050	-372.410	256.092	
1200	20.878	13.903	12.550		0.407	-396.055	-372.272	254.303	
1300	20.973	14.026	12.550		0.444	-396.060	-372.134	252.514	
1400	21.068	14.149	12.550		0.481	-396.065	-371.996	250.725	
1500	21.163	14.272	12.550		0.518	-396.070	-371.858	248.936	
1600	21.258	14.395	12.550		0.555	-396.075	-371.720	247.147	
1700	21.353	14.518	12.550		0.592	-396.080	-371.582	245.358	
1800	21.448	14.641	12.550		0.629	-396.085	-371.444	243.569	
1900	21.543	14.764	12.550		0.666	-396.090	-371.306	241.780	
2000	21.638	14.887	12.550		0.703	-396.095	-371.168	239.991	
2100	21.733	15.010	12.550		0.740	-396.100	-371.030	238.202	
2200	21.828	15.133	12.550		0.777	-396.105	-370.892	236.413	
2300	21.923	15.256	12.550		0.814	-396.110	-370.754	234.624	
2400	22.018	15.379	12.550		0.851	-396.115	-370.616	232.835	
2500	22.113	15.502	12.550		0.888	-396.120	-370.478	231.046	
2600	22.208	15.625	12.550		0.925	-396.125	-370.340	229.257	
2700	22.303	15.748	12.550		0.962	-396.130	-370.202	227.468	
2800	22.398	15.871	12.550		0.999	-396.135	-370.064	225.679	
2900	22.493	15.994	12.550		1.036	-396.140	-369.926	223.890	
3000	22.588	16.117	12.550		1.073	-396.145	-369.788	222.101	

Al_2O_3

MOL. WT. = 101.9612

(CRYSTAL)

ALUMINUM OXIDE, GAMMA (γ - Al_2O_3)

ΔH_f° 0 = Unknown

ΔH_f° 298.15 = [-396.0 $\pm$ 0.5] kcal. mole⁻¹

ΔH_m° = [20.9] kcal. mole⁻¹

$S_{298.15}^\circ$ = [12.55] cal. deg.⁻¹ mole⁻¹

T_m = 2323°K.

Heat of Formation.

The enthalpy change (ΔH_f°) for the transition $\text{Al}_2\text{O}_3(\delta, c) \rightarrow \text{Al}_2\text{O}_3(\alpha', c)$ has been determined by (1) V. Kostomarov and M. Rey, *Silicates Ind.* 29, 9 (1963); and (2) T. Yokokawa and O. J. Kleppa, *J. Phys. Chem.* 68, 3246 (1964). The results obtained are presented in the table. The enthalpies of solution for $\text{Al}_2\text{O}_3(\delta, c)$ and $\text{Al}(c)$ in 2N KOH(aq.) have been measured by (3) K. K. Kelley, C. H. Shonster, F. E. Young, B. F. Naylor, A. E. Salo and E. H. Huffman, U. S. Bur. Mines Tech. Rept. 688 (1946). Based on their reported values, -16.13 $\pm$ 1.0 and -196.02 $\pm$ 0.25 kcal. mole⁻¹, respectively, the heat of formation (ΔH_f° 298.15) for $\text{Al}_2\text{O}_3(\delta, c)$ was evaluated to be -384.84 $\pm$ 1.1 kcal. mole⁻¹. Hence, the enthalpy of transition ($\delta - \alpha'$) was calculated as -15.6 $\pm$ 1.1 kcal. mole⁻¹, using ΔH_f° 298.15 ($\text{Al}_2\text{O}_3, \alpha', c$) = -400.4 kcal. mole⁻¹.

Source	Method	Temperature, °K.	ΔH_f° , kcal. mole ⁻¹	ΔH_t° 298.15, kcal. mole ⁻¹
(2)	solution calorimetry	978	-5.3	-4.4
(1)	differential thermal analysis	1473	-11.0	-9.4
(3)	solution calorimetry	298.15	-15.6	-15.6

The heat of formation for $\text{Al}_2\text{O}_3(\delta, c)$ was calculated from that for $\text{Al}_2\text{O}_3(\alpha', c)$ and the ΔH_t° values reported by Yokokawa and Kleppa, loc. cit., which was arbitrarily selected.

Heat Capacity and Entropy.

The heat capacities were assumed to be larger than those for $\text{Al}_2\text{O}_3(\alpha', c)$ by 5% at each temperature. The value of $S_{298.15}^\circ$ was estimated such that at T_m , ΔH_m° ($\text{Al}_2\text{O}_3, \delta, c$) $>$ ΔH_f° ($\text{Al}_2\text{O}_3, \alpha', c$).

Melting Data.

T_m was reported by M. Plummer, *J. Appl. Chem.* 9, 35 (1959). The difference between ΔH_f° for $\text{Al}_2\text{O}_3(\delta, c)$ and $\text{Al}_2\text{O}_3(1)$ at T_m is ΔH_m° .

Al_2O_3

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0						
100	18.889	23.728	0.000	- 373.356	- 354.478	259.827
200	18.889	23.728	0.000	- 373.356	- 354.478	259.827
300	18.889	23.728	0.000	- 373.356	- 354.478	259.827
400	18.889	23.728	0.000	- 373.356	- 354.478	259.827
500	18.889	23.728	0.000	- 373.356	- 354.478	259.827
600	26.689	40.062	28.080	- 373.264	- 335.276	122.118
700	27.969	44.291	30.060	- 373.060	- 328.961	102.701
800	28.158	45.001	32.114	- 372.859	- 322.615	78.432
900	28.158	45.001	32.114	- 372.859	- 322.615	78.432
1000	28.158	45.001	32.114	- 372.859	- 322.615	78.432
1100	30.176	57.481	37.808	- 377.141	- 303.034	60.208
1200	30.176	57.481	37.808	- 377.141	- 303.034	60.208
1300	30.176	57.481	37.808	- 377.141	- 303.034	60.208
1400	30.176	57.481	37.808	- 377.141	- 303.034	60.208
1500	31.420	67.060	44.387	- 375.432	- 276.323	40.264
1600	34.623	69.110	45.869	- 375.070	- 269.766	36.847
1700	34.623	71.209	47.598	- 374.431	- 263.208	33.836
1800	34.623	73.188	48.682	- 373.602	- 250.213	28.185
1900	34.623	74.836	49.111	- 372.859	- 240.213	24.638
2000	34.623	76.836	51.318	- 372.170	- 243.780	24.638
2100	34.623	78.525	52.374	- 371.465	- 237.378	24.703
2200	34.623	80.136	53.790	- 370.771	- 231.009	22.948
2300	34.623	81.676	55.195	- 369.982	- 224.563	18.438
2400	34.623	83.162	56.582	- 369.093	- 218.053	18.540
2500	34.623	84.562	57.923	- 368.137	- 212.085	18.540
2600	34.623	85.920	59.301	- 368.069	- 205.833	17.301
2700	34.623	87.226	59.348	- 367.413	- 199.607	16.156
2800	34.623	88.406	60.366	- 367.413	- 190.966	14.827
2900	34.623	89.474	61.366	- 367.413	- 182.966	13.427
3000	34.623	90.874	62.321	- 367.413	- 167.469	12.200
3100	34.623	92.010	63.261	- 367.413	- 156.207	11.012
3200	34.623	93.109	64.177	- 367.413	- 144.983	9.801
3300	34.623	94.174	65.069	- 367.413	- 132.456	7.982
3400	34.623	95.201	65.908	- 367.413	- 122.456	6.962
3500	34.623	96.211	66.791	- 367.413	- 111.496	6.962

$S_{298.15}^{\circ} = [23.728] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{298.15}^{\circ} = [373.356] \text{ kcal. mole}^{-1}$
 $\Delta F_{298.15}^{\circ} = 28.30 \pm 0.55 \text{ kcal. mole}^{-1}$
 $T_m = 2315^{\circ}\text{K.}$

Heat of Formation.

The heat of formation for the liquid was obtained from $\Delta H_f^{\circ} 298.15$ for Δ crystal by adding on ΔH_m plus the difference between H_{2315}° and $H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacities of the liquid alpha-Al₂O₃ was taken from the crystal heat capacities up to 1600°K. where a glass transition was assumed. From 1600°K. to 3500°K. the heat capacities were assumed to be the constant value of 34.623 measured by P. B. Kantor, L. S. Lazareva, V. V. Kandyba and E. M. Pomichev (2300-2500°K.) Ukr. Fiz. Zh. 7, 205-10 (1962).

The entropy at 298.15°K. was obtained in a manner analogous to the heat of formation.

Melting Data.

The melting data was taken from the measurements of P. B. Kantor, et al., loc. cit. S. J. Schneider, "Compilation of the Melting Points of the Metal Oxides," NBS Monograph 68 p. 6, Oct. 10, 1963, gives a review of the melting points that range from 2267 to 2345°K.

Sillimanite (Al₂SiO₅)
(Crystal)



GFW = 162.046

T, °K	C _p ^a	S ^b	-(C _p ^a - H ₂₉₈ ³⁰⁰)/T	H ^c - H ₂₉₈ ³⁰⁰	kcal/mol ΔH ^f	ΔG ^f	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	7.714	3.609	42.687	4.164	-614.830	-614.830	INFINITE
200	20.500	13.048	25.407	3.908	-606.175	-606.175	1324.794
298	29.210	22.987	22.987	2.472	-595.168	-595.168	450.369
300	29.342	23.169	22.988	2.472	-595.168	-595.168	427.907
400	35.248	32.474	24.217	3.303	-583.543	-583.543	425.111
500	39.005	40.769	26.714	7.027	-571.736	-571.736	312.382
600	41.354	46.090	29.680	11.051	-559.912	-559.912	244.737
700	42.215	50.420	32.682	19.631	-548.125	-548.125	199.654
800	42.994	53.882	35.882	28.107	-536.384	-536.384	163.340
900	43.694	56.491	38.906	36.685	-524.691	-524.691	124.583
1000	44.326	59.144	41.829	45.423	-513.039	-513.039	109.505
1100	44.900	61.844	44.641	54.324	-501.435	-501.435	97.141
1200	45.428	64.584	47.393	63.374	-489.876	-489.876	86.148
1300	45.912	67.264	50.084	72.574	-478.358	-478.358	76.483
1400	46.352	69.894	52.724	81.924	-466.788	-466.788	70.429
1500	46.752	72.474	55.324	91.424	-455.168	-455.168	64.229
1600	47.124	75.004	57.884	101.074	-443.508	-443.508	58.586
1700	47.464	77.484	60.394	110.874	-431.808	-431.808	53.600
1800	47.774	79.914	62.854	120.824	-420.068	-420.068	49.079
1900	48.054	82.294	65.264	130.924	-408.288	-408.288	45.079
2000	48.304	84.624	67.624	141.174	-396.468	-396.468	41.466
2100	48.524	86.904	69.934	151.574	-384.608	-384.608	38.201
2200	48.714	89.134	72.194	162.124	-372.708	-372.708	35.238
2300	48.874	91.314	74.404	172.824	-360.768	-360.768	32.538
2400	49.004	93.444	76.564	183.674	-348.788	-348.788	30.067
2500	49.114	95.524	78.674	194.674	-336.768	-336.768	27.799
2600	49.204	97.554	80.734	205.824	-324.708	-324.708	25.709
2700	49.274	99.544	82.744	217.124	-312.608	-312.608	23.759
2800	49.324	101.484	84.704	228.574	-300.468	-300.468	21.924
2900	49.354	103.384	86.614	240.174	-288.288	-288.288	19.824
3000	49.374	105.244	88.474	251.924	-276.068	-276.068	17.930

SILLIMANITE (Al₂SiO₅)

(CRYSTAL)

GFW = 162.046

$$\Delta H_f^0 = -614.83 \pm 0.5 \text{ kcal/mol}$$

$$\Delta H_f^{298,15} = -618.81 \pm 0.5 \text{ kcal/mol}$$

$$S_{298,15} = 22.987 \pm 0.1 \text{ gibbs/mol}$$

Heat of Formation

The heat of the reaction $\text{Al}_2\text{O}_3(\text{c}) + \text{SiO}_2(\text{quartz}) \rightarrow \text{Al}_2\text{SiO}_5(\text{sillimanite})$ has been determined at 968°K by J. L. Holm and O. J. Kleppa, J. Phys. Chem. **70**, 1690 (1966) and Am. Mineralogist **51**, 1808 (1966), to be -1.51 ± 0.15 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta H_f^0 = -0.71$ kcal/mol, which is used to calculate the adopted value.

The above value is in serious disagreement with the solution data of F. Neumann, Z. Anorg. Allgem. Chem. **145**, 193 (1925); this work, however, has recently been questioned by several workers. H. Flood and W. J. Knapp, J. Am. Ceram. Soc. **40**, 206 (1957) suggested that ΔH_f^0 was between 0 and -10 kcal/mol. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964, conclude that ΔH_f^0 should lie between 0 and -6 kcal/mol. C. R. Waldhaug, Am. Mineralogist **50**, 186 (1965), calculated $\Delta H_f^0 = -0.356$ kcal/mol from high temperature - high pressure equilibria. These later values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.4° to 286.5°K by S. S. Todd, J. Am. Chem. Soc. **72**, 4742 (1950). The entropy is based on $S_{21}^0 = 0.73$ gibbs/mol. The high temperature enthalpy has been measured to 1500°K by L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964. The low and high temperature data were joined smoothly together by means of a Shomate function plot (C. H. Shomate, J. Phys. Chem. **58**, 368 (1954)). The crystal structure of sillimanite, L. Bragg and G. F. Claringbull, "Crystal Structure of Minerals," Vol. IV, G. Bell and Sons Ltd., London, 1965, indicates that there is no mixing of the tetra-coordinated aluminum and silicon atoms. Thus there should be no residual entropy at 0°K.



T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	7.000	INFINITE	4.085	- 615.461	- 615.461	INFINITE
100	20.271	3.282	3.66	- 615.461	- 615.461	1.471E
200	20.271	21.695	2.66	- 616.752	- 595.735	650.989
298	29.339	22.240	2.000	- 619.520	- 584.259	428.273
300	29.474	22.482	.054	- 619.529	- 584.041	425.473
400	35.747	31.654	3.334	- 619.732	- 572.161	312.607
500	39.524	40.286	7.111	- 619.589	- 560.247	244.791
600	41.710	47.675	11.178	- 619.295	- 548.454	199.774
700	43.276	54.227	15.430	- 618.943	- 536.673	167.557
800	44.484	60.086	35.312	- 618.562	- 524.947	143.409
900	45.495	65.363	28.320	- 618.253	- 513.261	125.527
1000	46.377	70.223	28.914	- 623.016	- 501.243	109.547
1100	47.175	74.683	33.592	- 622.589	- 489.089	97.173
1200	47.916	78.620	46.664	- 622.117	- 476.974	86.869
1300	48.617	82.683	49.472	- 621.604	- 464.898	78.156
1400	49.289	86.311	48.069	- 621.051	- 452.864	70.655
1500	49.940	89.734	54.360	- 620.460	- 440.872	64.235
1600	50.578	92.977	58.057	- 619.830	- 428.919	58.588
1700	51.195	96.062	56.917	- 631.152	- 416.002	53.586
1800	51.806	99.005	61.063	- 630.391	- 404.317	49.091
1900	52.410	101.823	63.135	- 629.565	- 391.782	45.065
2000	53.007	104.526	78.777	- 628.732	- 379.290	41.447
2100	53.599	107.127	84.108	- 627.832	- 366.840	38.178
2200	54.186	109.634	89.497	- 626.891	- 354.437	35.210
2300	54.768	112.055	94.845	- 625.899	- 342.069	32.504
2400	55.345	114.388	100.450	- 624.867	- 329.746	30.027
2500	55.917	116.669	106.013	- 623.792	- 317.482	27.754
2600	56.484	118.873	111.634	- 622.669	- 305.246	25.658
2700	57.046	121.016	117.310	- 621.506	- 293.064	23.722
2800	57.603	123.100	123.043	- 759.119	- 279.256	21.797
2900	58.155	125.131	40.707	- 757.345	- 262.150	19.656
3000	58.705	127.112	134.673	- 755.529	- 245.104	17.656

ΔHf° = -615.46 ± 0.5 kcal/mol

ΔHf°_{298.15} = -619.52 ± 0.5 kcal/mol

S°_{298.15} = 22.28 ± 0.1 gibbs/mol

Heat of Formation

The heat of the reaction Al₂O₃(c) + SiO₂(quartz) + Al₂SiO₅(andalusite) has been determined at 968°K by J. L. Holm and O. J. Kleppa, J. Phys. Chem. 70, 1690 (1966) and Am. Mineralogist 51, 1608 (1966), to be -1.99 ± 0.17 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to ΔHf°₂₉₈ = -1.42 kcal/mol, which is used to calculate the adopted value.

The above value is in serious disagreement with the solution data of F. Neumann, Z. Anorg. Allgem. Chem. 115, 193 (1925); this work, however, has recently been questioned by several workers. H. Flood and W. J. Knapp, J. Am. Ceram. Soc. 40, 206 (1957), suggested that ΔHf° was between 0 and -10 kcal/mol. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964, conclude that ΔHf° should lie between 0 and -6 kcal/mol. C. R. Waldbaum, Am. Mineralogist 50, 186 (1965), calculated ΔHf° = -1.108 kcal/mol from high temperature - high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.9° to 296.2°K by S. S. Todd, J. Am. Chem. Soc. 72, 4742 (1950). The entropy is based on S°₂₉₈ = 0.62 gibbs/mol. The high temperature enthalpy has been measured to 1600°K by L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964. The low and high temperature data were joined smoothly together by means of a Shomate function plot [C. H. Shomate, J. Phys. Chem. 58, 368 (1954)]. Since all the aluminum and silicon atoms occupy differently coordinated sites, there is no possibility of any residual entropy of mixing in this polymorph.

Kyanite (Al₂SiO₅)

(Crystal)

GF_W = 162.046

T, °K	C _p ^a	S ^b	-(C _p ^a - H ²⁹⁸)/T	H ²⁹⁸ - H ²⁹⁸	ΔH ^f	ΔG ^f	Log K _p
0	-	-	INFINITE	-	-	-	INFINITE
100	5.043	10.00	10.00	3.835	-615.750	-615.750	19.701
200	10.354	16.143	22.411	3.678	-607.037	-607.037	651.080
298	20.099	20.032	20.032	2.414	-619.245	-595.818	651.080
300	20.239	20.213	20.213	.000	-620.060	-584.159	626.178
400	29.439	29.439	29.439	3.054	-620.070	-593.907	475.376
500	35.555	35.498	35.498	7.007	-620.173	-599.607	312.439
600	42.120	42.120	42.120	11.158	-619.855	-587.619	199.470
700	43.795	43.795	43.795	15.437	-619.456	-585.609	167.225
800	45.000	45.000	45.000	19.899	-619.043	-583.663	143.058
900	45.845	45.845	45.845	24.536	-618.618	-581.751	124.752
1000	46.890	46.890	46.890	29.402	-618.188	-579.863	109.173
1100	47.744	47.744	47.744	33.825	-617.755	-577.999	96.793
1200	48.558	48.558	48.558	38.641	-617.320	-576.160	86.084
1300	49.259	49.259	49.259	43.532	-616.885	-574.346	77.769
1400	49.849	49.849	49.849	48.501	-616.449	-572.557	70.305
1500	50.338	50.338	50.338	53.534	-616.012	-570.791	63.944
1600	51.178	51.178	51.178	58.600	-615.575	-569.047	58.197
1700	51.799	51.799	51.799	63.749	-615.138	-567.322	53.206
1800	52.414	52.414	52.414	68.959	-614.699	-565.616	48.701
1900	53.028	53.028	53.028	74.231	-614.259	-563.929	44.676
2000	53.628	53.628	53.628	79.564	-613.818	-562.257	41.059
2100	54.220	54.220	54.220	84.956	-613.375	-560.600	37.791
2200	54.809	54.809	54.809	90.408	-612.930	-558.957	34.825
2300	55.396	55.396	55.396	95.918	-612.483	-557.327	32.121
2400	55.980	55.980	55.980	101.486	-612.035	-555.712	29.646
2500	56.562	56.562	56.562	107.114	-611.586	-554.113	27.376
2600	57.141	57.141	57.141	112.799	-611.139	-552.529	25.281
2700	57.718	57.718	57.718	118.535	-610.691	-550.952	23.347
2800	58.293	58.293	58.293	124.323	-610.242	-549.384	21.564
2900	58.866	58.866	58.866	130.164	-609.792	-547.825	19.921
3000	59.438	59.438	59.438	136.056	-609.341	-546.274	18.417

(CRYSTAL)

KYANITE (Al₂SiO₅)

GF_W = 162.046

Al₂O₅Si

ΔH_f⁰ = -615.75 ± 0.5 kcal/mol

ΔH_f⁰_{298.15} = -620.06 ± 0.5 kcal/mol

S⁰_{298.15} = 20.032 ± 0.1 gibbs/mol

Heat of Formation

The heat of the reaction Al₂O₃(g) + SiO₂(quartz) → Al₂SiO₅(kyanite) has been determined at 968° by J. L. Holm and O. J. Kleppa, J. Phys. Chem. 70, 1690 (1966) and Am. Mineralogist 51, 1608 (1966), to be -2.37 ± 0.15 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to ΔH_f⁰₂₉₈ = -1.95 kcal/mol, which is used to calculate the adopted value.

The above value is in serious disagreement with the solution data of F. Neumann, Z. Anorg. Allgem. Chem. 145, 183 (1925); this work, however, has recently been questioned by several workers. H. Flood and W. J. Knapp, J. Am. Ceram. Soc. 40, 206 (1957), suggested that ΔH_f⁰ was between 0 and -10 kcal/mol. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964, conclude that ΔH_f⁰ should lie between 0 and -6 kcal/mol. R. W. Haskell and R. C. DeVries, J. Am. Ceram. Soc. 47, 202 (1964), from phase equilibria obtained ΔH_f⁰ = -2 ± 7 kcal/mol. C. R. Waldbaum, Am. Mineralogist 50, 186 (1965), calculated ΔH_f⁰ = -0.622 kcal/mol from high temperature - high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.8° to 296.3° by S. S. Todd, J. Am. Chem. Soc. 72, 4742 (1950). The entropy is based on S_{298.15}⁰ = 0.33 gibbs/mol. The high temperature enthalpy has been measured to 1500°K by L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964. The low and high temperature data were joined smoothly together by means of a Shomate function plot [C. H. Shomate, J. Phys. Chem. 58, 368 (1954)]. The high temperature heat capacity has been measured between 100° and 1200°C by V. Ya. Leonidov, Yu. P. Barskii and N. I. Khitarov, Geochemistry (English Transl.) 1964, 409 (1964). The values reported are in excellent agreement with the adopted functions. Since the aluminum atoms and the silicon atoms occupy different types of sites there is no possibility of any residual entropy of mixing in this polymorph.

T, °K	C _p ^o	S ^o	gibbs/mol	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	kcal/mol	ΔH ^o	ΔG ^o	Log K _p
0	-0.00	-0.00	INFINITE	INFINITE	-11.011	-1619.252	-1619.252	-1619.252	INFINITE
100	20.379	14.508	117.851	10.334	-10.334	-1623.850	-1623.850	-1597.221	3490.722
200	54.005	39.385	72.126	6.554	-6.554	-1627.808	-1627.808	-1566.994	1714.516
298	77.830	65.700	65.700	0.000	0.000	-1629.830	-1629.830	-1539.639	1124.600
300	78.142	66.193	65.701	0.148	8.767	-1629.854	-1629.854	-1539.101	1121.234
400	93.390	90.882	68.966	16.425	16.425	-1630.461	-1630.461	-1508.724	824.328
500	103.250	112.840	75.590	20.290	20.290	-1630.228	-1630.228	-1478.303	646.165
600	109.900	132.283	83.481	20.290	20.290	-1629.552	-1629.552	-1442.980	527.424
700	114.100	145.136	90.932	52.177	52.177	-1627.700	-1627.700	-1417.783	442.652
800	118.100	155.136	97.933	64.119	64.119	-1626.845	-1626.845	-1387.783	379.110
900	120.650	179.196	107.933	76.288	76.288	-1624.297	-1624.297	-1357.783	329.715
1000	122.700	192.016	115.728	88.435	88.435	-1620.928	-1620.928	-1326.823	289.977
1100	124.212	203.782	123.295	101.627	101.627	-1616.092	-1616.092	-1295.030	257.379
1200	125.960	214.720	131.254	111.757	111.757	-1609.891	-1609.891	-1263.141	230.231
1300	127.960	224.720	137.254	119.751	119.751	-1602.635	-1602.635	-1230.941	207.276
1400	130.134	234.212	143.846	126.512	126.512	-1594.635	-1594.635	-1201.835	187.615
1500	132.470	243.092	150.169	133.384	133.384	-1585.329	-1585.329	-1170.827	170.589
1600	135.097	251.461	156.281	139.352	139.352	-1574.985	-1574.985	-1139.003	155.703
1700	137.973	259.237	162.107	144.401	144.401	-1563.597	-1563.597	-1108.452	142.552
1800	141.073	266.460	167.693	148.536	148.536	-1550.091	-1550.091	-1076.666	130.725
1900	144.351	273.024	173.103	151.751	151.751	-1534.548	-1534.548	-1044.578	120.154
2000	147.760	280.844	178.320	205.046	205.046	-1516.956	-1516.956	-1012.577	110.649
2100	151.240	288.844	183.359	216.419	216.419	-1498.220	-1498.220	-980.443	102.255
2200	154.812	296.957	188.167	226.395	226.395	-1478.361	-1478.361	-947.603	94.725
2300	158.496	305.229	192.624	235.003	235.003	-1457.361	-1457.361	-914.018	87.137
2400	162.304	313.618	201.940	242.695	242.695	-1435.167	-1435.167	-879.309	80.618
2500	166.240	322.142	206.240	249.482	249.482	-1411.896	-1411.896	-843.713	74.632
2600	170.312	330.812	210.438	255.312	255.312	-1387.561	-1387.561	-807.151	69.108
2700	174.520	339.612	214.438	260.240	260.240	-1362.167	-1362.167	-769.683	64.001
2800	178.860	348.536	218.240	264.240	264.240	-1335.667	-1335.667	-731.249	59.249
2900	183.336	357.584	221.840	267.312	267.312	-1308.061	-1308.061	-691.849	54.849
3000	187.952	366.856	225.144	269.491	269.491	-1279.349	-1279.349	-651.456	50.756

MULLITE (Al₆Si₂O₁₃)

GFW = 426.053

(CRYSTAL)

ΔH_f^o = -1619.25 ± 1.5 kcal/mol

ΔH_f^o 298.15 = -1629.83 ± 1.5 kcal/mol

S_{298.15} = 65.7 ± 3 gibbs/mol

T_m = 2023°K

Heat of Formation

The heat of the reaction 3Al₂O₃(s) + 2SiO₂(quartz) → Al₆Si₂O₁₃ has been determined at 968°K by J. L. Holm and G. J. Kleppa, J. Phys. Chem., 70, 1690 (1966) and Am. Mineralogist 51, 1608 (1966), to be +5.44 ± 0.35 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to ΔH_f^o 298 = +4.11 kcal/mol, which is used to calculate the adopted value.

Heat Capacity and Entropy

The low temperature heat capacity and high temperature enthalpy of mullite have been measured by L. B. Pankratz, W. W. Waller and K. K. Kelley, U. S. Bur. Mines RI 6287, 1963. The low temperature investigations extended from 53.5°K to 295.4°K; the Debye-Einstein equation 3D(182/T) + 15E(350/T) + 10E(502/T) + 15E(897/T) represented the data from 53.5° to 114.6°K within 1.4 percent and gave a smooth extrapolation to zero. From this equation the entropy at 51°K was found to be 2.17 gibbs/mol as opposed to the value 1.96 gibbs/mol found by Pankratz et al. However, since it is known that mullite has some of its Al atoms on Si sites, there will be configurational entropy remaining at 0°K. This is borne out by the free energy determinations of R. H. Rein and J. Chipman, Trans. Met. Soc. AIME 233, 415 (1965), and D. A. R. Kay and J. Taylor, Trans. Faraday Soc. 56, 1372 (1960), who obtain ΔG_f^o 1823 = -5.7 ± 0.1 kcal/mol for the formation from oxide. If the entropies and enthalpies reported by Pankratz et al. are used with the heat of formation, they yield ΔG_f^o 1823 = +2.9 kcal/mol. Holm and Kleppa, loc. cit., calculate that random mixing of tetra-coordinated aluminum and silicon atoms could produce 7 eu residual entropy. We have added 4.7 eu in order to match the measured ΔG_f^o 1823.

A review of the enthalpy determination indicated that the values might easily be 2 percent low if as little as 4 percent of kyanite remained unchanged in the sample used for measurement. Since X-ray could not detect this amount, it is not an unreasonable assumption. Accordingly we have checked the effect of increasing the heat capacity above 298°K by 2 percent; this then gives ΔG_f^o 1823 = -2.10 kcal/mol. In order to bring this within reasonable agreement with the observations a residual configurational entropy of 2 gibbs/mol would be needed. Thus the uncertainty in the residual entropy is of the order of 2 eu due to possible uncertainty in the high temperature heat capacity.

Melting Data

The congruent melting point of mullite was reported by S. Aramaki and R. Roy, Nature 184, 631 (1959).

Boron (B)

(Reference State) At. Wt. = 10.82

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	H ^o - H ₂₉₈ ^o	keal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	•000	INFINITE	•	•292	•000	•000	INFINITE	•000
100	•000	•000	•000	•286	•000	•000	•000	•000
200	1.447	•588	1.418	•206	•000	•000	•000	•000
298	2.650	1.403	1.403	•000	•000	•000	•000	•000
300	2.666	1.419	1.403	•005	•000	•000	•000	•000
400	3.760	2.459	1.471	•427	•000	•000	•000	•000
500	4.450	3.257	1.777	•740	•000	•000	•000	•000
600	4.990	4.122	2.097	1.215	•000	•000	•000	•000
700	5.320	4.917	2.444	1.731	•000	•000	•000	•000
800	5.560	5.664	2.769	2.276	•000	•000	•000	•000
900	5.760	6.410	3.153	2.852	•000	•000	•000	•000
1000	5.950	6.957	3.500	3.427	•000	•000	•000	•000
1100	6.120	7.502	3.838	4.031	•000	•000	•000	•000
1200	6.260	8.041	4.166	4.650	•000	•000	•000	•000
1300	6.410	8.548	4.483	5.284	•000	•000	•000	•000
1400	6.540	9.028	4.791	5.931	•000	•000	•000	•000
1500	6.670	9.493	5.089	6.592	•000	•000	•000	•000
1600	6.790	9.918	5.377	7.265	•000	•000	•000	•000
1700	6.900	10.333	5.657	7.950	•000	•000	•000	•000
1800	7.000	10.730	5.927	8.645	•000	•000	•000	•000
1900	7.092	11.110	6.190	9.348	•000	•000	•000	•000
2000	7.170	11.474	6.445	10.057	•000	•000	•000	•000
2100	7.177	11.823	6.693	10.772	•000	•000	•000	•000
2200	7.228	12.158	6.934	11.492	•000	•000	•000	•000
2300	7.274	12.480	7.168	12.217	•000	•000	•000	•000
2400	7.315	12.791	7.395	12.947	•000	•000	•000	•000
2500	7.350	13.098	7.602	13.682	•000	•000	•000	•000
2600	7.300	13.575	7.961	19.798	•000	•000	•000	•000
2700	7.300	15.851	8.248	20.528	•000	•000	•000	•000
2800	7.300	16.116	8.524	21.258	•000	•000	•000	•000
2900	7.300	16.381	8.799	21.988	•000	•000	•000	•000
3000	7.300	16.650	9.077	22.718	•000	•000	•000	•000
3100	7.300	16.850	9.296	23.448	•000	•000	•000	•000
3200	7.300	17.091	9.536	24.178	•000	•000	•000	•000
3300	7.300	17.316	9.768	24.908	•000	•000	•000	•000
3400	7.300	17.536	9.993	25.638	•000	•000	•000	•000
3500	7.300	17.745	10.212	26.368	•000	•000	•000	•000
3600	7.300	17.951	10.424	27.098	•000	•000	•000	•000
3700	7.300	18.151	10.630	27.828	•000	•000	•000	•000
3800	7.300	18.346	10.830	28.558	•000	•000	•000	•000
3900	7.300	18.535	11.026	29.288	•000	•000	•000	•000
4000	4.252	43.551	11.752	151.157	•000	•000	•000	•000
4100	4.985	49.674	12.675	151.596	•000	•000	•000	•000
4200	4.988	49.795	13.558	152.194	•000	•000	•000	•000
4300	4.993	49.912	14.402	152.693	•000	•000	•000	•000
4400	4.997	50.027	15.200	153.193	•000	•000	•000	•000
4500	5.002	50.139	15.995	153.693	•000	•000	•000	•000
4600	5.008	50.249	16.729	154.193	•000	•000	•000	•000
4700	5.015	50.357	17.443	154.694	•000	•000	•000	•000
4800	5.022	50.463	18.130	155.196	•000	•000	•000	•000
4900	5.029	50.568	18.812	155.697	•000	•000	•000	•000
5000	5.039	50.668	19.427	156.202	•000	•000	•000	•000
5100	5.048	50.768	20.041	156.707	•000	•000	•000	•000
5200	5.058	50.866	20.633	157.212	•000	•000	•000	•000
5300	5.069	50.962	21.204	157.718	•000	•000	•000	•000
5400	5.079	51.057	21.776	158.226	•000	•000	•000	•000
5500	5.093	51.151	22.290	158.734	•000	•000	•000	•000
5600	5.107	51.242	22.806	159.244	•000	•000	•000	•000
5700	5.121	51.333	23.306	159.756	•000	•000	•000	•000
5800	5.135	51.424	23.806	160.268	•000	•000	•000	•000
5900	5.152	51.510	24.290	160.783	•000	•000	•000	•000
6000	5.168	51.597	24.714	161.299	•000	•000	•000	•000

Dec. 31, 1960; Dec. 31, 1984

B

(REFERENCE STATE)

BORON (B)

AT. WT. = 10.82

0 to 2450°K. Crystal
2450 to 3931°K. Liquid
3931 to 6000°K. Ideal Monatomic Gas

See crystal, liquid and ideal monatomic gas for details.

B

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	-	.292	.000	INFINITE	
100	1.256	2.941	-	.266	.000	.000	
200	2.406	5.016	-	.260	.000	.000	
298	2.650	14.403	-	.000	.000	.000	
300	2.667	14.419	1.403	.005	.000	.000	
400	3.720	2.339	1.521	.327	.000	.000	
500	4.460	3.257	1.777	.740	.000	.000	
600	4.900	4.122	2.007	1.215	.000	.000	
700	5.320	4.917	2.444	1.731	.000	.000	
800	5.560	5.644	2.799	2.276	.000	.000	
900	5.760	6.310	3.153	2.842	.000	.000	
1000	5.950	6.927	3.500	3.427	.000	.000	
1100	6.120	7.502	3.838	4.031	.000	.000	
1200	6.260	8.041	4.166	4.650	.000	.000	
1300	6.410	8.548	4.483	5.284	.000	.000	
1400	6.540	9.028	4.791	5.931	.000	.000	
1500	6.670	9.483	5.089	6.592	.000	.000	
1600	6.790	9.918	5.377	7.265	.000	.000	
1700	6.900	10.333	5.657	7.940	.000	.000	
1800	7.000	10.730	5.927	8.645	.000	.000	
1900	7.082	11.110	6.190	9.368	.000	.000	
2000	7.120	11.474	6.443	10.097	.000	.000	
2100	7.176	11.823	6.693	10.772	.000	.000	
2200	7.228	12.158	6.934	11.492	.000	.000	
2300	7.274	12.480	7.168	12.217	.000	.000	
2400	7.314	12.791	7.396	12.947	.000	.000	
2500	7.350	13.090	7.618	13.680	.000	.010	
2600	7.374	13.379	7.834	14.416	.000	.028	
2700	7.396	13.657	8.044	15.155	.000	.045	
2800	7.416	13.927	8.250	15.895	.000	.067	
2900	7.434	14.187	8.450	16.639	.000	.089	
3000	7.450	14.440	8.646	17.382	.000	.109	
3100	7.464	14.684	8.836	18.128	.000	.128	
3200	7.476	14.921	9.023	18.875	.000	.142	
3300	7.486	15.151	9.205	19.623	.000	.151	
3400	7.494	15.375	9.383	20.372	.000	.159	
3500	7.500	15.592	9.558	21.122	.000	.165	

Dec. 31, 1960; Dec. 31, 1964

$S_{298.15}^{\circ} = 1.403 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 2450 \pm 20^{\circ} \text{K.}$
 $\Delta H_f^{\circ} = 0 \text{ kcal. mole}^{-1}$
 $\Delta H_g^{\circ} = [5.39] \text{ kcal. mole}^{-1}$
 $\Delta H_g^{\circ} 298.15 = 132.8 \pm 4.0 \text{ kcal. mole}^{-1}$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Low temperature heat capacities, 16.90 - 303.71°K., were measured by H. L. Johnston, H. N. Hersh and E. C. Kerr, J. Am. Chem. Soc. 73, 1112 (1951). The high temperature heat capacities, 282.8 - 1667.8°K., were measured by R. A. McDonald and D. R. Stull, J. Chem. Eng. Data, 7, 84 (1962). These two sets of data were joined smoothly at 298.15°K. by graphical method. The heat capacity values above 1667.8°K. were estimated by graphical extrapolation. The high temperature Cp, 530 - 800°K., were also determined by S. S. Wise, J. L. Margrave and R. L. Altman, J. Phys. Chem. 64, 915 (1960). The other principal investigators are: (1) J. A. Robertson, Ph. D. Thesis, Cornell University, 1944; (2) A. Magnus and H. Danz, Ann. Phys. [4] 81, 407 (1926); (3) H. Molau and H. Gautier, Compt. rend. 116, 924 (1893); (4) H. P. Weber, Ann. Phys. [2] 154, 367, 553 (1875); (5) H. Kopp, Trans. Roy. Soc. [London] 155, 71 (1865); and (6) V. Regnault, Ann. chim. et phys. [3] 63, 5 (1861) and Phil. Mag. [4] 23, 103 (1862). The value of S_{298.15} was obtained from H. L. Johnston, H. N. Hersh and E. C. Kerr, loc. cit., based on S₁₇ = 0.00139 cal. deg.⁻¹ mole⁻¹.

Melting Data.

The melting point (T_m) has been measured by many investigators. The values of T_m reported are in the range 2273 - 2673°K. Based on the relationship between the values of T_m determined and the purities of the boron sample used, the value T_m = 2450 ± 20°K. was estimated. The data employed for estimation are those reported by C. F. Glue, J. Electrochem. Soc. 106 (4), 332 (1959), and A. W. Seary and C. E. Myers, J. Phys. Chem. 61, 957 (1957). The estimated value for T_m is in agreement with the value taken by H. L. Schick, et al., "Thermodynamics of Certain Refractory Compounds", ASD-TR-61-260, Part I, Vol. 1, May 1962, in which the reported melting points of boron were reviewed. The heat of melting was calculated assuming entropy of melting is 2.2 cal. deg.⁻¹ mole⁻¹ at 2450°K.

Heat of Sublimation.

The adopted value of ΔH_g^o 298.15 is the weighted average of eight ΔH_g^o 298.15 values derived from vapor pressure data. See B(g) table for details.

Boron (B)

(Liquid) At. Wt. = 10.82

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0							
100							
200							
298	2.650	3.533	3.533	0.000	5.260	4.625	- 3.390
300	2.666	3.549	3.533	0.005	5.260	4.621	- 3.366
400	3.720	4.469	3.577	0.327	5.260	4.408	- 2.408
500	4.490	5.367	3.507	0.740	5.260	4.195	- 1.833
600	4.990	6.252	4.227	1.215	5.260	3.982	- 1.450
700	5.320	7.047	4.574	1.731	5.260	3.769	- 1.177
800	5.560	7.774	4.929	2.276	5.260	3.556	- 0.971
900	5.760	8.440	5.283	2.842	5.260	3.343	- 0.812
1000	5.930	9.057	5.630	3.427	5.260	3.130	- 0.684
1100	6.120	9.632	5.968	4.031	5.240	2.917	- 0.580
1200	6.260	10.171	6.296	4.650	5.260	2.704	- 0.492
1300	6.410	10.678	6.613	5.284	5.260	2.491	- 0.419
1400	6.540	11.158	6.921	5.931	5.260	2.278	- 0.356
1500	6.670	11.613	7.219	6.592	5.260	2.065	- 0.301
1600	6.790	12.046	7.507	7.262	5.257	1.852	- 0.253
1700	7.300	12.474	7.787	7.968	5.278	1.639	- 0.211
1800	7.300	12.891	8.059	8.698	5.313	1.423	- 0.173
1900	7.300	13.286	8.324	9.428	5.340	1.208	- 0.136
2000	7.300	13.660	8.581	10.158	5.361	0.989	- 0.108
2100	7.300	14.016	8.832	10.888	5.376	0.771	- 0.080
2200	7.300	14.356	9.075	11.618	5.386	0.551	- 0.055
2300	7.300	14.681	9.312	12.348	5.391	0.329	- 0.031
2400	7.300	14.993	9.542	13.078	5.391	0.111	- 0.010
2500	7.300	15.289	9.766	13.808	5.391	0.000	0.000
2600	7.300	15.576	9.984	14.538	0.000	0.000	0.000
2700	7.300	15.851	10.196	15.268	0.000	0.000	0.000
2800	7.300	16.116	10.403	15.998	0.000	0.000	0.000
2900	7.300	16.373	10.604	16.728	0.000	0.000	0.000
3000	7.300	16.620	10.801	17.458	0.000	0.000	0.000
3100	7.300	16.860	10.992	18.188	0.000	0.000	0.000
3200	7.300	17.091	11.179	18.918	0.000	0.000	0.000
3300	7.300	17.316	11.362	19.648	0.000	0.000	0.000
3400	7.300	17.534	11.540	20.378	0.000	0.000	0.000
3500	7.300	17.745	11.715	21.108	0.000	0.000	0.000
3600	7.300	17.951	11.885	21.838	0.000	0.000	0.000
3700	7.300	18.151	12.052	22.568	0.000	0.000	0.000
3800	7.300	18.346	12.215	23.298	0.000	0.000	0.000
3900	7.300	18.535	12.375	24.028	0.000	0.000	0.000
4000	7.300	18.720	12.531	24.758	0.000	0.000	0.000
4100	7.300	18.900	12.684	25.488	- 121.119	2.145	- 0.117
4200	7.300	19.076	12.834	26.218	- 120.948	5.226	- 0.279
4300	7.300	19.248	12.981	26.948	- 120.716	8.304	- 0.432
4400	7.300	19.416	13.125	27.678	- 120.485	11.370	- 0.578
4500	7.300	19.580	13.267	28.408	- 120.255	14.434	- 0.717
4600	7.300	19.740	13.406	29.138	- 120.025	17.491	- 0.849
4700	7.300	19.897	13.543	29.868	- 119.795	20.547	- 0.976
4800	7.300	20.051	13.677	30.598	- 119.566	23.596	- 1.097
4900	7.300	20.201	13.811	31.328	- 119.338	26.640	- 1.213
5000	7.300	20.349	13.938	32.058	- 119.111	29.678	- 1.323
5100	7.300	20.494	14.065	32.788	- 118.884	32.711	- 1.430

BORON (B) (LIQUID) AT. WT. = 10.82

$$\Delta H_f^o 298.15 = [5.260] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^o = [5.39] \text{ kcal. mole}^{-1}$$

$$\Delta H_v^o = [121.3 \pm 4] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = [3.533] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = [2450 \pm 20]^{\circ}\text{K.}$$

$$T_b = [5931]^{\circ}\text{K.}$$

Heat of Formation.

$\Delta H_f^o 298.15$ for B(l) was obtained from $\Delta H_f^o 298.15$ for B(c) by adding ΔH_m^o and the difference between H_m^o - $H_{298.15}^o$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of liquid was estimated by comparison with the heat capacity of solid at the melting temperature. The value of $S_{298.15}^o$ was obtained in a manner analogous to that of the heat of formation. A glass transition temperature at 1800°K. is assumed.

Melting Data.

See B(c) table for details.

Vaporization Data.

The boiling point was calculated as the temperature at which the free energies of formation (ΔF_f^o) for both B(l) and B(g) are equal. The difference in heat of formation (ΔH_f^o) of B(l) and B(g) at the boiling point is the heat of vaporization (ΔH_v^o).

Ground State Configuration $2p_{1/2}^2$
 $S_{298.15}^\circ = 36.649 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ 298.15 = 131.6 \pm 4 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = 132.8 \pm 4 \text{ kcal. mole}^{-1}$

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f kcal. mole ⁻¹	ΔF _f	Log K _p
0	∞	INFINITE	-1.511	131.581	131.581	INFINITE
100	4.933	31.411	-1.501	131.581	131.581	13.994
200	4.971	31.466	-1.498	132.518	132.518	13.994
298	4.971	36.649	-1.498	132.600	122.793	13.994
300	4.971	36.680	-1.498	132.604	122.793	13.994
400	4.970	38.110	-1.506	132.604	118.671	13.994
500	4.969	39.219	-1.505	132.604	115.083	13.994
600	4.969	40.125	-1.500	132.604	111.484	13.994
700	4.969	40.891	-1.497	132.604	107.885	13.994
800	4.969	41.554	-1.494	132.604	104.286	13.994
900	4.968	42.139	-1.491	132.604	100.687	13.994
1000	4.968	42.663	-1.487	132.604	97.088	13.994
1100	4.968	43.136	-1.484	132.753	93.489	13.994
1200	4.968	43.569	-1.481	132.631	89.890	13.994
1300	4.968	43.966	-1.478	132.631	86.291	13.994
1400	4.968	44.335	-1.475	132.344	82.692	13.994
1500	4.968	44.677	-1.472	132.180	79.093	13.994
1600	4.968	44.998	-1.468	132.003	75.494	13.994
1700	4.968	45.299	-1.465	131.815	71.895	13.994
1800	4.968	45.583	-1.462	131.617	68.296	13.994
1900	4.968	45.852	-1.459	131.411	64.697	13.994
2000	4.968	46.107	-1.456	131.199	61.098	13.994
2100	4.968	46.349	-1.453	130.981	57.499	13.994
2200	4.968	46.580	-1.450	130.757	53.900	13.994
2300	4.968	46.801	-1.447	130.529	50.301	13.994
2400	4.968	47.012	-1.443	130.296	46.702	13.994
2500	4.968	47.215	-1.440	129.062	43.103	13.994
2600	4.968	47.410	-1.437	128.839	39.504	13.994
2700	4.968	47.598	-1.434	128.615	35.905	13.994
2800	4.969	47.778	-1.431	128.392	32.306	13.994
2900	4.969	47.953	-1.428	128.169	28.707	13.994
3000	4.969	48.121	-1.425	127.946	25.108	13.994
3100	4.969	48.284	-1.422	127.723	21.509	13.994
3200	4.970	48.442	-1.418	127.500	17.910	13.994
3300	4.970	48.595	-1.415	127.277	14.311	13.994
3400	4.971	48.743	-1.412	127.054	10.712	13.994
3500	4.972	48.887	-1.409	126.831	7.113	13.994
3600	4.973	49.027	-1.406	126.608	3.514	13.994
3700	4.973	49.164	-1.403	126.385	-0.085	13.994
3800	4.977	49.296	-1.401	126.162	-3.686	13.994
3900	4.977	49.423	-1.398	125.939	-7.287	13.994
4000	4.982	49.552	-1.395	125.716	-10.888	13.994
4100	4.985	49.675	-1.396	125.493	-14.489	13.994
4200	4.988	49.795	-1.394	125.270	-18.090	13.994
4300	4.993	49.912	-1.393	125.047	-21.691	13.994
4400	4.997	50.027	-1.392	124.824	-25.292	13.994
4500	5.002	50.140	-1.390	124.601	-28.893	13.994
4600	5.008	50.250	-1.389	124.378	-32.494	13.994
4700	5.015	50.357	-1.388	124.155	-36.095	13.994
4800	5.022	50.463	-1.387	123.932	-39.696	13.994
4900	5.030	50.567	-1.386	123.709	-43.297	13.994
5000	5.039	50.668	-1.385	123.486	-46.898	13.994
5100	5.048	50.768	-1.384	123.263	-50.499	13.994
5200	5.058	50.866	-1.383	123.040	-54.100	13.994
5300	5.069	50.963	-1.382	122.817	-57.701	13.994
5400	5.081	51.058	-1.381	122.594	-61.302	13.994
5500	5.093	51.151	-1.380	122.371	-64.903	13.994
5600	5.107	51.243	-1.379	122.148	-68.504	13.994
5700	5.121	51.333	-1.378	121.925	-72.105	13.994
5800	5.136	51.423	-1.377	121.702	-75.706	13.994
5900	5.152	51.512	-1.376	121.479	-79.307	13.994
6000	5.168	51.597	-1.375	121.256	-82.908	13.994

Dec. 31, 1960; Dec. 31, 1964

Heat of Formation.

The vapor pressures of B(g) over condensed phases B(c) and B₂(c), respectively, were determined by many investigators. Using the vapor pressure data reported, the corresponding heats of sublimation and decomposition were evaluated by both the third and second law methods. The values of ΔH_f° 298.15 for B(g) were then calculated. The results obtained are listed as follows (all calculations were made employing JANAF Functions).

Investigator	Process or Reaction	ΔH _f ° 298.15 ^a kcal. mole ⁻¹	Second Law Value	ΔH _f ° 298.15 ^a kcal. mole ⁻¹
Hildenbrand and Hall ¹	0.25CB ₄ (c) → 0.25C(c) + B(g)	138.5	137.6 ± 1.2	135.3 ± 1.3
Hildenbrand ²	B(c) → B(g)	136.1	136.3 ± 3	136.1 ± 0.3
Paule and Margrave ³	B(c) → B(g)	136.4	135.4 ± 1.6	136.4 ± 1.0
Robson and Gilles ⁴	0.25CB ₄ (c) → 0.25C(c) + B(g)	137.7	142 ± 4	134.5 ± 1.3
Searcy and Myers ⁵	B(c) → B(g)	139.1	148.4 ± 8.4	139.1 ± 2.5
Schissel and Williams ⁶	B(c) → B(g)	129.2	129 ± 5	129 ± 5
Chupka ⁷	B(c) → B(g)	131.7	131.7	129.2
Akshin et al. ⁸	B(am.) → B(g)	131.7	131.7	131.7 ± 5
Linevsky, et al. ¹⁰	0.25CB ₄ (c) → 0.25C(c) + B(g)	—	129.1 ± 5	130.3 ± 5**
Schissel and Trulsson ¹¹	B(c) → B(g)	—	134.4 ± 5	131.2 ± 5
	B(c) → B(g)	—	131.4	131.4
	B(c) → B(g)	—	132.8 ± 1.4	132.8 ± 1.4

^aCalculation based on the third law values available.

^bBased on a heat of transition of 1.2 kcal. mole⁻¹ for B(c) to B(am.).

- 1 D. L. Hildenbrand and W. F. Hall, J. Phys. Chem. **69**, 989 (1964) - torsion-effusion.
- 2 D. L. Hildenbrand, "Thermodynamic Properties of Propellant Combustion Products", QLR-64-10, Philco Corporation, California, 1960-2140°K., torsion-Langmuir method. Listed ΔH_f° 298.15 value is the average of three reported values.
- 3 R. O. Paule and J. L. Margrave, J. Phys. Chem. **67**, 1368 (1963) - 1761-2152°K. - free-evaporation.
- 4 H. E. Robson and P. W. Gilles, J. Phys. Chem. **69**, 983 (1964) - 2164-2522°K. - Knudsen-effusion.
- 5 A. W. Searcy and C. E. Myers, J. Phys. Chem. **61**, 957 (1957) - 2115-2413°K. - Knudsen-effusion.
- 6 P. O. Schissel and W. S. Williams, Bull. Am. Phys. Soc. **4**, 139 (1959). The quoted value of ΔH_f° was derived from vapor pressure data determined by the mass spectrometer-effusion method.
- 7 The third and second law values of ΔH_f° 298.15 were calculated from the respective values of ΔH_f° 0 quoted by O. Verhaegen and J. Drowart, J. Chem. Phys. **37**, 1367 (1962). Vapor pressure data obtained by mass spectrometer-effusion method.
- 8 P. A. Akshin, D. O. Hikitin and L. N. Gorbokhov, Proc. Acad. Sci., USSR, **129**, 1075 (1959). The vapor pressure data (2024 - 2231°K.) were determined by the mass spectrometric method.
- 9 The second law values were recalculated from ΔH_f° 2080 = 127.4 and ΔH_f° 2080 = 133.1 kcal. mole⁻¹ for the first and second reactions in the above table, respectively. The data were reported by O. Verhaegen and J. Drowart, J. Phys. Chem. **51**, 1381 (1952), which were derived from vapor pressures determined by the mass spectrometric method.
- 10 M. J. Linevsky, O. M. Kibler, T. P. Lyon and V. J. Desantis, "Refractory Materials Research", WADD-TR-60-646, Part IV, August 1964, General Electric Co., Ohio.
- 11 P. O. Schissel and O. C. Trulsson, J. Phys. Chem. **66**, 1492 (1962).

The adopted value of ΔH_f° 298.15 for B(g) is the weighted average of the 12 ΔH_f° 298.15 values given in the above table.

Heat Capacity and Entropy.

The electronic levels and quantum weights used were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, National Bureau of Standards Circular 467, 1949.

Boron Unipositive Ion (B⁺)

(Ideal Gas)

GF_W = 10.81045

B⁺

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG_f°	Log Kp
0							
100	4.968	33.086	33.086	+0.00	324.084	313.151	-229.54
200	4.968	33.117	33.086	-0.09	324.097	313.042	-228.040
300	4.968	33.147	33.086	-0.09	324.109	312.930	-226.997
400	4.968	33.177	33.086	-0.09	324.121	312.817	-225.978
500	4.968	33.207	33.086	-0.09	324.133	312.704	-224.978
600	4.968	33.237	33.086	-0.09	324.145	312.591	-223.997
700	4.968	33.267	33.086	-0.09	324.157	312.478	-223.026
800	4.968	33.297	33.086	-0.09	324.169	312.365	-222.065
900	4.968	33.327	33.086	-0.09	324.181	312.252	-221.114
1000	4.968	33.357	33.086	-0.09	324.193	312.139	-220.173
1100	4.968	33.387	33.086	-0.09	324.205	312.026	-219.242
1200	4.968	33.417	33.086	-0.09	324.217	311.913	-218.321
1300	4.968	33.447	33.086	-0.09	324.229	311.800	-217.400
1400	4.968	33.477	33.086	-0.09	324.241	311.687	-216.479
1500	4.968	33.507	33.086	-0.09	324.253	311.574	-215.558
1600	4.968	33.537	33.086	-0.09	324.265	311.461	-214.637
1700	4.968	33.567	33.086	-0.09	324.277	311.348	-213.716
1800	4.968	33.597	33.086	-0.09	324.289	311.235	-212.795
1900	4.968	33.627	33.086	-0.09	324.301	311.122	-211.874
2000	4.968	33.657	33.086	-0.09	324.313	311.009	-210.953
2100	4.968	33.687	33.086	-0.09	324.325	310.896	-210.032
2200	4.968	33.717	33.086	-0.09	324.337	310.783	-209.111
2300	4.968	33.747	33.086	-0.09	324.349	310.670	-208.190
2400	4.968	33.777	33.086	-0.09	324.361	310.557	-207.269
2500	4.968	33.807	33.086	-0.09	324.373	310.444	-206.348
2600	4.968	33.837	33.086	-0.09	324.385	310.331	-205.427
2700	4.968	33.867	33.086	-0.09	324.397	310.218	-204.506
2800	4.968	33.897	33.086	-0.09	324.409	310.105	-203.585
2900	4.968	33.927	33.086	-0.09	324.421	310.000	-202.664
3000	4.968	33.957	33.086	-0.09	324.433	309.887	-201.743
3100	4.968	33.987	33.086	-0.09	324.445	309.774	-200.822
3200	4.968	34.017	33.086	-0.09	324.457	309.661	-199.901
3300	4.968	34.047	33.086	-0.09	324.469	309.548	-198.980
3400	4.968	34.077	33.086	-0.09	324.481	309.435	-198.059
3500	4.968	34.107	33.086	-0.09	324.493	309.322	-197.138
3600	4.968	34.137	33.086	-0.09	324.505	309.209	-196.217
3700	4.968	34.167	33.086	-0.09	324.517	309.096	-195.296
3800	4.968	34.197	33.086	-0.09	324.529	308.983	-194.375
3900	4.968	34.227	33.086	-0.09	324.541	308.870	-193.454
4000	4.968	34.257	33.086	-0.09	324.553	308.757	-192.533
4100	4.968	34.287	33.086	-0.09	324.565	308.644	-191.612
4200	4.968	34.317	33.086	-0.09	324.577	308.531	-190.691
4300	4.968	34.347	33.086	-0.09	324.589	308.418	-189.770
4400	4.968	34.377	33.086	-0.09	324.601	308.305	-188.849
4500	4.968	34.407	33.086	-0.09	324.613	308.192	-187.928
4600	4.968	34.437	33.086	-0.09	324.625	308.079	-187.007
4700	4.968	34.467	33.086	-0.09	324.637	307.966	-186.086
4800	4.968	34.497	33.086	-0.09	324.649	307.853	-185.165
4900	4.968	34.527	33.086	-0.09	324.661	307.740	-184.244
5000	4.968	34.557	33.086	-0.09	324.673	307.627	-183.323
5100	4.968	34.587	33.086	-0.09	324.685	307.514	-182.402
5200	4.968	34.617	33.086	-0.09	324.697	307.401	-181.481
5300	4.968	34.647	33.086	-0.09	324.709	307.288	-180.560
5400	4.968	34.677	33.086	-0.09	324.721	307.175	-179.639
5500	4.968	34.707	33.086	-0.09	324.733	307.062	-178.718
5600	4.968	34.737	33.086	-0.09	324.745	306.949	-177.797
5700	4.968	34.767	33.086	-0.09	324.757	306.836	-176.876
5800	4.968	34.797	33.086	-0.09	324.769	306.723	-175.955
5900	4.968	34.827	33.086	-0.09	324.781	306.610	-175.034
6000	4.968	34.857	33.086	-0.09	324.793	306.497	-174.113

BORON UNIPOSITIVE ION (B⁺)

(IDEAL GAS)

GF_W = 10.81045

Ground State Configuration 1S₀

$\Delta H_f^\circ = 322.9 \pm 4.0$ kcal/mol

$\Delta H_f^\circ = 324.1 \pm 4.0$ kcal/mol

$S_{298.15}^\circ = 33.086$ gibbs/mol

Electronic Levels and Quantum Weights

E_i, cm^{-1}	g_i	E_i, cm^{-1}	g_i
0.0	1	144019.32	12
37348.4	9	151658.48	20
73386.7	3	166741.85	4
100152.89	14	174212.71	57
129245.18	4	181473.27	12
135946.0	1		

We calculate the heat of formation at 0°K from the reaction B(g) + e⁻(g) + B⁺(g) using the JANAF auxiliary value for B(g) and an ionization potential of 191.34 kcal/mol from C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, Vol. I, 1949.

Heat Capacity and Entropy

We obtain the electronic levels and quantum weights from C. E. Moore, loc. cit. $H_0^\circ - H_{298}^\circ = -1.481$ kcal/mol at 0°K.

Boron Monobromide (BBR)

(Ideal Gas) Mol. Wt. = 90.736

BBR

MOL. WT. = 90.736

(IDEAL GAS)

BORON MONOBROMIDE (BBR)

T, °K.	C _p ^o	S ^o - (R°-H ₂₉₈)/T	h ^o - H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞.000	INFINITE	2.150	57.071	57.071	INFINITE
100	6.968	45.817	57.426	53.496	-116.910	-
200	7.323	50.728	54.451	49.533	-54.125	-
298	7.837	53.750	51.745	45.817	-33.583	-
300	7.845	53.790	53.751	45.993	-33.330	-
400	8.216	56.111	54.063	43.087	-23.541	-
500	8.451	57.971	54.465	40.771	-17.820	-
600	8.604	59.526	55.349	38.464	-14.010	-
700	8.783	60.950	56.079	36.151	-11.292	-
800	8.973	62.409	57.212	33.839	-8.573	-
900	9.189	63.907	58.567	31.526	-5.854	-
1000	9.428	65.440	60.151	29.210	-3.135	-
1100	9.691	67.009	61.985	26.894	-0.416	-
1200	9.978	68.613	63.978	24.578	2.297	-
1300	10.289	70.252	66.131	22.262	5.012	-
1400	10.624	71.926	68.455	19.946	7.727	-
1500	10.983	73.635	70.956	17.630	10.442	-
1600	11.366	75.379	73.603	15.314	13.157	-
1700	11.773	77.158	76.400	13.000	15.872	-
1800	12.204	78.972	79.349	10.686	18.587	-
1900	12.659	80.821	82.455	8.372	21.302	-
2000	13.138	82.695	85.718	6.058	24.017	-
2100	13.641	84.595	89.140	3.744	26.732	-
2200	14.168	86.520	92.722	1.430	29.447	-
2300	14.719	88.470	96.465	-0.884	32.162	-
2400	15.294	90.445	100.378	-3.200	34.877	-
2500	15.892	92.445	104.460	-5.516	37.592	-
2600	16.513	94.470	108.712	-7.832	40.307	-
2700	17.156	96.520	113.134	-10.148	43.022	-
2800	17.821	98.595	117.736	-12.464	45.737	-
2900	18.508	100.695	122.518	-14.780	48.452	-
3000	19.217	102.820	127.480	-17.096	51.167	-
3100	19.948	104.970	132.622	-19.412	53.882	-
3200	20.701	107.145	137.944	-21.728	56.597	-
3300	21.475	109.345	143.456	-24.044	59.312	-
3400	22.270	111.570	149.158	-26.360	62.027	-
3500	23.086	113.820	155.050	-28.676	64.742	-
3600	23.923	116.095	161.132	-30.992	67.457	-
3700	24.781	118.395	167.404	-33.308	70.172	-
3800	25.660	120.720	173.866	-35.624	72.887	-
3900	26.560	123.070	180.518	-37.940	75.602	-
4000	27.481	125.445	187.360	-40.256	78.317	-
4100	28.423	127.845	194.392	-42.572	81.032	-
4200	29.386	130.270	201.614	-44.888	83.747	-
4300	30.369	132.720	209.026	-47.204	86.462	-
4400	31.372	135.195	216.628	-49.520	89.177	-
4500	32.395	137.695	224.420	-51.836	91.892	-
4600	33.438	140.220	232.402	-54.152	94.607	-
4700	34.501	142.770	240.574	-56.468	97.322	-
4800	35.583	145.345	248.936	-58.784	100.037	-
4900	36.685	147.945	257.488	-61.100	102.752	-
5000	37.807	150.570	266.230	-63.416	105.467	-
5100	38.949	153.220	275.162	-65.732	108.182	-
5200	40.111	155.895	284.284	-68.048	110.897	-
5300	41.293	158.595	293.596	-70.364	113.612	-
5400	42.495	161.320	303.098	-72.680	116.327	-
5500	43.717	164.070	312.790	-74.996	119.042	-
5600	44.959	166.845	322.672	-77.312	121.757	-
5700	46.221	169.645	332.744	-79.628	124.472	-
5800	47.493	172.470	343.006	-81.944	127.187	-
5900	48.785	175.320	353.458	-84.260	129.902	-
6000	50.097	178.195	364.100	-86.576	132.617	-

Dec. 31, 1961; Sept. 30, 1962; Dec. 31, 1964

Ground State Configuration $1s^2 +$

$\Delta H_f^o = 53.750 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^o = 57 \pm 10 \text{ kcal. mole}^{-1}$

$\Delta H_f^o = 56 \pm 10 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{E_i}{0}, \text{ cm.}^{-1} \quad \frac{g_i}{1}$$

$\omega_e = 3.57 \text{ cm.}^{-1}$

$\omega_e = 669.04 \text{ cm.}^{-1}$

$\omega_e = 0.0036 \text{ cm.}^{-1}$

$\omega_e = 0.497 \text{ cm.}^{-1}$

$\omega_e = 1.887 \text{ Å}$

Heat of Formation.

G. Herzberg, "Spectra of Diatomic Molecules" D. Van Nostrand Co. New York 1950 reports a D_0 of 4.1 e.v. which corresponds to a heat of formation of 64 kcal. mole⁻¹ A. G. Gaydon "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, London 1953, gives essentially the same value, with a rider that the value is unreliable due to the ionic nature of the bonding. R. F. Barrow, Trans. Farad. Soc. 56, 952 (1960) made a critical evaluation of the bond dissociation energies of the group III halides and concluded $D_0 \text{ BBr} = 103.5$ which gives $\Delta H_f^o = 56 \text{ kcal. mole}^{-1}$. An estimate of the dissociation energy by taking the ratio $D(\text{Br})/(\Delta H_f^o(\text{Br}_2)/3) = 1.177$ and applying this to Br_2 yields $D(\text{BBR}) = 103 \text{ kcal. mole}^{-1}$, this was the value adopted.

Heat Capacity and Entropy.

The vibrational and rotational constants were all taken from National Bureau Standards Report 7033, Jan. 1, 1962.

BBR

Boron Bromide Chloride (BBrCl)

(Ideal Gas) Mol. Wt. = 126.193

BORON BROMIDE CHLORIDE (BBrCl)

(IDEAL GAS)

MOL. WT. = 126.193

Point Group C_{2v}
 $S_{298.15}^\circ = [69.056] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ 0 = [-1.0 \pm 10] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [-2.5 \pm 10] \text{ kcal. mole}^{-1}$

Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies

$\Delta G_f^\circ \text{ cm.}^{-1}$
[660](1)
[195](1)
[905](1)

Bond Distance B-Cl = $[1.73] \text{ \AA}$ B-Br = $[1.87] \text{ \AA}$
 Bond Angle Cl-B-Br = $[120^\circ]$
 $\sigma = 1$

Product of the Moments of Inertia: $I_A I_B I_C = [2.192176] \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_f^\circ = 0$ for the reaction $\text{BCl}_2 + \text{Br}_2 \rightarrow 2\text{BBrCl}$.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for BBr_2 and BCl_2 . The bond distances, angles, and quantum weight were assumed the same as in the dihalides. The individual moments of inertia were $I_A = 1.2937 \times 10^{-39} \text{ g. cm.}^2$, $I_B = 40.4239 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 41.7236 \times 10^{-39} \text{ g. cm.}^2$.

Dec. 31, 1962; Dec. 31, 1964

T, °K	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	INFINITE	-2.842	-1.023	-1.023	INFINITE
100	6.035	50.183	78.289	-2.011	-0.893	-3.790	8.282
200	10.141	60.141	80.046	-1.466	-0.861	-4.000	6.819
298	11.197	69.056	80.000	-0.000	-2.500	-9.303	
300	11.214	69.126	69.057	0.021	-2.508	-9.345	6.809
400	12.003	72.467	62.507	1.184	-6.202	-10.868	5.938
500	12.531	75.206	70.391	2.413	-6.234	-12.059	5.258
600	12.882	77.324	71.383	3.684	-6.336	-13.176	4.799
700	13.120	79.529	72.407	4.985	-6.437	-14.309	4.467
800	13.287	81.292	73.410	6.306	-6.552	-15.426	4.214
900	13.407	82.864	74.374	7.641	-6.677	-16.528	4.013
1000	13.496	84.282	75.295	8.986	-6.814	-17.615	3.850
1100	13.564	85.572	76.172	10.340	-6.964	-18.689	3.713
1200	13.617	86.754	77.005	11.699	-7.125	-19.747	3.596
1300	13.659	87.846	77.798	13.063	-7.289	-20.792	3.495
1400	13.692	88.859	78.552	14.430	-7.463	-21.822	3.406
1500	13.720	89.805	79.271	15.801	-7.651	-22.842	3.328
1600	13.742	90.691	79.957	17.174	-7.859	-23.844	3.257
1700	13.761	91.525	80.614	18.549	-8.108	-24.834	3.193
1800	13.777	92.312	81.242	19.926	-8.337	-25.813	3.134
1900	13.790	93.057	81.844	21.305	-8.574	-26.776	3.080
2000	13.802	93.765	82.423	22.684	-8.818	-27.729	3.030
2100	13.812	94.438	82.979	24.065	-9.067	-28.667	2.983
2200	13.821	95.081	83.515	25.447	-9.322	-29.595	2.940
2300	13.828	95.696	84.031	26.829	-9.582	-30.511	2.899
2400	13.835	96.284	84.529	28.212	-9.849	-31.413	2.860
2500	13.841	96.840	85.011	29.596	-10.125	-32.308	2.815
2600	13.846	97.392	85.477	30.980	-10.410	-33.198	2.762
2700	13.851	97.915	85.928	32.365	-10.704	-34.083	2.713
2800	13.855	98.419	86.365	33.750	-11.005	-34.956	2.666
2900	13.859	98.905	86.789	35.136	-11.316	-35.818	2.621
3000	13.862	99.375	87.201	36.522	-11.635	-36.669	2.580
3100	13.865	99.829	87.601	37.908	-11.960	-37.502	2.540
3200	13.868	100.270	87.990	39.295	-12.291	-38.326	2.502
3300	13.870	100.696	88.369	40.682	-12.627	-39.146	2.465
3400	13.873	101.110	88.737	42.069	-12.967	-39.959	2.430
3500	13.875	101.513	89.097	43.457	-13.310	-40.764	2.397
3600	13.877	101.904	89.447	44.844	-13.654	-41.564	2.365
3700	13.879	102.284	89.789	46.232	-14.000	-42.356	2.335
3800	13.880	102.654	90.122	47.620	-14.348	-43.141	2.305
3900	13.882	103.014	90.448	49.008	-14.697	-43.927	2.277
4000	13.883	103.366	90.767	50.396	-15.047	-44.714	2.252
4100	13.885	103.709	91.078	51.785	-15.398	-45.502	2.227
4200	13.886	104.043	91.383	53.173	-15.750	-46.292	2.202
4300	13.887	104.370	91.681	54.562	-16.104	-47.083	2.177
4400	13.888	104.689	91.973	55.940	-16.459	-47.876	2.152
4500	13.889	105.002	92.259	57.319	-16.814	-48.671	2.127
4600	13.890	105.307	92.540	58.700	-17.169	-49.467	2.102
4700	13.891	105.606	92.815	60.077	-17.525	-50.264	2.077
4800	13.892	105.898	93.084	61.456	-17.882	-51.062	2.052
4900	13.892	106.184	93.349	62.836	-18.240	-51.861	2.027
5000	13.893	106.465	93.608	64.219	-18.598	-52.661	2.002
5100	13.894	106.740	93.863	65.604	-18.957	-53.462	1.977
5200	13.894	107.010	94.113	67.004	-19.316	-54.264	1.952
5300	13.895	107.275	94.359	68.403	-19.675	-55.067	1.927
5400	13.896	107.534	94.601	69.803	-20.034	-55.871	1.902
5500	13.896	107.789	94.838	71.202	-20.393	-56.676	1.877
5600	13.897	108.040	95.072	72.602	-20.752	-57.481	1.852
5700	13.897	108.286	95.301	74.002	-21.111	-58.286	1.827
5800	13.898	108.527	95.527	75.402	-21.470	-59.091	1.802
5900	13.898	108.765	95.750	76.802	-21.829	-59.896	1.777
6000	13.899	108.999	95.968	78.202	-22.188	-60.701	1.752

Boron Bromide Dichloride (BBrCl₂)
(Ideal Gas) Mol. Wt. = 161.65

BBrCl₂

MOL. WT. = 161.65

(IDEAL GAS)

BORON BROMIDE DICHLORIDE (BBrCl₂)

Point Group C_{2v}

$\Delta H_f^\circ = -78.5 \pm 10 \text{ kcal. mole}^{-1}$

$S_{298.15}^\circ = 74.163 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^\circ = -80.5 \pm 10 \text{ kcal. mole}^{-1}$

Ground State Quantum Weight [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
885(1)	959(1)
406(1)	[208](1)
218(1)	433(1)

Bond Distances: B-Cl = 1.73 Å B-Br = 1.87 Å

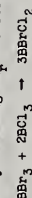
Bond Angle: Cl-B-Cl = [120°] Br-B-Cl = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = 9.19303 \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$

$\sigma = 2$

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_f^\circ = 0$ for the reaction



Heat Capacity and Entropy.

Vibrational frequencies were obtained from L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956). The b_1 mode was the only unobserved frequency and was calculated from a normal coordinate treatment. Bond distances were reported by T. Wentink and V. H. Tienau, J. Chem. Phys. 28, 826 (1956). Bond angles were estimated by analogy with the other trihalides of boron. The individual moments of inertia were $I_A = 26.4242 \times 10^{-39} \text{ g. cm.}^2$, $I_B = 47.3327 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 73.6569 \times 10^{-39} \text{ g. cm.}^2$.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	kerl. mole ⁻¹ H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	+0.00	INFINITE	-3.477	-78.561	-	INFINITE
100	10.218	60.250	2.616	-78.414	-78.561	173.049
200	13.421	68.410	1.421	-78.933	-79.596	87.826
298	15.392	74.163	-0.000	-80.500	-80.881	59.285
300	15.422	74.258	-0.029	-80.508	-80.884	58.921
400	16.743	78.689	1.441	-84.167	-80.257	43.848
500	17.607	82.725	3.362	-84.154	-79.281	34.652
600	18.170	85.998	5.153	-84.151	-78.307	28.522
700	18.469	88.822	6.992	-84.143	-77.350	23.815
800	18.642	91.321	8.863	-84.163	-76.350	20.489
900	18.040	93.552	10.758	-84.171	-75.383	18.305
1000	14.188	95.566	12.660	-84.188	-74.405	16.260
1100	14.300	97.400	14.594	-84.216	-73.426	14.588
1200	14.354	99.084	16.528	-84.252	-72.444	13.193
1300	14.358	100.658	18.467	-84.293	-71.468	11.969
1400	14.311	102.082	20.419	-84.353	-70.497	10.892
1500	14.256	103.430	22.372	-84.421	-69.526	9.953
1600	14.193	104.693	24.330	-84.499	-68.575	9.033
1700	14.116	105.882	26.291	-84.587	-67.670	8.173
1800	14.027	107.000	28.257	-84.684	-66.802	7.367
1900	13.927	108.057	30.221	-84.790	-65.962	6.604
2000	13.818	109.077	32.189	-84.902	-65.144	5.883
2100	13.709	110.058	34.159	-85.019	-64.348	5.208
2200	13.591	110.999	36.131	-85.144	-63.576	4.579
2300	13.464	111.892	38.106	-85.276	-62.828	3.993
2400	13.329	112.737	40.078	-85.409	-62.092	3.451
2500	13.186	113.540	42.053	-85.539	-61.366	2.948
2600	13.035	114.304	44.029	-85.669	-60.641	2.481
2700	12.876	115.030	46.006	-85.797	-59.916	2.048
2800	12.710	115.719	47.984	-85.921	-59.191	1.651
2900	12.537	116.371	49.962	-86.041	-58.466	1.288
3000	12.358	116.994	51.941	-86.159	-57.741	0.959
3100	12.173	117.584	53.920	-86.274	-57.016	0.663
3200	11.982	118.143	55.899	-86.386	-56.291	0.398
3300	11.785	118.671	57.878	-86.495	-55.566	0.163
3400	11.582	119.166	59.856	-86.601	-54.841	0.058
3500	11.373	120.137	61.834	-86.704	-54.116	0.000
3600	11.158	120.695	63.812	-86.804	-53.391	-0.151
3700	10.938	121.252	65.790	-86.901	-52.666	-0.302
3800	10.713	121.767	67.768	-86.995	-51.941	-0.453
3900	10.484	122.282	69.746	-87.086	-51.216	-0.604
4000	10.250	122.783	71.724	-87.174	-50.491	-0.755
4100	10.011	123.273	73.702	-87.259	-49.766	-0.906
4200	9.768	123.741	75.680	-87.341	-49.041	-1.057
4300	9.520	124.188	77.658	-87.420	-48.316	-1.208
4400	9.268	124.614	79.636	-87.496	-47.591	-1.359
4500	9.011	125.019	81.614	-87.569	-46.866	-1.510
4600	8.750	125.404	83.592	-87.639	-46.141	-1.661
4700	8.484	125.769	85.570	-87.706	-45.416	-1.812
4800	8.213	126.114	87.548	-87.770	-44.691	-1.963
4900	7.938	126.439	89.526	-87.831	-43.966	-2.114
5000	7.659	126.744	91.504	-87.889	-43.241	-2.265
5100	7.375	127.030	93.482	-87.944	-42.516	-2.416
5200	7.086	127.297	95.460	-87.996	-41.791	-2.567
5300	6.792	127.545	97.438	-88.045	-41.066	-2.718
5400	6.494	127.774	99.416	-88.091	-40.341	-2.869
5500	6.191	127.984	101.394	-88.134	-39.616	-3.020
5600	5.884	128.174	103.372	-88.174	-38.891	-3.171
5700	5.572	128.344	105.350	-88.211	-38.166	-3.322
5800	5.256	128.494	107.328	-88.245	-37.441	-3.473
5900	4.936	128.624	109.306	-88.276	-36.716	-3.624
6000	4.611	128.734	111.284	-88.304	-35.991	-3.775

Boron Bromide Fluoride (BBrF)

(Ideal Gas) Mol. Wt. = 109.736

MOL. WT. = 109.736

BORON BROMIDE FLUORIDE (BBrF)

(IDEAL GAS)

Point Group C_2

$\Delta H_f^\circ = [65.887] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^\circ 298.15 = [57.5 \pm 10] \text{ kcal. mole}^{-1}$

Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies

$\Delta G, \text{ cm.}^{-1}$

[860](1)

[310](1)

[1140](1)

Bond Distance: B-Br = $[1.3] \text{ \AA}$ B-Br = $[1.87] \text{ \AA}$

Bond Angle: Br-B-Br = $[120^\circ]$

Product of the Moments of Inertia: $I_A I_B I_C = [4.13196] \times 10^{-115} \text{ g. cm.}^6$

$\sigma = 1$

Heat of Formation

The heat of formation was estimated by assuming $\Delta H_f^\circ = 0$ for the reaction $\text{BBr}_2 + \text{BrF}_2 \rightarrow 2\text{BBrF}$.

Heat Capacity and Entropy

The vibrational frequencies, bond lengths, angles and quantum weight were estimated by comparison with the respective dihalides. The individual moments of inertia were $I_A = 0.8407 \times 10^{-39} \text{ g. cm.}^2$, $I_B = 21.7537 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 22.5944 \times 10^{-39} \text{ g. cm.}^2$.

BBrF

Dec. 31, 1962; Dec. 31, 1964

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	8.418	55.751	74.445	-1.873	-55.784	-55.902	-55.902	INFINITE
200	9.477	61.928	86.809	-1.976	-55.903	-56.673	-56.673	128.224
298	10.408	65.887	95.887	-2.000	-57.500	-61.526	-61.526	67.230
300	10.425	65.931	95.887	-2.010	-57.500	-61.526	-61.526	46.969
400	11.261	69.069	106.306	-2.063	-61.349	-66.628	-66.628	46.709
500	11.900	71.654	111.125	-2.105	-65.255	-71.652	-71.652	46.709
600	12.362	73.867	118.069	-2.140	-69.227	-76.686	-76.686	24.649
700	12.696	75.811	124.032	-2.168	-73.255	-81.718	-81.718	24.649
800	12.936	77.511	129.045	-2.191	-77.255	-86.740	-86.740	19.440
900	13.116	79.045	133.116	-2.210	-81.255	-91.762	-91.762	17.164
1000	13.251	80.434	136.251	-2.225	-85.255	-96.784	-96.784	15.659
1100	13.356	81.702	138.561	-2.238	-89.227	-101.796	-101.796	14.424
1200	13.436	82.867	140.936	-2.249	-93.191	-106.799	-106.799	13.424
1300	13.504	83.947	143.374	-2.258	-97.146	-111.792	-111.792	12.517
1400	13.557	84.949	145.864	-2.265	-101.084	-116.775	-116.775	11.764
1500	13.601	85.886	148.401	-2.270	-105.000	-121.748	-121.748	11.110
1600	13.637	86.765	150.975	-2.273	-108.896	-126.702	-126.702	10.535
1700	13.665	87.593	153.588	-2.275	-112.771	-131.637	-131.637	10.035
1800	13.685	88.374	156.239	-2.276	-116.626	-136.552	-136.552	9.572
1900	13.714	89.116	158.916	-2.276	-120.461	-141.447	-141.447	9.164
2000	13.733	89.820	161.616	-2.275	-124.276	-146.322	-146.322	8.796
2100	13.748	90.490	164.336	-2.273	-128.071	-151.177	-151.177	8.461
2200	13.763	91.124	167.071	-2.270	-131.846	-156.012	-156.012	8.153
2300	13.773	91.722	169.820	-2.266	-135.591	-160.827	-160.827	7.875
2400	13.776	92.288	172.583	-2.261	-139.316	-165.622	-165.622	7.617
2500	13.776	92.821	175.360	-2.255	-143.021	-170.397	-170.397	7.369
2600	13.764	93.323	178.150	-2.248	-146.706	-175.152	-175.152	7.130
2700	13.753	93.793	180.953	-2.240	-150.371	-179.887	-179.887	6.900
2800	13.743	94.234	183.770	-2.231	-154.016	-184.602	-184.602	6.700
2900	13.733	94.644	186.600	-2.221	-157.641	-189.297	-189.297	6.525
3000	13.730	95.016	189.441	-2.210	-161.246	-193.972	-193.972	6.353
3100	13.725	95.354	192.293	-2.200	-164.831	-198.627	-198.627	6.185
3200	13.720	95.653	195.156	-2.189	-168.396	-203.262	-203.262	6.025
3300	13.714	95.920	198.030	-2.177	-171.941	-207.877	-207.877	5.873
3400	13.708	96.154	200.914	-2.165	-175.466	-212.472	-212.472	5.725
3500	13.702	96.354	203.808	-2.152	-178.961	-217.047	-217.047	5.585
3600	13.695	96.520	206.712	-2.139	-182.436	-221.602	-221.602	5.453
3700	13.688	96.654	209.626	-2.126	-185.881	-226.137	-226.137	5.326
3800	13.681	96.756	212.549	-2.113	-189.306	-230.652	-230.652	5.203
3900	13.673	96.826	215.481	-2.100	-192.711	-235.147	-235.147	5.083
4000	13.665	96.863	218.421	-2.087	-196.096	-239.622	-239.622	4.966
4100	13.656	96.777	221.369	-2.074	-199.461	-244.077	-244.077	4.854
4200	13.646	96.673	224.326	-2.061	-202.806	-248.512	-248.512	4.746
4300	13.635	96.550	227.291	-2.048	-206.131	-252.927	-252.927	4.642
4400	13.624	96.408	230.263	-2.035	-209.436	-257.322	-257.322	4.542
4500	13.612	96.246	233.241	-2.022	-212.721	-261.697	-261.697	4.446
4600	13.600	96.063	236.226	-2.009	-215.986	-266.052	-266.052	4.354
4700	13.587	95.860	239.217	-1.996	-219.231	-270.387	-270.387	4.266
4800	13.574	95.636	242.214	-1.983	-222.456	-274.702	-274.702	4.182
4900	13.560	95.391	245.217	-1.970	-225.661	-279.007	-279.007	4.101
5000	13.546	95.126	248.226	-1.957	-228.846	-283.292	-283.292	4.023
5100	13.532	94.841	251.240	-1.944	-232.011	-287.557	-287.557	3.948
5200	13.518	94.536	254.259	-1.931	-235.156	-291.802	-291.802	3.876
5300	13.503	94.211	257.283	-1.918	-238.281	-296.027	-296.027	3.806
5400	13.488	93.866	260.312	-1.905	-241.386	-300.232	-300.232	3.738
5500	13.472	93.501	263.346	-1.892	-244.471	-304.417	-304.417	3.672
5600	13.456	93.116	266.385	-1.879	-247.546	-308.582	-308.582	3.608
5700	13.439	92.711	269.429	-1.866	-250.601	-312.727	-312.727	3.546
5800	13.422	92.286	272.478	-1.853	-253.636	-316.852	-316.852	3.486
5900	13.405	91.841	275.532	-1.840	-256.651	-320.957	-320.957	3.428
6000	13.388	91.376	278.591	-1.827	-259.646	-325.042	-325.042	3.372

Boron Bromide Difluoride (BBrF₂)
(Ideal Gas) Mol. Wt. 128.736

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	+0.00	INFINITE	-	3.054	-193.723	-193.723	INFINITE
100	8.742	56.536	78.971	2.243	-193.479	-193.479	425.888
200	11.472	69.443	68.424	0.000	-193.400	-193.400	213.811
298	13.492	80.424	68.424	0.000	-196.000	-196.114	149.746
300	13.524	68.508	68.424	0.025	-196.011	-196.115	142.863
400	14.097	72.611	68.974	1.455	-199.793	-195.378	106.745
500	16.088	76.089	70.057	3.012	-199.897	-194.263	84.908
600	16.896	79.089	71.117	4.663	-199.997	-193.127	70.343
700	17.496	81.741	72.621	6.384	-200.089	-191.874	59.934
800	17.944	84.108	73.611	8.157	-200.175	-190.810	52.124
900	18.283	86.242	75.165	9.969	-200.254	-189.635	46.047
1000	18.545	88.182	76.171	11.811	-200.332	-188.449	41.184
1100	18.749	89.959	77.527	13.676	-200.414	-187.258	37.203
1200	18.911	91.598	78.632	15.560	-200.498	-186.087	33.684
1300	19.041	93.117	79.688	17.457	-200.590	-184.850	31.075
1400	19.148	94.532	80.699	19.367	-200.687	-183.635	28.665
1500	19.235	95.856	81.665	21.286	-200.794	-182.414	26.576
1600	19.308	97.100	82.592	23.214	-200.909	-181.185	24.747
1700	19.369	98.273	83.480	25.147	-201.034	-179.948	23.133
1800	19.421	99.381	84.333	27.087	-201.166	-178.706	21.697
1900	19.465	100.432	85.153	29.031	-201.305	-177.452	20.411
2000	19.504	101.432	85.942	30.980	-201.450	-176.194	19.253
2100	19.537	102.384	86.742	32.932	-201.600	-174.927	18.204
2200	19.566	103.294	87.446	34.887	-201.755	-173.655	17.250
2300	19.591	104.164	88.145	36.845	-201.916	-172.372	16.378
2400	19.613	104.998	88.830	38.805	-202.083	-171.083	15.576
2500	19.633	105.799	89.482	40.768	-202.257	-169.779	14.833
2600	19.651	106.570	90.135	42.732	-202.437	-168.463	14.134
2700	19.667	107.312	90.787	44.698	-202.620	-167.139	13.487
2800	19.681	108.027	91.361	46.665	-202.805	-165.806	12.886
2900	19.694	108.718	91.948	48.634	-202.992	-164.463	12.323
3000	19.705	109.386	92.518	50.604	-203.181	-163.111	11.802
3100	19.716	110.032	93.073	52.575	-203.372	-161.755	11.312
3200	19.725	110.658	93.612	54.547	-203.565	-160.395	10.852
3300	19.734	111.265	94.138	56.520	-203.760	-159.030	10.419
3400	19.742	111.855	94.651	58.494	-203.957	-157.665	10.012
3500	19.749	112.427	95.150	60.468	-204.155	-156.300	9.627
3600	19.756	112.984	95.638	62.443	-204.354	-154.935	9.264
3700	19.762	113.525	96.114	64.419	-204.554	-153.570	8.920
3800	19.768	114.052	96.579	66.396	-204.754	-152.205	8.594
3900	19.773	114.566	97.034	68.373	-204.954	-150.840	8.284
4000	19.778	115.066	97.479	70.350	-205.154	-149.475	7.987
4100	19.782	115.555	97.914	72.328	-205.354	-148.110	7.701
4200	19.786	116.031	98.339	74.307	-205.554	-146.745	7.431
4300	19.790	116.497	98.756	76.286	-205.754	-145.380	7.170
4400	19.794	116.952	99.165	78.265	-205.954	-144.015	6.920
4500	19.797	117.397	99.565	80.244	-206.154	-142.650	6.679
4600	19.801	117.832	99.957	82.224	-206.354	-141.285	6.447
4700	19.804	118.258	100.342	84.205	-206.554	-139.920	6.226
4800	19.807	118.675	100.720	86.185	-206.754	-138.555	6.014
4900	19.809	119.083	101.090	88.166	-206.954	-137.190	5.811
5000	19.812	119.484	101.454	90.147	-207.154	-135.825	5.617
5100	19.814	119.876	101.812	92.128	-207.354	-134.460	5.431
5200	19.816	120.261	102.163	94.110	-207.554	-133.095	5.254
5300	19.818	120.638	102.508	96.091	-207.754	-131.730	5.087
5400	19.820	121.009	102.847	98.073	-207.954	-130.365	4.930
5500	19.822	121.372	103.180	100.056	-208.154	-128.999	4.782
5600	19.824	121.729	103.508	102.038	-208.354	-127.634	4.643
5700	19.826	122.080	103.831	104.020	-208.554	-126.269	4.514
5800	19.827	122.425	104.149	106.003	-208.754	-124.904	4.394
5900	19.829	122.764	104.461	107.986	-208.954	-123.539	4.284
6000	19.830	123.097	104.769	109.969	-209.154	-122.174	4.184

Sept. 30, 1962, Dec. 31, 1964

Boron Bromide Difluoride (BBrF₂)
(Ideal Gas)

MOL. WT. = 128.736

Point Group C_{2v}
S_{298.15} = 68.424 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight [1]
ΔH_f⁰ = [-193.7 ± 10] kcal. mole⁻¹
ΔH_f⁰ 298.15 = [-196.0 ± 10] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω _i , cm. ⁻¹	ω _i , cm. ⁻¹
1215 (1)	1427 (1)
653 (1)	[346](1)
[330](1)	575 (1)

Bond Distance: B-F = 1.295 Å B-Br = 1.87 Å

Bond Angle: F-B-F = [120°] Br-B-F = [120°]

Product of the Moments of Inertia: I_AI_BI_C = 8.46916 X 10⁻¹¹⁴ g.³ cm.⁶

σ = 2

Heat of Formation.

The heat of formation was estimated by assuming ΔH_f = 0 for the reaction 2BF₃ + BBr₃ → 3BBrF₂.

Heat Capacity and Entropy.

All but two of the vibrational frequencies have been observed and assigned by L. P. Lindeman and M. K. Wilson J. Chem. Phys. 24, 242 (1956), the two remaining frequencies were calculated by a normal coordinate treatment. The bond distances were reported by T. Kuntink and V. H. Tienau, J. Chem. Phys. 28, 826 (1958). The bond angles were estimated by analogy with the other boron trihalides. The individual moments of inertia were I_A = 7.9349 X 10⁻³⁹ g. cm.², I_B = 28.9426 X 10⁻²⁹ g. cm.² and I_C = 36.8775 X 10⁻³⁹ g. cm.².

Boron Oxide Bromide (BOBr)

(Ideal Gas) Mol. Wt. = 106.736

BORON OXIDE BROMIDE (BOBr)

(IDEAL GAS)

MOL. WT. = 106.736

$$\Delta H_f^\circ 0 = [-58 \pm 7] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ 298.15 = [-60 \pm 7] \text{ kcal. mole}^{-1}$$

Point Group [C_{∞v}]

$$S_{298.15}^\circ = [59.48] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$$\omega, \text{ cm.}^{-1}$$

$$[550] (1)$$

$$[370] (2)$$

$$[1800] (1)$$

$$\text{Bond Distance: O-B} = [1.20] \text{ \AA} \quad \text{B-Br} = [1.87] \text{ \AA}$$

$$\text{Bond Angle: O-B-Br} = [180]^\circ$$

$$\text{Rotation Constant: } B_0 = [0.11742] \text{ cm.}^{-1}$$

$$\sigma^- = 1$$

Heat of Formation.

The value of $\Delta H_f^\circ 298.15$ for BOBr (g) was calculated based on an assumption that $D(\text{BO-Br}) = 92.5 \text{ kcal. mole}^{-1}$ which was estimated by comparison with the following related bond energy values: $D(\text{BF}_2\text{-F}) = 159$, $D(\text{BO-F}) = 169$, $D(\text{BCl}_2\text{-Cl}) = 105$, $D(\text{BO-Cl}) = 110$ and $D(\text{BBr}_2\text{-Br}) = 90.5 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The vibrational frequencies (ω) were estimated from the ω values calculated by the valence force method described by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., 1945, using estimated force constants, $k_1 = 4.2 \times 10^5$, $k_2 = 16.9 \times 10^5 \text{ dynes cm.}^{-1}$ and $k_3 = 0.37 \times 10^{-11} \text{ dynes cm. rad.}^{-1}$. The B-O and B-Br bond distances were assumed to be the same as those in BO(g) and BBr₃(g), respectively. The moment of inertia is $2.58357 \times 10^{-38} \text{ g. cm.}^2$.

BBrO

T, K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f °	Log K _p
0	∞	∞	∞	∞	INFINITE
100	7.000	40.000	2.620	58.361	18.561
200	9.687	55.293	6.040	50.482	15.039
298	11.188	59.463	10.000	60.000	12.837
300	11.206	59.463	10.021	60.007	12.806
400	11.968	62.869	15.482	63.643	12.776
500	12.498	65.800	20.407	65.836	12.746
600	12.909	67.916	24.786	66.664	12.716
700	13.239	69.932	28.696	66.705	12.686
800	13.505	71.718	32.131	66.422	12.656
900	13.720	73.321	35.166	65.860	12.626
1000	13.893	74.776	37.859	65.067	12.596
1100	14.034	76.107	40.163	64.053	12.566
1200	14.149	77.333	42.045	62.836	12.536
1300	14.244	78.470	43.552	61.448	12.506
1400	14.323	79.528	44.821	60.000	12.476
1500	14.390	80.519	45.886	58.500	12.446
1600	14.445	81.449	46.680	56.957	12.416
1700	14.493	82.326	47.245	55.369	12.386
1800	14.534	83.156	47.697	53.732	12.356
1900	14.569	83.963	48.045	52.049	12.326
2000	14.599	84.691	48.290	50.322	12.296
2100	14.626	85.404	48.440	48.551	12.266
2200	14.649	86.085	48.500	46.736	12.236
2300	14.670	86.736	48.470	44.876	12.206
2400	14.688	87.361	48.350	42.976	12.176
2500	14.704	87.961	48.140	41.036	12.146
2600	14.719	88.538	47.850	39.056	12.116
2700	14.732	89.094	47.490	37.036	12.086
2800	14.743	89.630	47.060	34.976	12.056
2900	14.754	90.147	46.570	32.876	12.026
3000	14.764	90.648	46.020	30.736	11.996
3100	14.772	91.132	45.410	28.556	11.966
3200	14.780	91.601	44.740	26.326	11.936
3300	14.787	92.056	44.010	24.056	11.906
3400	14.794	92.498	43.230	21.746	11.876
3500	14.800	92.926	42.400	19.396	11.846
3600	14.805	93.344	41.520	17.006	11.816
3700	14.811	93.749	40.590	14.576	11.786
3800	14.816	94.144	39.610	12.106	11.756
3900	14.820	94.529	38.580	9.596	11.726
4000	14.824	94.904	37.500	7.046	11.696
4100	14.828	95.271	36.360	4.456	11.666
4200	14.831	95.628	35.170	1.826	11.636
4300	14.835	95.977	33.930	-0.846	11.606
4400	14.838	96.318	32.640	-3.476	11.576
4500	14.841	96.651	31.300	-6.066	11.546
4600	14.843	96.978	29.910	-8.616	11.516
4700	14.846	97.297	28.470	-11.126	11.486
4800	14.848	97.615	26.980	-13.596	11.456
4900	14.851	97.916	25.440	-16.026	11.426
5000	14.853	98.216	23.850	-18.416	11.396
5100	14.855	98.510	22.210	-20.766	11.366
5200	14.857	98.798	20.520	-23.076	11.336
5300	14.858	99.081	18.780	-25.346	11.306
5400	14.860	99.359	16.990	-27.576	11.276
5500	14.862	99.632	15.150	-29.766	11.246
5600	14.863	99.900	13.260	-31.916	11.216
5700	14.865	100.163	11.320	-34.026	11.186
5800	14.866	100.421	9.330	-36.096	11.156
5900	14.867	100.675	7.290	-38.126	11.126
6000	14.868	100.925	5.200	-40.116	11.096

Dec. 31, 1962; Mar. 31, 1965

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	9.4000	∞	∞	∞	∞	18.233	18.233	INFINITE
100	9.3444	56.220	79.888	-	2.067	18.410	13.783	-30.122
200	10.4444	56.029	79.888	-	1.078	18.148	9.239	-10.096
298	11.4866	70.402	70.402	∞	∞	15.000	5.276	-3.867
300	11.503	70.473	70.402	∞	∞	14.983	5.216	-3.800
400	12.248	76.680	76.680	2.211	7.493	14.431	2.471	-1.457
500	12.726	76.680	71.756	2.462	7.566	12.440	2.440	-1.067
600	13.035	79.030	72.778	3.751	7.492	1.422	-	-5.18
700	13.242	81.056	73.819	5.066	7.398	∞	∞	-1.130
800	13.488	84.416	75.812	7.721	7.568	-	-	4.57
900	13.564	85.842	76.748	9.094	7.036	-	-	4.58
1000	13.621	87.137	77.634	10.454	6.890	-	-	4.687
1100	13.666	88.325	78.476	11.818	6.732	-	-	4.800
1200	13.706	89.426	79.278	13.181	6.566	-	-	4.910
1300	13.742	90.443	80.038	14.548	6.380	-	-	5.016
1400	13.775	91.384	80.763	15.932	6.185	-	-	5.111
1500	13.806	92.272	81.455	17.308	5.979	-	-	5.199
1600	13.835	93.108	82.116	18.686	5.762	-	-	5.281
1700	13.861	93.899	82.750	20.066	5.535	-	-	5.358
1800	13.884	94.642	83.353	21.446	5.301	-	-	5.431
1900	13.905	95.351	83.937	22.827	5.059	-	-	5.499
2000	13.924	96.026	84.497	24.210	4.813	-	-	5.562
2100	13.942	96.669	85.036	25.594	4.560	-	-	5.620
2200	13.958	97.280	85.556	26.979	4.300	-	-	5.673
2300	13.972	97.863	86.056	28.362	4.039	-	-	5.721
2400	13.985	98.430	86.540	29.747	3.778	-	-	5.765
2500	13.997	98.982	87.008	31.132	3.517	-	-	5.806
2600	13.857	98.982	87.008	31.132	3.256	-	-	5.844
2700	13.861	100.005	87.462	32.518	2.995	-	-	5.879
2800	13.867	100.496	88.327	33.901	2.734	-	-	5.911
2900	13.870	100.966	88.740	36.678	2.473	-	-	5.940
3000	13.873	101.421	89.142	38.065	2.212	-	-	5.966
3100	13.875	101.862	89.533	39.452	1.951	-	-	5.990
3200	13.877	102.297	90.000	40.838	1.690	-	-	6.012
3300	13.879	102.730	90.463	42.228	1.429	-	-	6.033
3400	13.881	103.105	90.644	43.616	1.168	-	-	6.053
3500	13.883	103.496	90.995	45.004	0.907	-	-	6.072
3600	13.884	103.827	91.338	46.392	0.646	-	-	6.090
3700	13.885	104.124	91.673	47.782	0.385	-	-	6.107
3800	13.887	104.408	92.000	49.169	0.124	-	-	6.123
3900	13.888	104.695	92.320	50.558	-0.137	-	-	6.138
4000	13.889	105.002	92.632	51.947	-0.400	-	-	6.152
4100	13.890	105.320	92.938	53.336	-0.663	-	-	6.165
4200	13.891	105.664	93.239	54.726	-0.926	-	-	6.177
4300	13.892	106.028	93.540	56.114	-1.189	-	-	6.188
4400	13.893	106.595	93.817	57.503	-1.452	-	-	6.198
4500	13.894	106.901	94.098	58.893	-1.715	-	-	6.207
4600	13.895	107.249	94.373	60.282	-1.978	-	-	6.215
4700	13.896	107.638	94.649	61.671	-2.241	-	-	6.222
4800	13.896	107.778	94.909	63.061	-2.504	-	-	6.228
4900	13.896	108.059	95.169	64.451	-2.767	-	-	6.233
5000	13.897	108.334	95.425	65.840	-3.030	-	-	6.238
5100	13.897	108.609	95.680	67.229	-3.293	-	-	6.242
5200	13.898	108.869	95.935	68.618	-3.556	-	-	6.246
5300	13.898	109.129	96.184	70.009	-3.819	-	-	6.249
5400	13.899	109.384	96.402	71.399	-4.082	-	-	6.252
5500	13.899	109.634	96.636	72.789	-4.345	-	-	6.255
5600	13.899	109.884	96.869	74.179	-4.608	-	-	6.258
5700	13.900	110.120	97.095	75.569	-4.871	-	-	6.260
5800	13.900	110.360	97.316	76.959	-5.134	-	-	6.262
5900	13.900	110.593	97.535	78.349	-5.397	-	-	6.264
6000	13.901	110.820	97.753	79.739	-5.660	-	-	6.266

Mar. 31, 1962; Dec. 31, 1962; Dec. 31, 1964

BORON DIBROMIDE (BBr₂) (IDEAL GAS)

MOL. WT. = 170.652

Point Group [C_{2v}]
 $\Delta H_f^0 = [18.2 \pm 15] \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = [70.402] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = [15.0 \pm 15] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies

ω , cm.⁻¹
 [600](1)
 [150](1)
 [830](1)

Bond Distance: [1.87] Å

Bond Angle: [120°]

Product of the Moments of Inertia: $I_A I_B I_C = 7.26584 \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$ $\sigma = 2$

Heat of Formation.

The heat of formation was estimated by analogy with BP₃, specifically the ratio

$$\Delta H_f^0(\text{BX}_3) \rightarrow \text{BX}_2 + \text{X} / \Delta H_f^0(\text{BX}_3) \rightarrow \text{B} + 3\text{X}$$

was taken as 0.347.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from force constants transferred from the trihalide given by G. Herzberg "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., (1945). The bond length was taken between those of the mono and trihalide and the angle was estimated to be the same as that in the trihalides. The ground state quantum weight was taken as two on account of the one unpaired electron.

The individual moments of inertia were $I_B = 1.4708 \times 10^{-39} \text{ g. cm.}^2$, $I_A = 69.5532 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 71.0240 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF ⁰	Log K _p
0	.000	INFINITE	- 3.607	- 61.359	- 61.359	INFINITE
100	10.827	62.411	89.591	- 61.495	- 61.495	140.261
200	13.932	70.977	78.299	- 61.852	- 61.852	72.921
298	15.781	76.909	76.909	- 65.000	- 68.720	50.371
300	15.810	77.007	76.910	- 65.016	- 68.743	50.077
400	17.038	81.736	77.546	- 65.016	- 68.479	37.614
500	17.833	85.630	78.785	- 65.016	- 67.516	29.510
600	18.354	88.930	80.208	- 65.016	- 66.556	24.242
700	18.706	91.788	81.089	- 65.016	- 65.601	20.468
800	18.953	94.303	81.697	- 65.016	- 64.641	17.658
900	19.131	96.546	82.062	- 65.016	- 63.683	15.464
1000	19.262	98.569	82.773	- 65.016	- 62.732	13.707
1100	19.365	100.409	87.021	- 65.016	- 61.783	12.271
1200	19.440	102.098	90.888	- 65.016	- 60.832	11.058
1300	19.502	103.656	94.337	- 65.016	- 59.882	10.058
1400	19.551	105.103	97.412	- 65.016	- 58.932	9.168
1500	19.591	106.454	101.437	- 65.016	- 57.981	8.434
1600	19.626	107.719	105.466	- 65.016	- 57.030	7.773
1700	19.657	108.910	109.500	- 65.016	- 56.079	7.189
1800	19.675	109.934	113.538	- 65.016	- 55.128	6.670
1900	19.695	110.908	117.580	- 65.016	- 54.177	6.204
2000	19.712	111.829	121.626	- 65.016	- 53.226	5.785
2100	19.727	112.701	125.675	- 65.016	- 52.275	5.405
2200	19.740	113.529	129.726	- 65.016	- 51.324	5.059
2300	19.751	114.317	133.779	- 65.016	- 50.373	4.742
2400	19.761	115.067	137.834	- 65.016	- 49.422	4.451
2500	19.769	115.781	141.891	- 65.016	- 48.471	4.174
2600	19.777	116.461	145.948	- 65.016	- 47.520	3.908
2700	19.784	117.117	150.006	- 65.016	- 46.569	3.659
2800	19.790	117.750	154.064	- 65.016	- 45.618	3.432
2900	19.796	118.361	158.122	- 65.016	- 44.667	3.218
3000	19.801	118.950	162.180	- 65.016	- 43.716	3.018
3100	19.805	119.517	166.238	- 65.016	- 42.765	2.830
3200	19.809	120.061	170.296	- 65.016	- 41.814	2.652
3300	19.813	120.590	174.354	- 65.016	- 40.863	2.488
3400	19.817	121.104	178.412	- 65.016	- 39.912	2.332
3500	19.820	121.603	182.470	- 65.016	- 38.961	2.185
3600	19.823	122.087	186.528	- 65.016	- 38.010	2.045
3700	19.825	122.557	190.586	- 65.016	- 37.059	1.913
3800	19.828	123.013	194.644	- 65.016	- 36.108	1.787
3900	19.830	123.456	198.702	- 65.016	- 35.157	1.667
4000	19.832	123.887	202.760	- 65.016	- 34.206	1.537
4100	19.834	124.306	206.818	- 65.016	- 33.255	1.417
4200	19.836	124.713	210.876	- 65.016	- 32.304	1.307
4300	19.837	125.109	214.934	- 65.016	- 31.353	1.207
4400	19.839	125.494	218.992	- 65.016	- 30.402	1.117
4500	19.841	125.869	223.050	- 65.016	- 29.451	1.037
4600	19.842	126.234	227.108	- 65.016	- 28.500	0.967
4700	19.843	126.589	231.166	- 65.016	- 27.549	0.907
4800	19.844	126.934	235.224	- 65.016	- 26.598	0.857
4900	19.846	127.270	239.282	- 65.016	- 25.647	0.817
5000	19.847	127.597	243.340	- 65.016	- 24.696	0.787
5100	19.848	127.914	247.398	- 65.016	- 23.745	0.757
5200	19.849	128.221	251.456	- 65.016	- 22.794	0.727
5300	19.850	128.518	255.514	- 65.016	- 21.843	0.697
5400	19.851	128.805	259.572	- 65.016	- 20.892	0.667
5500	19.851	129.082	263.630	- 65.016	- 19.941	0.637
5600	19.852	129.350	267.688	- 65.016	- 18.990	0.607
5700	19.853	129.607	271.746	- 65.016	- 18.039	0.577
5800	19.853	129.854	275.804	- 65.016	- 17.088	0.547
5900	19.854	130.091	279.862	- 65.016	- 16.137	0.517
6000	19.855	130.318	283.920	- 65.016	- 15.186	0.487

Sept. 30, 1962; Dec. 31, 1964

Point Group C_{2v}
 $\Delta H_f^0 = 76.909 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = [-61.4 \pm 10] \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = [-65 \pm 10] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight [1]

Vibrational Levels and Degeneracies
$\omega_e, \text{cm.}^{-1}$
925(1)
344(1)
166(1)
409(1)

Bond Distance: B-Br = 1.87 Å B-Cl = 1.75 Å
 Bond Angle: Br-B-Br = [120°] Cl-B-Br = [120°]
 Product of the Moments of Inertia: $I_A I_B I_C = 2.55478 \times 10^{-112} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation

The heat of formation was estimated by assuming $\Delta H_f^0 = 0$ for the reaction
 $2\text{BBr}_2 + \text{BCl}_3 \rightarrow 3\text{BBr}_2\text{Cl}$

Heat Capacity and Entropy

The vibrational frequencies have all been observed and assigned by L. P. Lindeman and M. K. Wilson, J. Chem. Phys., 24, 242 (1956). The bond lengths were reported by T. Wentink and V. H. Tienau, J. Chem. Phys., 28, 826 (1958). Bond angles were estimated by analogy with the other trihalides of boron. Individual moments of inertia are $I_B = 35.0754 \times 10^{-39} \text{ g. cm.}^2$, $I_A = 69.5934 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 104.6668 \times 10^{-39} \text{ g. cm.}^2$.

Boron Dibromide Fluoride (BBr₂F)
(Ideal Gas) Mol. Wt. = 189.652

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0	-0.000	INFINITE	-	3.387	-119.181	INFINITE	INFINITE	
100	9.538	60.594	75.373	-2.553	-119.239	-124.788	245.788	
200	12.998	68.496	85.373	-1.373	-119.792	-136.193	136.193	
298	14.894	74.066	94.066	-0.000	-123.000	-126.594	92.792	
300	14.923	74.159	94.067	-0.028	-123.017	-126.617	92.236	
400	15.213	78.640	94.669	1.588	-130.404	-126.301	65.005	
500	17.110	82.360	95.846	3.571	-130.434	-125.274	54.754	
600	17.742	85.538	97.203	5.001	-130.469	-124.237	45.251	
700	18.194	88.309	98.596	6.836	-130.505	-123.196	38.662	
800	18.424	90.761	99.966	8.636	-130.543	-122.150	33.368	
900	18.560	92.848	101.290	10.502	-130.579	-121.099	29.406	
1000	18.596	94.846	102.557	12.388	-130.620	-120.043	26.234	
1100	19.100	96.759	103.767	14.291	-130.669	-118.983	23.639	
1200	19.214	98.426	104.920	16.207	-130.724	-117.917	21.475	
1300	19.305	99.968	106.019	18.133	-130.788	-116.848	19.643	
1400	19.376	101.411	107.061	20.068	-130.860	-115.772	18.072	
1500	19.439	102.741	108.058	22.009	-130.944	-114.694	16.710	
1600	19.489	103.997	109.025	23.955	-131.037	-113.607	15.517	
1700	19.531	105.180	109.941	25.906	-131.140	-112.514	14.464	
1800	19.566	106.297	110.819	27.861	-131.252	-111.417	13.427	
1900	19.595	107.345	111.661	29.824	-131.371	-110.310	12.408	
2000	19.623	108.332	112.471	31.780	-131.496	-109.199	11.432	
2100	19.645	109.319	113.251	33.744	-131.627	-108.080	10.427	
2200	19.665	110.234	114.002	35.709	-131.764	-106.957	9.425	
2300	19.682	111.108	114.727	37.676	-131.906	-105.824	8.425	
2400	19.696	111.945	115.424	39.644	-132.054	-104.684	7.425	
2500	19.711	112.751	116.104	41.614	-132.204	-103.539	6.425	
2600	19.723	113.524	116.760	43.588	-132.354	-102.385	5.425	
2700	19.734	114.269	117.394	45.560	-132.504	-101.225	4.425	
2800	19.743	114.984	118.004	47.534	-132.654	-100.060	3.425	
2900	19.750	115.670	118.594	49.509	-132.804	-98.894	2.425	
3000	19.760	116.349	119.169	51.485	-132.954	-97.729	1.425	
3100	19.767	116.997	119.752	53.461	-133.104	-96.564	0.425	
3200	19.773	117.625	120.301	55.438	-133.254	-95.399	-0.575	
3300	19.778	118.234	120.819	57.414	-133.404	-94.234	-1.575	
3400	19.784	118.824	121.365	59.390	-133.554	-93.069	-2.575	
3500	19.789	119.398	121.945	61.372	-133.704	-91.904	-3.575	
3600	19.794	119.955	122.531	63.352	-133.854	-90.739	-4.575	
3700	19.798	120.497	123.124	65.331	-134.004	-89.574	-5.575	
3800	19.801	121.024	123.694	67.309	-134.154	-88.409	-6.575	
3900	19.805	121.546	124.246	69.287	-134.304	-87.244	-7.575	
4000	19.809	122.041	124.773	71.272	-134.454	-86.079	-8.575	
4100	19.812	122.531	125.284	73.253	-134.604	-84.914	-9.575	
4200	19.815	123.008	125.773	75.235	-134.754	-83.749	-10.575	
4300	19.818	123.474	126.246	77.217	-134.904	-82.584	-11.575	
4400	19.820	123.934	126.694	79.199	-135.054	-81.419	-12.575	
4500	19.822	124.375	127.124	81.180	-135.204	-80.254	-13.575	
4600	19.824	124.811	127.534	83.162	-135.354	-79.089	-14.575	
4700	19.826	125.237	127.924	85.145	-135.504	-77.924	-15.575	
4800	19.828	125.654	128.294	87.127	-135.654	-76.759	-16.575	
4900	19.830	126.064	128.644	89.111	-135.804	-75.594	-17.575	
5000	19.832	126.464	128.974	91.094	-135.954	-74.429	-18.575	
5100	19.833	126.857	129.284	93.077	-136.104	-73.264	-19.575	
5200	19.835	127.242	129.574	95.060	-136.254	-72.099	-20.575	
5300	19.837	127.617	129.844	97.043	-136.404	-70.934	-21.575	
5400	19.839	127.991	130.094	99.026	-136.554	-69.769	-22.575	
5500	19.840	128.357	130.324	101.011	-136.704	-68.604	-23.575	
5600	19.841	128.712	130.534	102.995	-136.854	-67.439	-24.575	
5700	19.841	129.063	130.724	104.979	-137.004	-66.274	-25.575	
5800	19.841	129.404	130.894	106.962	-137.154	-65.109	-26.575	
5900	19.843	129.748	131.044	108.946	-137.304	-63.944	-27.575	
6000	19.844	130.081	131.174	110.930	-137.454	-62.779	-28.575	

Sept. 30, 1962; Dec. 31, 1964

BBr₂F

BORON DIBROMIDE FLUORIDE (BBr₂F) (IDEAL GAS)

MOL. WT. = 189.652

Point Group C_{2v}
 $\Delta H_f^\circ = [-119.2 \pm 10] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [-123 \pm 10] \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [74.066] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
1310 (1)	869 (1)
[418](1)	[283](1)
[183](1)	[496](1)

Bond Distance: B-Br = 1.87 Å B-Cl = 1.295 Å
 Bond Angle: Br-B-Br = [120°] Br-B-F = [120°]
 $\sigma = 2$

Product of the Moments of Inertia: $I_A I_B I_C = 8.72359 \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_f^\circ = 0$ for the reaction $2\text{BBr}_3 + \text{BF}_3 \rightarrow 3\text{BBr}_2\text{F}$.

Heat Capacity and Entropy.

Two of the vibrational frequencies were observed and assigned by L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956), the remaining frequencies were calculated by a normal coordinate treatment using force constants obtained by comparison with the other mixed trihalides. The bond distances were reported by T. Wentink and V. H. Hienau, J. Chem. Phys. 28, 826 (1958). The bond angles were estimated by analogy with the other trihalides. The individual moments of inertia were $I_B = 14.8452 \times 10^{-59} \text{ g. cm.}^2$, $I_A = 69.5934 \times 10^{-59} \text{ g. cm.}^2$ and $I_C = 84.4386 \times 10^{-59} \text{ g. cm.}^2$.

BBr₂F

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈ °	ΔH _f °	Log K _P
0	0.000	INFINITE	0.017	20.854	20.854	INFINITE
100	9.255	98.132	21.889	21.889	21.889	21.889
200	12.726	69.617	25.000	25.000	25.000	25.000
298	12.726	69.617	25.000	25.000	25.000	21.915
300	12.757	69.896	25.021	25.021	25.021	21.802
400	14.209	73.776	32.578	32.578	32.578	16.403
500	15.247	77.065	32.562	32.562	32.562	12.635
600	16.006	79.915	32.555	32.555	32.555	10.444
700	16.589	82.428	33.025	33.025	33.025	8.729
800	17.054	84.675	33.136	33.136	33.136	7.438
900	17.434	86.706	33.231	33.231	33.231	6.431
1000	17.748	88.500	33.316	33.316	33.316	5.623
1100	18.011	90.264	33.396	33.396	33.396	4.960
1200	18.231	91.841	33.473	33.473	33.473	4.407
1300	18.418	93.308	33.551	33.551	33.551	3.937
1400	18.577	94.678	33.631	33.631	33.631	3.533
1500	18.713	95.965	33.718	33.718	33.718	3.183
1600	18.830	97.176	33.812	33.812	33.812	2.876
1700	18.931	98.321	33.912	33.912	33.912	2.604
1800	19.018	99.406	34.019	34.019	34.019	2.361
1900	19.095	100.436	34.132	34.132	34.132	2.143
2000	19.162	101.417	34.249	34.249	34.249	1.947
2100	19.221	102.354	34.371	34.371	34.371	1.768
2200	19.273	103.249	34.498	34.498	34.498	1.605
2300	19.319	104.107	34.631	34.631	34.631	1.456
2400	19.361	104.930	34.769	34.769	34.769	1.324
2500	19.398	105.721	34.910	34.910	34.910	1.192
2600	19.431	106.482	40.0436	40.0436	40.0436	1.066
2700	19.461	107.216	40.576	40.576	40.576	0.920
2800	19.488	107.924	41.115	41.115	41.115	0.803
2900	19.512	108.609	41.659	41.659	41.659	0.693
3000	19.534	109.271	42.218	42.218	42.218	0.590
3100	19.555	109.911	42.792	42.792	42.792	0.494
3200	19.573	110.533	43.376	43.376	43.376	0.403
3300	19.590	111.135	43.969	43.969	43.969	0.317
3400	19.606	111.720	44.570	44.570	44.570	0.236
3500	19.620	112.289	45.178	45.178	45.178	0.160
3600	19.633	112.842	45.793	45.793	45.793	0.087
3700	19.646	113.380	46.414	46.414	46.414	0.019
3800	19.657	113.904	47.041	47.041	47.041	-0.047
3900	19.668	114.415	47.673	47.673	47.673	-0.119
4000	19.677	114.913	48.310	48.310	48.310	-0.194
4100	19.686	115.399	48.952	48.952	48.952	-0.274
4200	19.695	115.873	49.600	49.600	49.600	-0.358
4300	19.703	116.337	50.253	50.253	50.253	-0.446
4400	19.711	116.791	50.911	50.911	50.911	-0.538
4500	19.717	117.233	51.574	51.574	51.574	-0.634
4600	19.724	117.666	52.242	52.242	52.242	-0.734
4700	19.730	118.090	52.915	52.915	52.915	-0.838
4800	19.735	118.506	53.593	53.593	53.593	-0.946
4900	19.741	118.913	54.276	54.276	54.276	-1.058
5000	19.746	119.312	54.964	54.964	54.964	-1.174
5100	19.751	119.703	55.657	55.657	55.657	-1.294
5200	19.755	120.086	56.365	56.365	56.365	-1.418
5300	19.759	120.463	57.078	57.078	57.078	-1.546
5400	19.763	120.836	57.796	57.796	57.796	-1.678
5500	19.767	121.199	58.519	58.519	58.519	-1.814
5600	19.771	121.551	59.247	59.247	59.247	-1.954
5700	19.774	121.901	59.980	59.980	59.980	-2.098
5800	19.778	122.245	60.718	60.718	60.718	-2.246
5900	19.781	122.584	61.461	61.461	61.461	-2.398
6000	19.784	122.913	62.209	62.209	62.209	-2.554

Mar. 31, 1966

BORON DIBROMIDE HYDRIDE (BBr₂H₂) (IDEAL GAS) MOL. WT. = 171.63697

Point Group C_{2v}

$\Delta H_f^\circ = [-21 \pm 5] \text{ kcal. mole}^{-1}$

$\Delta H_f^\circ 298.15 = [-25 \pm 5] \text{ kcal. mole}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}
2600 (1)	1044 (1)
[532](1)	775 (1)
[158](1)	783 (1)

Bond Distance : B-H = 1.20 Å B-Br = [1.87] Å

Bond Angle: Br-B-Br = 119.3 ± 2° Br-B-H = 120.3 ± 1°

Product of the Moments of Inertia: $I_A I_B I_C = 1.08645 \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$

$\sigma = 2$

Heat of Formation.

The value of $\Delta H_f^\circ 298.15$ (BBr₂H₂, g) was derived by assuming the B-H bond strength to be 92 kcal. mole⁻¹, the same as that in BCl₂H(g).

Heat Capacity and Entropy.

The molecular structure, B-H bond distance and bond angle were obtained from L. Lynds and C. D. Bass, J. Chem. Phys. 41, 3165 (1964). The B-Br bond distance was taken from that in BBr₃(g) molecule. The vibrational frequencies adopted and corrected to the average isotopic species were assigned by O. Brioux de Mandirola and J. F. Westerkamp, Spectrochim. Acta, 21, 1101 (1965), from infrared spectrum. The values in brackets are calculated by the Wilson's FO-method. Infrared spectrum of BBr₂H(g) was also reported by S. K. Mason and R. P. Porter, J. Phys. Chem. 69, 2461 (1965), and three frequencies, ν_1 , ν_2 and ν_3 , were assigned. The three principal moments of inertia are: $I_A = 6.87842 \times 10^{-38}$, $I_B = 2.2244 \times 10^{-38}$ and $I_C = 7.10086 \times 10^{-38} \text{ g. cm.}^2$

Boron Tribromide (BB₃)

(Liquid) Mol. Wt. = 250.568

BB₃

T, °K.	C _p ^o	$\frac{S^o - (F^o - H_{298}^o)/T}{\text{cal. mole}^{-1}\text{deg.}^{-1}}$	$\frac{H^o - H_{298}^o}{\text{kcal. mole}^{-1}}$	ΔH_f^o	ΔF_f^o	Log K _P
0						
200						
258						
300	30.600	54.760	54.700	0.000	- 57.000	- 56.610
350	30.600	54.889	54.701	0.057	- 56.998	- 56.616
400	30.600	54.987	54.901	0.117	- 66.620	- 56.639
500	30.600	55.052	55.181	0.177	- 65.297	- 51.550
600	30.600	55.099	60.705	9.237	- 64.044	- 48.919
700	30.600	55.129	63.249	12.297	- 62.840	- 46.494
800	30.600	55.157	65.706	15.357	- 61.669	- 44.240
900	30.600	55.183	68.083	18.417	- 60.522	- 42.130
1000	30.600	55.206	70.253	21.477	- 59.397	- 40.145

BORON TRIBROMIDE (BB₃)

(LIQUID)

MOL. WT. = 250.568

$S_{298.15}^o = 54.7 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 227.2^\circ\text{K}$
 $T_b = 364.4^\circ\text{K}$
 $\Delta H_f^o = 298.15 = -57.0 \pm 0.2 \text{ kcal. mole}^{-1}$
 $\Delta H_m^o = \text{Unknown}$
 $\Delta H_v^o = 7.30 \text{ kcal. mole}^{-1}$

Heat of Formation.

The heat of formation of boron tribromide liquid has been determined by H. A. Skinner and N. B. Smith, Trans. Farad. Soc. 51, 19 (1955) by hydrolysis to H₃BO₃ and HBr. The adopted heat of formation was calculated from Skinner's hydrolysis data using $\Delta H_f^o \text{ H}_3\text{BO}_3(\text{c})$ from these tables, $\Delta H_{\text{soln}}^o \text{ H}_3\text{BO}_3$ from L. G. Faallino, National Research Corporation Special Report NMR-3608 (OO) June 2, 1964, with the dilution data of J. Smisko and L. S. Mason, J. Am. Chem. Soc. 72, 3679 (1950). The $\Delta H_f^o \text{ HBr}(\text{aq})$ was taken from W. H. Evans, Appendix III, Natl. Bureau of Standards Report 8504, 1 July 1964.

Heat Capacity and Entropy.

The heat capacity was estimated from that of the gas by K. K. Kelley USNM Bulletin 383. The entropy was back calculated from that of the gas by adjusting the free energy functions to give the best fit of the vapor pressure data.

Melting Data.

The temperature of melting was reported by J. Goubeau and H. Keller, Z. anorg. allgem. Chem. 267, 1 (1951) and A. Stock and E. Kusa, Ber. 47, 3113 (1914). This value was recently confirmed by the triple point measurement of 227.31°K by W. F. Barber, C. F. Boynton and P. E. Gallagher J. Chem. Eng. Data 9, 137 (1964).

Boiling Data.

The boiling point is from the data of Stock and Kusa, loc. cit. A second and third law analysis of the vapor pressure data of Stock and Kusa (1) and Barber et. al. (2) loc. cit. indicated that the data of Stock gave the best agreement as indicated below.

	Second Law	Third Law
$\Delta H_v^o 298.15 \text{ kcal. mole}^{-1}$	$S_{298}^o = 54.7$	$S_{298}^o = 54.26$
Ref. 1.	8.175 $\pm$ 0.03	8.222 (-0.02)
Ref. 2.	8.229 $\pm$ 0.03	8.203 (-0.44)
		8.361 (0.42)
		8.347 (0.00)

Ref. 1. had the first eight data points rejected due to a statistical test on the third law values. The values in parentheses are values of the third law drift measured as $\Delta(\Delta H) / \Delta T$. The second law entropy also confirmed the choice of the data of ref. 1 and an entropy of 54.7 cal. deg.⁻¹ mole⁻¹.

BB₃

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	(F°-H ₂₉₈)/T	II°-II ₂₉₈	ΔH _f ^o	Log K _f
0	-0.000	-0.000	INFINITE	-3.755	-43.475	-43.475	INFINITE
100	11.546	62.344	90.633	-2.829	-43.556	-47.852	10.576
200	14.474	71.364	78.918	-1.511	-44.075	-51.061	56.777
298	16.198	77.487	77.487	-0.000	-48.800	-55.213	40.470
300	16.224	77.588	77.488	0.000	-48.825	-55.252	40.249
400	17.478	86.350	70.404	3.468	-50.786	-53.069	23.560
500	18.079	89.720	80.852	5.321	-50.760	-52.807	10.234
600	18.545	92.604	82.329	7.192	-50.745	-51.650	16.125
700	18.857	95.060	83.775	9.080	-50.736	-50.605	20.984
800	19.120	97.133	85.175	11.000	-50.736	-49.680	25.000
900	19.345	98.842	86.491	12.934	-50.740	-48.883	28.550
1000	19.532	100.200	87.750	14.880	-50.750	-48.200	31.750
1100	19.682	101.273	88.951	16.873	-50.758	-47.628	34.633
1200	19.800	102.067	89.999	18.919	-50.765	-47.150	37.250
1300	19.895	102.620	90.900	21.000	-50.773	-46.750	39.650
1400	19.968	103.000	91.660	23.125	-50.780	-46.400	41.800
1500	20.020	103.234	92.296	25.291	-50.784	-46.100	43.650
1600	20.055	103.360	92.820	27.500	-50.786	-45.850	45.250
1700	20.078	103.400	93.250	29.750	-50.788	-45.650	46.650
1800	20.092	103.440	93.590	32.040	-50.789	-45.500	47.850
1900	20.098	103.470	93.850	34.370	-50.790	-45.400	48.900
2000	20.105	103.490	94.040	36.740	-50.791	-45.350	49.850
2100	20.112	103.500	94.180	39.150	-50.792	-45.300	50.750
2200	20.118	103.510	94.280	41.600	-50.793	-45.250	51.600
2300	20.124	103.520	94.350	44.090	-50.794	-45.200	52.400
2400	20.129	103.530	94.400	46.620	-50.795	-45.150	53.150
2500	20.134	103.540	94.440	49.190	-50.796	-45.100	53.850
2600	20.138	103.550	94.470	51.800	-50.797	-45.050	54.500
2700	20.142	103.560	94.490	54.450	-50.798	-45.000	55.100
2800	20.145	103.570	94.500	57.140	-50.799	-44.950	55.650
2900	20.148	103.580	94.510	59.870	-50.800	-44.900	56.150
3000	20.151	103.590	94.520	62.640	-50.801	-44.850	56.600
3100	20.154	103.600	94.530	65.450	-50.802	-44.800	57.000
3200	20.157	103.610	94.540	68.300	-50.803	-44.750	57.350
3300	20.160	103.620	94.550	71.190	-50.804	-44.700	57.650
3400	20.162	103.630	94.560	74.120	-50.805	-44.650	57.900
3500	20.165	103.640	94.570	77.090	-50.806	-44.600	58.100
3600	20.167	103.650	94.580	80.100	-50.807	-44.550	58.250
3700	20.169	103.660	94.590	83.150	-50.808	-44.500	58.350
3800	20.171	103.670	94.600	86.240	-50.809	-44.450	58.400
3900	20.173	103.680	94.610	89.370	-50.810	-44.400	58.450
4000	20.175	103.690	94.620	92.540	-50.811	-44.350	58.500
4100	20.177	103.700	94.630	95.750	-50.812	-44.300	58.550
4200	20.179	103.710	94.640	99.000	-50.813	-44.250	58.600
4300	20.181	103.720	94.650	102.290	-50.814	-44.200	58.650
4400	20.183	103.730	94.660	105.620	-50.815	-44.150	58.700
4500	20.185	103.740	94.670	108.990	-50.816	-44.100	58.750
4600	20.187	103.750	94.680	112.400	-50.817	-44.050	58.800
4700	20.189	103.760	94.690	115.850	-50.818	-44.000	58.850
4800	20.191	103.770	94.700	119.340	-50.819	-43.950	58.900
4900	20.193	103.780	94.710	122.870	-50.820	-43.900	58.950
5000	20.195	103.790	94.720	126.440	-50.821	-43.850	59.000
5100	20.197	103.800	94.730	130.050	-50.822	-43.800	59.050
5200	20.199	103.810	94.740	133.700	-50.823	-43.750	59.100
5300	20.201	103.820	94.750	137.390	-50.824	-43.700	59.150
5400	20.203	103.830	94.760	141.120	-50.825	-43.650	59.200
5500	20.205	103.840	94.770	144.890	-50.826	-43.600	59.250
5600	20.207	103.850	94.780	148.700	-50.827	-43.550	59.300
5700	20.209	103.860	94.790	152.550	-50.828	-43.500	59.350
5800	20.211	103.870	94.800	156.440	-50.829	-43.450	59.400
5900	20.213	103.880	94.810	160.370	-50.830	-43.400	59.450
6000	20.215	103.890	94.820	164.340	-50.831	-43.350	59.500

Dec. 31, 1961; Sept. 30, 1962; Dec. 31, 1964

Point Group D_{3h}
 $S_{298.15}^o = 77.487 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = -43.5 \pm 0.22 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o 298.15 = -48.8 \pm 0.22 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = {1}

Vibrational Frequencies and Degeneracies

$\omega_e, \text{cm.}^{-1}$	Deg.
278 (1)	278 (1)
379 (1)	379 (1)
827 (2)	827 (2)
150 (2)	150 (2)

Bond Distance: B-Br = $1.87 \pm 0.02 \text{ \AA}$
 Bond Angle: Br-B-Br = $120^\circ \pm 6^\circ$
 Product of the Moments of Inertia: $I_A I_B I_C = 6.74115 \times 10^{-112} \text{ g. cm.}^6$
 $\sigma = 8$

Heat of Formation.

ΔH_f^o 298 was obtained from the heat of formation of the liquid plus the heat of vaporization at 298°K, taken as 8.20 kcal. mole⁻¹ as the average second and third law values derived from the vapor pressures of A. Stock and E. Kuas, Ber. 47, 3113 (1914). See BBr₃(1) for details.

Heat Capacity and Entropy.

Vibrational frequencies were obtained from T. Wentink, Jr., and V. H. Tiensuu, J. Chem. Phys., 28, 825 (1958) modified for the natural isotopic abundances (B10 16.83%, B11 81.17%) given by J. R. Bredford, "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., 1958. B-Br bond distance was reported by T. Wentink, Jr., and V. H. Tiensuu, loc. cit. Br-B-Br angle was taken from L. E. Sutton (editor), "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958. The individual moments of inertia were $I_A = I_B = 419.167 \times 10^{-39} \text{ g. cm.}^2$, $I_C = 836.375 \times 10^{-39} \text{ g. cm.}^2$.

BORON MONOCHLORIDE (BCl)

(IDEAL GAS)

MOL. WT. = 46.277

Boron Monochloride (BCl)

(Ideal Gas) Mol. Wt. = 46.277

Ground State Configuration 1^2

$$\Delta H_f^0 = 33.1 \pm 4.0 \text{ kcal mole}^{-1}$$

$$\Delta H_f^{298.15} = 50.942 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{298.15} = 33.8 \pm 4.0 \text{ kcal mole}^{-1}$$

Electronic Levels and Quantum Weight

$$\frac{g_i}{g_0} \text{ cm}^{-1}$$

$$\frac{g_i}{g_0}$$

$$\omega_e x_e = 5.167 \text{ cm}^{-1}$$

$$\sigma = 1$$

$$\omega_e = 843.65 \text{ cm}^{-1}$$

$$B_e = 0.6914 \text{ cm}^{-1}$$

$$a_e = 0.00857 \text{ cm}^{-1}$$

$$r_e = 1.7157 \text{ \AA}$$

Heat of Formation

The dissociation energy (D_0^0) of BCl(g) has been reported by G. Herzberg¹, A. G. Gaydon² and R. F. Barrow³, respectively. Hence the corresponding values of $\Delta H_f^{298.15}$ for BCl(g) were derived. The results are given as follows.

$$\Delta H_f^{298.15}$$

$$\text{kcal mole}^{-1}$$

$$62.6$$

$$41.8 \pm 9.2$$

$$33.8 \pm 4$$

$$127$$

$$96.9$$

$$4.2$$

$$5.1 \pm 0.4$$

$$117.6 \pm 9.2$$

$$127$$

$$96.9$$

$$4.2$$

$$5.1 \pm 0.4$$

$$117.6 \pm 9.2$$

$$127$$

$$96.9$$

$$4.2$$

$$5.1 \pm 0.4$$

$$117.6 \pm 9.2$$

$$127$$

$$96.9$$

$$4.2$$

$$5.1 \pm 0.4$$

$$117.6 \pm 9.2$$

$$127$$

$$96.9$$

$$4.2$$

$$5.1 \pm 0.4$$

$$117.6 \pm 9.2$$

$$127$$

$$96.9$$

$$4.2$$

$$5.1 \pm 0.4$$

$$117.6 \pm 9.2$$

$$127$$

1 G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950.

2 A. G. Gaydon, "Association Energies", Chapman and Hall Ltd., London, 1953.

3 R. F. Barrow, Trans. Faraday Soc. **56**, 952 (1960).

The last value of $\Delta H_f^{298.15}$ listed in the above table is adopted. Using the bond energy, $D^0(\text{B-Cl})$, obtained from BCl₃(g) molecule, the heat of formation ($\Delta H_f^{298.15}$) for BCl(g) was calculated as $37.8 \text{ kcal mole}^{-1}$ employing the same ratio of $D^0(\text{B-X})$ /average bond energy of B₃ as found in B₂(g) and B₃(g), which is within the uncertainty of the value evaluated from dissociation energy.

Heat Capacity and Entropy

The spectroscopic constants were obtained from G. Herzberg, loc. cit. and corrected to the average isotopic species. The principal moment of inertia (I) is $4.0514 \times 10^{-39} \text{ g cm}^2$.

T, °K	C _p ^o	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	0.000	INFINITE	2.118	33.071	33.071	INFINITE
100	6.959	43.155	57.486	1.423	33.409	31.362	-68.537
200	7.140	46.013	57.619	0.721	33.671	29.202	-31.908
298	7.267	50.942	58.842	0.000	33.800	26.974	-15.772
300	7.575	50.988	59.042	0.014	33.802	26.932	-15.619
400	7.967	53.224	51.244	0.792	33.843	24.633	-13.458
500	8.248	55.034	51.827	1.604	33.815	22.333	-9.761
600	8.442	56.556	52.491	2.439	33.760	20.043	-7.300
700	8.579	57.868	53.168	3.299	33.637	17.769	-5.547
800	8.678	59.020	53.829	4.153	33.512	15.510	-4.237
900	8.752	60.047	54.464	5.025	33.372	13.267	-3.222
1000	8.810	60.972	55.069	5.903	33.219	11.042	-2.413
1100	8.856	61.814	55.645	6.786	33.049	8.832	-1.755
1200	8.894	62.586	56.191	7.674	32.868	6.639	-1.209
1300	8.926	63.300	56.711	8.565	32.674	4.460	-0.750
1400	8.954	63.962	57.206	9.459	32.469	2.298	-0.359
1500	8.978	64.581	57.677	10.356	32.252	0.149	-0.022
1600	9.000	65.161	58.127	11.255	32.024	-1.083	0.271
1700	9.020	65.707	58.557	12.156	31.785	-2.300	0.527
1800	9.038	66.223	58.968	13.059	31.538	-3.525	0.753
1900	9.054	66.712	59.363	13.963	31.283	-4.754	0.954
2000	9.070	67.177	59.742	14.869	31.023	-5.979	1.133
2100	9.085	67.620	60.107	15.777	30.758	-7.203	1.294
2200	9.099	68.043	60.458	16.686	30.488	-8.428	1.439
2300	9.112	68.448	60.797	17.597	30.214	-9.653	1.570
2400	9.125	68.836	61.124	18.509	29.936	-10.878	1.689
2500	9.138	69.209	61.440	19.422	29.656	-12.103	1.788
2600	9.150	69.567	61.746	20.336	29.368	-13.328	1.869
2700	9.162	69.913	62.042	21.252	29.071	-14.553	1.943
2800	9.174	70.246	62.329	22.169	28.764	-15.778	2.011
2900	9.185	70.568	62.607	23.087	28.452	-16.999	2.074
3000	9.196	70.880	62.878	24.006	28.132	-18.217	2.132
3100	9.207	71.182	63.141	24.926	27.804	-19.432	2.186
3200	9.218	71.474	63.397	25.847	27.464	-20.647	2.235
3300	9.229	71.758	63.646	26.770	27.114	-21.862	2.281
3400	9.240	72.034	63.889	27.693	26.754	-23.077	2.323
3500	9.250	72.302	64.125	28.618	26.384	-24.292	2.363
3600	9.261	72.562	64.356	29.543	25.994	-25.507	2.400
3700	9.271	72.816	64.581	30.470	25.591	-26.722	2.435
3800	9.281	73.064	64.801	31.397	25.174	-27.937	2.467
3900	9.292	73.305	65.016	32.326	24.744	-29.152	2.497
4000	9.302	73.540	65.226	33.256	24.294	-30.367	2.528
4100	9.312	73.770	65.432	34.186	23.824	-31.582	2.558
4200	9.322	73.995	65.633	35.118	23.334	-32.797	2.588
4300	9.332	74.214	65.830	36.051	22.824	-34.012	2.618
4400	9.342	74.429	66.023	36.984	22.294	-35.227	2.648
4500	9.352	74.639	66.212	37.919	21.744	-36.442	2.678
4600	9.361	74.844	66.398	38.855	21.174	-37.657	2.708
4700	9.371	75.046	66.579	39.791	20.584	-38.872	2.738
4800	9.381	75.243	66.758	40.729	19.974	-40.087	2.768
4900	9.391	75.437	66.933	41.668	19.344	-41.302	2.798
5000	9.401	75.627	67.105	42.607	18.684	-42.517	2.828
5100	9.410	75.813	67.274	43.548	17.994	-43.732	2.858
5200	9.420	75.996	67.440	44.489	17.284	-44.947	2.888
5300	9.430	76.175	67.603	45.432	16.554	-46.162	2.918
5400	9.439	76.351	67.763	46.375	15.794	-47.377	2.948
5500	9.449	76.525	67.921	47.320	14.994	-48.592	2.978
5600	9.459	76.695	68.076	48.265	14.154	-49.807	3.008
5700	9.468	76.863	68.229	49.211	13.274	-51.022	3.038
5800	9.478	77.027	68.379	50.159	12.354	-52.237	3.068
5900	9.488	77.186	68.527	51.107	11.394	-53.452	3.098
6000	9.497	77.349	68.673	52.056	10.394	-54.667	3.128

Mar. 31, 1961, Dec. 31, 1964

T, °K	C _p ^o	S ^o - (C _p ^o - H _{298.15})/T	ΔH ^o kcal/mol	ΔG ^o	Log K _p
0					
100					
200					
298	7.563	52.347	52.346	.000	286.268 - 209.840
300	7.571	52.393	52.347		286.213 - 208.506
400	7.563	54.628	52.649	.792	283.198 - 154.732
500	7.643	54.836	53.231	1.603	286.056 - 122.412
600	8.437	57.058	53.895	2.937	286.439 - 100.833
700	8.437	57.249	53.871	2.964	276.431 - 85.397
800	8.472	60.420	55.232	4.151	297.202 - 73.406
900	8.746	61.446	55.667	5.022	297.559 - 64.779
1000	8.803	62.371	56.872	5.699	297.902 - 57.550
1100	8.689	63.212	57.087	6.782	289.229 - 51.428
1200	8.684	64.984	57.593	7.669	286.544 - 46.668
1300	8.918	64.696	58.112	8.559	292.620 - 42.503
1400	8.945	65.358	58.607	9.452	289.136 - 38.913
1500	8.969	65.976	59.077	10.348	285.697 - 35.768
1600	8.990	66.556	59.527	11.244	289.483 - 33.070
1700	9.009	67.101	59.957	12.144	289.990 - 30.662
1800	9.026	67.617	60.368	13.048	284.679 - 28.518
1900	9.043	68.105	60.762	13.951	281.246 - 26.599
2000	9.058	68.569	61.141	14.856	287.599 - 24.871
2100	9.072	69.012	61.506	15.742	293.939 - 23.304
2200	9.084	69.434	61.857	16.620	290.269 - 21.882
2300	9.096	69.838	62.195	17.500	296.586 - 20.561
2400	9.111	70.226	62.521	18.400	292.901 - 19.367
2500	9.123	70.598	62.837	19.300	289.385 - 18.268
2600	9.135	70.956	63.142	20.215	295.823 - 17.301
2700	9.146	71.300	63.436	21.229	292.359 - 16.377
2800	9.157	71.634	63.725	22.144	297.036 - 15.519
2900	9.168	71.955	64.003	23.060	297.252 - 14.719
3000	9.179	72.266	64.274	23.978	297.468 - 13.972
3100	9.190	72.567	64.546	24.896	297.484 - 13.273
3200	9.201	72.859	64.792	25.816	297.900 - 12.617
3300	9.212	73.143	65.041	26.736	298.115 - 12.000
3400	9.223	73.418	65.283	27.658	298.329 - 11.419
3500	9.235	73.685	65.519	28.581	298.543 - 10.871
3600	9.246	73.946	65.750	29.505	298.758 - 10.353
3700	9.258	74.199	65.975	30.430	298.972 - 9.863
3800	9.270	74.446	66.194	31.357	299.187 - 9.398
3900	9.282	74.687	66.409	32.284	299.401 - 8.956
4000	9.295	74.922	66.619	33.213	299.614 - 8.534
4100	9.308	75.152	66.828	34.143	299.828 - 8.116
4200	9.322	75.376	67.025	35.075	299.997 - 7.719
4300	9.336	75.596	67.222	36.007	299.773 - 7.341
4400	9.351	75.811	67.415	36.942	299.219 - 6.984
4500	9.366	76.021	67.604	37.878	298.664 - 6.682
4600	9.382	76.227	67.789	38.815	298.112 - 6.425
4700	9.399	76.429	67.971	39.744	297.560 - 6.227
4800	9.416	76.627	68.149	40.665	297.007 - 6.044
4900	9.434	76.821	68.324	41.637	296.455 - 5.885
5000	9.453	77.017	68.496	42.582	295.904 - 5.742
5100	9.472	77.199	68.665	43.528	295.354 - 5.625
5200	9.492	77.384	68.830	44.476	294.805 - 5.524
5300	9.513	77.565	68.994	45.426	294.257 - 5.437
5400	9.534	77.743	69.154	46.379	293.709 - 5.360
5500	9.557	77.918	69.312	47.333	293.163 - 5.291
5600	9.580	78.090	69.467	48.289	292.616 - 5.231
5700	9.603	78.260	69.620	49.249	292.070 - 5.180
5800	9.627	78.427	69.770	50.211	291.526 - 5.136
5900	9.652	78.592	69.918	51.175	290.983 - 5.099
6000	9.678	78.754	70.064	52.141	290.441 - 5.064

June 30, 1968

(IDEAL GAS)

BORON MONOCHLORIDE UNIPosITIVE ION (BCl⁺)

Ground State Configuration [2_g]

ΔH_f^o = [299.3 ± 10] kcal/mol

GFW = 42.2634

S_{298.15} = [52.3 ± 0.5] gibbs/mol

ΔH_f^o_{298.15} = [295 ± 10] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[2]
[28000]	[4]
ω_e = [845] cm ⁻¹	$\sigma = 1$
B_e = [0.68] cm ⁻¹	$r_g = [1.73] \text{ \AA}$
$\omega_e x_e$ = [5] cm ⁻¹	
a_g = [0.0056] cm ⁻¹	

Heat of Formation

Several values of the appearance potential of BCl⁺ from BCl₃ have been reported. Oberghaus (1) gave 19.2eV, Harriott and Craggs (2) reported 16.54 ± 0.07eV, and Koski et al. (3) obtained two values of 17.2 ± 0.2eV and 20 ± 0.2eV. We make the presumption that the higher values, 19.2 and 20, refer to the reaction BCl₃(g) + e⁻ → BCl⁺ + 2Cl₂(g) + 2e⁻ and the other values to BCl₃(g) + e⁻ → BCl⁺ + Cl₂(g) + 2e⁻. Using the lower value in each case to help eliminate any excess kinetic energy, we obtain ΔH_f^o₂₉₈(BCl⁺, g) = 289 and 300 kcal/mol, respectively. We adopt an average value of ΔH_f^o₂₉₈(BCl⁺, g) = 295 ± 10 kcal/mol, which corresponds to an ionization potential for BCl(g) of 11.3 ± 0.3eV.

Heat Capacity and Entropy

BCl⁺ is isoelectronic with BaCl and the ground state configuration and electronic levels are estimated by comparison with BaCl. The bond length, frequency and anharmonicity constant are estimated between the values for BCl and BaCl; the rotational constant is calculated from the bond length and atomic masses, and σ_e is obtained from the above constants assuming a Morse potential function.

The enthalpy at 0°K is -2.118 kcal/mol.

References

1. O. Oberghaus, Z. Phys. 128, 366 (1950).
2. J. Harriott and J. D. Craggs, J. Electron. Contr. 3, 194 (1957).
3. W. S. Koski, J. J. Kaufman and C. F. Paolucci, J. Am. Chem. Soc. 81, 1326 (1959).

Boron Chloride Difluoride (BCIF₂)

(Ideal Gas) Mol. Wt. = 84.277

BORON CHLORIDE DIFLUORIDE (BClF₂) (IDEAL GAS) MOL. WT. = 84.277

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞.000	INFINITE	2.945	-	211.046	-	211.046	INFINITE
100	8.428	54.323	75.737	-	211.046	-	210.389	459.783
200	10.902	60.893	66.789	-	211.472	-	208.400	228.870
298	13.018	65.667	65.667	∞.000	-	-	208.370	152.732
300	13.052	65.742	65.662	0.24	-	-	208.351	151.776
400	14.637	69.726	66.194	1.613	-	-	207.248	113.230
500	15.814	73.125	67.249	2.938	-	-	206.116	90.089
600	16.683	76.089	68.480	4.565	-	-	204.960	74.653
700	17.267	78.111	69.759	6.507	-	-	203.783	59.468
800	17.657	80.017	71.000	8.764	-	-	202.594	46.004
900	18.171	83.177	72.261	9.825	-	-	201.397	48.904
1000	18.451	85.107	73.456	11.656	-	-	200.188	43.749
1100	18.670	86.876	74.592	13.513	-	-	198.970	39.530
1200	18.834	88.489	75.689	15.389	-	-	197.742	36.032
1300	18.983	90.032	76.750	17.289	-	-	196.507	33.040
1400	19.097	91.433	77.770	19.185	-	-	195.265	30.481
1500	19.190	92.754	78.668	21.099	-	-	194.016	28.267
1600	19.268	93.995	79.606	23.022	-	-	192.759	26.328
1700	19.332	95.158	80.456	24.959	-	-	191.492	24.563
1800	19.389	96.272	81.248	26.889	-	-	190.223	23.005
1900	19.437	97.332	82.148	28.830	-	-	188.942	21.732
2000	19.478	98.320	82.932	30.776	-	-	187.653	20.505
2100	19.513	99.271	83.689	32.726	-	-	186.358	19.394
2200	19.543	100.189	84.421	34.684	-	-	185.057	18.349
2300	19.571	101.069	85.121	36.534	-	-	183.748	17.459
2400	19.595	101.883	85.802	38.393	-	-	182.428	16.612
2500	19.617	102.683	86.462	40.253	-	-	181.094	15.822
2600	19.638	103.453	87.100	42.116	-	-	179.744	15.083
2700	19.652	104.199	87.724	43.974	-	-	178.381	14.395
2800	19.668	104.909	88.321	45.840	-	-	177.019	13.762
2900	19.676	105.599	88.905	47.704	-	-	175.653	13.168
3000	19.684	106.267	89.473	49.573	-	-	174.284	12.615
3100	19.705	106.913	90.025	52.352	-	-	172.910	12.097
3200	19.724	107.539	90.562	55.139	-	-	171.530	11.610
3300	19.738	108.159	91.100	57.934	-	-	170.141	11.151
3400	19.753	108.774	91.597	60.746	-	-	168.749	10.721
3500	19.740	109.306	92.054	63.572	-	-	167.356	10.315
3600	19.748	109.863	92.580	66.411	-	-	165.961	9.930
3700	19.760	110.444	93.095	69.264	-	-	164.566	9.566
3800	19.766	111.044	93.671	72.132	-	-	163.171	9.221
3900	19.776	111.666	94.211	75.014	-	-	161.776	8.894
4000	19.771	111.945	94.671	77.910	-	-	160.381	8.584
4100	19.776	112.433	94.848	80.822	-	-	158.986	8.284
4200	19.785	113.375	95.668	83.756	-	-	157.591	7.994
4300	19.789	113.830	96.095	86.712	-	-	156.196	7.715
4400	19.789	113.830	96.095	89.689	-	-	154.801	7.446
4500	19.792	114.275	96.494	92.689	-	-	153.406	7.186
4600	19.796	114.710	96.885	95.712	-	-	152.011	6.936
4700	19.796	115.132	97.266	98.756	-	-	150.616	6.696
4800	19.802	115.552	97.646	101.810	-	-	149.221	6.466
4900	19.805	115.961	98.015	104.874	-	-	147.826	6.246
5000	19.807	116.361	98.379	107.948	-	-	146.431	6.036
5100	19.810	116.753	98.735	111.032	-	-	145.036	5.836
5200	19.815	117.135	99.089	114.126	-	-	143.641	5.646
5300	19.817	117.515	99.454	117.230	-	-	142.246	5.466
5400	19.817	117.885	99.768	120.344	-	-	140.851	5.296
5500	19.819	118.249	100.100	123.468	-	-	139.456	5.136
5600	19.821	118.606	100.428	126.602	-	-	138.061	4.986
5700	19.824	118.956	100.756	129.746	-	-	136.666	4.846
5800	19.824	119.302	101.084	132.890	-	-	135.271	4.716
5900	19.826	119.641	101.378	136.034	-	-	133.876	4.596
6000	19.827	119.974	101.666	139.178	-	-	132.481	4.486

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Dec. 31, 1964

Point Group = C_{2v} $\Delta H_f^o = -211 \pm 5 \text{ kcal. mole}^{-1}$ $S_{298.15}^o = 65.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^o 298.15 = -211.6 \pm 5 \text{ kcal. mole}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

 $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$

1250 (1)

1430 (1)

697 (1)

366 (1)

429 (1)

608 (1)

1250 (1)

1430 (1)

697 (1)

366 (1)

429 (1)

608 (1)

1250 (1)

1430 (1)

697 (1)

366 (1)

429 (1)

608 (1)

1250 (1)

1430 (1)

697 (1)

366 (1)

429 (1)

608 (1)

1250 (1)

1430 (1)

697 (1)

366 (1)

429 (1)

608 (1)

1250 (1)

1430 (1)

697 (1)

366 (1)

429 (1)

608 (1)

1250 (1)

1430 (1)

697 (1)

366 (1)

429 (1)

608 (1)

1250 (1)

1430 (1)

697 (1)

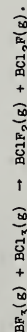
Bond Distances B-Cl = [1.73] Å B-F = [1.295] Å

Bond Angle: F-B-Cl = [120°] F-B-F = [120°]

Product of the Moments of Inertia: $I_{AB}I_C = 3567.6 \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The values for BCl₂F and BClF₂ of $\Delta H_f^o 298.15 = -154$ and $\Delta H_f^o 298.15 = -211.6 \text{ kcal. mole}^{-1}$, respectively, are obtained from the average bond energies of BF₃ and BCl₃. The calculated values were each made less negative by about 0.8 kcal. mole⁻¹ in order to make them consistent with the equilibrium measurements of T. H. Higgins, E. C. Leisegang, C. J. G. Raw, and A. J. Rosauw, J. Chem. Phys. **23**, 1544 (1955) and S. R. Gunn and R. H. Sanborn, J. Chem. Phys. **33**, 955 (1960) for the reaction



Values for the heat of reaction are $\Delta H_{298.15}^o = +1.68 \text{ kcal. mole}^{-1}$ and $\Delta H_{298.15}^o = 1.1$ (uncertainty of -0.5 to +0.8 kcal. mole⁻¹), the former calculated from the measured equilibrium constant and the statistical entropy change and the latter obtained from the variation of the equilibrium constant with temperature. Selection of $\Delta H_{298.15}^o = 1.6 \text{ kcal. mole}^{-1}$ fixes the sum of the heats of formation of BClF₂ and BCl₂F as -385.6 kcal. mole⁻¹, but it does not determine the individual values. Thus, the selected heats of formation are only as accurate as the average bond energy calculations on which they are based. A reasonable estimate of the uncertainty would be $\pm 5 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The observed frequencies of L. P. Lindeman and M. K. Wilson, J. Chem. Phys. **24**, 242 (1956), were adjusted to the normal isotopic composition of 81.2% ¹⁰B and 18.8% ¹¹B. The bond angles were assumed to be 120° and the bond lengths were taken to be the same as in the respective trihalides. As a result, the principal moments of inertia are: $I_A = 17.6044 \times 10^{-39}$, $I_B = 7.335 \times 10^{-39}$, and $I_C = 25.5394 \times 10^{-39} \text{ g. cm.}^2$.

Boron Oxide Chloride (BOCl)
(Ideal Gas) Mol. Wt. = 62.277

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(H°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	INFINITE	-2.536	-75.709	-75.709	INFINITE
100	46.062	55.792	-1.833	-75.720	-76.072	166.247
200	9.382	52.662	.995	-75.662	-76.443	89.520
298	10.765	56.720	.000	-75.600	-76.843	56.925
300	10.785	56.784	.020	-75.599	-76.851	55.983
400	11.642	60.015	1.144	-75.567	-77.275	42.210
500	12.241	62.681	2.340	-75.577	-77.701	33.061
600	12.703	64.955	3.288	-75.615	-78.122	28.455
700	13.053	66.875	4.049	-75.675	-78.542	24.565
800	13.333	68.707	6.109	-75.735	-78.962	21.555
900	13.599	70.295	7.548	-75.804	-79.339	19.265
1000	13.780	71.738	8.718	-75.880	-79.727	17.423
1100	13.845	73.060	43.462	-75.965	-80.108	15.915
1200	14.072	74.270	65.114	-76.055	-80.485	14.605
1300	14.176	75.409	65.318	-76.158	-80.845	13.591
1400	14.263	76.463	66.071	-76.267	-81.201	12.675
1500	14.336	77.450	66.803	-76.386	-81.551	11.881
1600	14.398	78.377	67.497	-76.515	-81.889	11.185
1700	14.450	79.251	68.162	-76.653	-82.216	10.572
1800	14.495	80.079	68.802	-76.801	-82.540	10.031
1900	14.534	80.864	69.417	-76.956	-82.860	9.531
2000	14.568	81.610	70.008	-77.117	-83.166	9.088
2100	14.597	82.321	70.577	-77.284	-83.463	8.686
2200	14.623	83.000	71.128	-77.457	-83.750	8.320
2300	14.645	83.652	71.657	-77.633	-84.038	7.985
2400	14.666	84.275	72.160	-77.823	-84.309	7.677
2500	14.683	84.874	72.646	-78.020	-84.567	7.384
2600	14.699	85.451	73.147	-78.222	-84.808	7.103
2700	14.717	86.000	73.673	-78.429	-85.033	6.830
2800	14.737	86.521	74.205	-78.641	-85.253	6.565
2900	14.758	87.058	74.750	-78.857	-85.468	6.314
3000	14.779	87.558	75.311	-79.076	-85.678	6.074
3100	14.788	88.042	75.886	-79.299	-85.881	5.841
3200	14.797	88.500	76.466	-79.526	-86.078	5.614
3300	14.775	88.965	76.144	-79.757	-86.270	5.401
3400	14.782	89.406	76.528	-79.992	-86.456	5.196
3500	14.789	89.835	76.902	-80.231	-86.638	5.000
3600	14.795	90.251	77.267	-80.474	-86.815	4.813
3700	14.801	90.657	77.623	-80.721	-86.988	4.636
3800	14.806	91.052	77.972	-80.972	-87.156	4.468
3900	14.811	91.436	78.312	-81.226	-87.320	4.307
4000	14.816	91.811	78.645	-81.481	-87.480	4.153
4100	14.820	92.177	78.970	-81.740	-87.636	4.005
4200	14.825	92.534	79.288	-82.002	-87.788	3.863
4300	14.827	92.883	79.601	-82.267	-87.936	3.726
4400	14.831	93.224	79.907	-82.536	-88.080	3.593
4500	14.834	93.557	80.207	-82.809	-88.220	3.464
4600	14.837	93.883	80.500	-83.086	-88.356	3.340
4700	14.840	94.203	80.788	-83.367	-88.488	3.221
4800	14.842	94.515	81.071	-83.650	-88.616	3.107
4900	14.845	94.821	81.349	-83.935	-88.741	2.998
5000	14.847	95.121	81.621	-84.214	-88.863	2.893
5100	14.849	95.415	81.889	-84.488	-88.982	2.792
5200	14.852	95.703	82.152	-84.758	-89.098	2.695
5300	14.853	95.986	82.410	-85.024	-89.211	2.601
5400	14.855	96.264	82.664	-85.286	-89.320	2.510
5500	14.857	96.537	82.914	-85.544	-89.426	2.421
5600	14.859	96.804	83.161	-85.798	-89.529	2.335
5700	14.860	97.067	83.413	-86.048	-89.628	2.251
5800	14.862	97.326	83.659	-86.294	-89.724	2.168
5900	14.863	97.580	83.873	-86.536	-89.817	2.086
6000	14.865	97.830	84.104	-86.774	-89.907	2.005

Dec. 31, 1960; Sept. 30, 1963; Mar. 31, 1965

BC10

BORON OXIDE CHLORIDE (BOCl) (IDEAL GAS) MOL. WT. = 62.277

Point Group [C_{∞v}]
S_{298.15} = [56.72] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

ΔH_f⁰ = -74.8 ± 7.0 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -75.6 ± 7.0 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω_e, cm.⁻¹
[690] (1)
[400] (2)
[1850] (1)

Bond Distance: Cl-B = [1.75] Å B-O [1.20] Å

Bond Angle: Cl-B-O = [180]°

Rotational Constant: B₀ = [0.18504] cm.⁻¹

σ = 1

Heat of Formation.

The vapor-phase equilibria existing in the B₂O₃ + BCl₃ system were determined by an effusion method in the temperature range 1234-1389°K. by J. Blauer and M. Farber, Trans. Faraday Soc. 60, 301 (1964). Based on the equilibrium constants reported for the reaction 1/3 B₂O₃(l) + 1/3 BCl₃(g) = BCl(g), the second and third law values of ΔH_f⁰ 298.15 were evaluated as 57.7 and 56.3 kcal. mole⁻¹, respectively. The third law value for ΔH_f⁰ 298.15 was adopted for the calculation of the heat of formation (ΔH_f⁰ 298.15) for BCl(g).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The vibrational frequencies (ω) were estimated from the ω values calculated by the valence force method described by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., 1945, using estimated force constants, k₁ = 5.2 X 10⁵, k₂ = 16.7 X 10⁵ dynes cm.⁻¹ and k₃ = 0.40 X 10⁻¹¹ dynes cm. rad.⁻¹. The B-O and B-Cl bond distances were assumed to be the same as those in BO(g) and BCl₃(g), respectively. The moment of inertia is 1.6958 X 10⁻³⁸ g. cm.²

BC10

Boron Dichloride (BCl₂)

(Ideal Gas) Mol. Wt. = 81.734

BORON DICHLORIDE (BCl₂)

(IDEAL GAS)

MOL. WT. = 81.734

Point Group [C_{2v}]
 $\Delta H_f^0 = [-20.3 \pm 15] \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = [-20 \pm 15] \text{ kcal. mole}^{-1}$

S_{298.15} = [64.956] cal. deg.⁻¹ mole⁻¹
 Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies

ω , cm.⁻¹
 [720](1)
 [240](1)
 [960](1)

Bond Distances: B-Cl = [1.73] Å

Bond Angle: Cl-B-Cl = [120°]

Product of the Moments of Inertia: I_AI_BI_C = [9.49841 X 10⁻¹¹⁵] g.³ cm.⁶

$\sigma = 2$

Heat of Formation

The heat of formation was estimated by analogy with BF₃, specifically the ratio

$$\Delta H_f(BX_3) \rightarrow BX_2 + X) / \Delta H_f(BX_3) \rightarrow B + 3X$$

was taken as 0.347.

Heat Capacity and Entropy

The vibrational frequencies were obtained from force constants transferred from the trichloride given by O. Harzberg "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., (1945). The bond length was taken between those of the mono and trichlorides and the angle was estimated to be the same as that in the trichlorides. The ground state quantum weight was taken as two on account of the one unpaired electron.

The individual moments of inertia were I_B = 1.1661 X 10⁻³⁹ g. cm.², I_A = 26.4189 X 10⁻³⁹ g. cm.² and I_C = 27.5851 X 10⁻³⁹ g. cm.²

BCl₂

T. °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH _f ⁰	Log K _p
0	0.000	INFINITE	-	2.775	- 20.289	-	20.289	INFINITE
100	6.756	54.374	73.050	- 1.058	- 20.179	-	21.089	44.088
200	9.898	60.810	65.023	- 1.023	- 20.045	-	22.058	24.102
298	10.919	64.956	-	+ 0.000	- 20.000	-	23.060	16.903
300	10.937	65.024	-	- 1.020	- 20.000	-	23.080	16.913
400	12.758	68.249	66.926	- 1.363	- 20.015	-	23.122	10.980
500	12.331	70.979	66.222	- 2.363	- 20.075	-	23.122	10.980
600	12.721	73.263	67.235	- 3.617	- 20.165	-	23.122	9.515
700	12.990	75.246	68.241	- 4.904	- 20.272	-	23.107	8.463
800	13.151	76.925	69.278	- 6.233	- 20.394	-	23.076	7.670
900	13.320	78.352	70.348	- 7.613	- 20.524	-	23.028	7.082
1000	13.424	79.663	71.088	- 8.975	- 20.667	-	22.966	6.549
1100	13.503	81.247	71.934	- 10.222	- 20.821	-	30.889	6.137
1200	13.565	82.424	72.778	- 11.575	- 20.987	-	31.796	5.791
1300	13.613	83.512	73.562	- 12.934	- 21.164	-	32.691	5.496
1400	13.652	84.512	74.302	- 14.302	- 21.351	-	33.576	5.244
1500	13.685	85.466	75.022	- 15.665	- 21.551	-	34.438	5.017
1600	13.711	86.350	75.703	- 17.035	- 21.762	-	35.289	4.820
1700	13.734	87.182	76.354	- 18.407	- 21.984	-	36.126	4.644
1800	13.756	87.967	76.977	- 19.781	- 22.216	-	36.952	4.486
1900	13.776	88.707	77.571	- 21.156	- 22.461	-	37.773	4.344
2000	13.782	89.418	78.110	- 22.535	- 22.701	-	38.583	4.214
2100	13.784	90.090	78.703	- 23.914	- 22.952	-	39.349	4.095
2200	13.804	90.732	79.235	- 25.293	- 23.211	-	40.124	3.986
2300	13.821	91.345	79.744	- 26.674	- 23.474	-	40.897	3.881
2400	13.833	91.946	80.228	- 28.056	- 23.743	-	41.667	3.781
2500	13.828	92.498	80.723	- 29.438	- 24.006	-	42.428	3.695
2600	13.834	93.041	81.186	- 30.821	- 24.278	-	43.179	3.596
2700	13.839	93.563	81.635	- 32.205	- 24.552	-	43.926	3.503
2800	13.844	94.066	82.070	- 33.589	- 24.829	-	44.674	3.416
2900	13.848	94.552	82.492	- 34.972	- 25.109	-	45.424	3.331
3000	13.853	95.022	82.902	- 36.359	- 30.788	-	46.174	3.257
3100	13.856	95.476	83.301	- 37.744	- 31.072	-	45.173	3.185
3200	13.860	95.916	83.688	- 39.130	- 31.358	-	45.623	3.116
3300	13.863	96.345	84.065	- 40.516	- 31.647	-	46.064	3.051
3400	13.866	96.757	84.435	- 41.901	- 31.937	-	46.506	2.986
3500	13.868	97.159	84.792	- 43.290	- 32.231	-	46.924	2.930
3600	13.870	97.549	85.139	- 44.676	- 32.528	-	47.334	2.873
3700	13.873	97.929	85.480	- 46.064	- 32.826	-	47.741	2.820
3800	13.875	98.300	85.817	- 47.451	- 33.127	-	48.143	2.769
3900	13.876	98.660	86.137	- 48.838	- 33.431	-	48.540	2.720
4000	13.878	99.011	86.454	- 50.226	- 154.916	-	46.772	2.555
4100	13.880	99.354	86.765	- 51.614	- 154.992	-	44.070	2.349
4200	13.881	99.688	87.069	- 53.002	- 155.070	-	41.359	2.132
4300	13.882	99.998	87.366	- 54.390	- 155.150	-	38.648	1.917
4400	13.884	100.294	87.657	- 55.779	- 155.232	-	35.940	1.705
4500	13.885	100.566	87.942	- 57.167	- 155.317	-	33.232	1.614
4600	13.886	100.951	88.222	- 58.556	- 155.401	-	30.516	1.440
4700	13.887	101.250	88.496	- 59.944	- 155.489	-	27.799	1.283
4800	13.888	101.546	88.763	- 61.332	- 155.578	-	25.086	1.137
4900	13.889	101.826	89.028	- 62.720	- 155.668	-	22.369	1.007
5000	13.890	102.109	89.287	- 64.111	- 155.760	-	19.640	.886
5100	13.891	102.384	89.541	- 65.500	- 155.853	-	16.914	.725
5200	13.891	102.654	89.791	- 66.889	- 155.947	-	14.190	.596
5300	13.892	102.920	89.999	- 68.278	- 156.043	-	11.469	.473
5400	13.893	103.178	90.206	- 69.667	- 156.140	-	8.748	.354
5500	13.893	103.433	90.514	- 71.057	- 156.238	-	6.000	.238
5600	13.894	103.684	90.747	- 72.446	- 156.338	-	3.279	.128
5700	13.895	103.930	90.976	- 73.835	- 156.441	-	.546	.021
5800	13.896	104.171	91.203	- 75.224	- 156.545	-	-	-
5900	13.896	104.400	91.423	- 76.615	- 156.647	-	-	-
6000	13.896	104.642	91.642	- 78.004	- 156.754	-	-	-

Dec. 31, 1960; Mar. 31, 1963; Dec. 31, 1964

Boron Dichloride Unipositive Ion (BCl₂⁺)

(Ideal Gas) GFW = 81.71645

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^c	Log Kp
0							
100	12.661	61.590	61.590	.000	148.000	144.956	-105.889
200							
250							
300	12.678	61.668	61.590	.023	148.012	144.934	-105.220
400	13.402	65.423	62.097	1.330	148.664	143.141	-78.209
500	13.886	68.465	63.076	2.695	149.260	141.691	-61.933
600	14.128	71.017	64.193	4.094	149.812	140.125	-51.040
700	14.313	73.209	65.128	5.517	150.337	138.468	-41.232
800	14.441	75.159	66.435	6.955	150.841	136.737	-37.355
900	14.532	76.836	67.488	8.404	151.331	134.945	-32.769
1000	14.599	78.371	68.510	9.861	151.806	133.098	-29.069
1100	14.650	79.744	69.471	11.323	152.264	131.205	-26.048
1200	14.689	81.091	70.382	12.790	152.709	129.272	-23.584
1300	14.720	82.218	71.248	14.261	153.140	127.300	-21.401
1400	14.745	83.101	72.071	15.734	153.559	125.298	-19.560
1500	14.765	84.328	72.855	17.210	153.965	123.263	-17.959
1600	14.781	85.281	73.602	18.687	154.358	121.204	-16.556
1700	14.795	86.178	74.315	20.166	154.740	119.122	-15.314
1800	14.807	87.024	74.998	21.646	155.110	117.013	-14.207
1900	14.818	87.825	75.652	23.127	155.473	114.890	-13.245
2000	14.827	88.585	76.280	24.609	155.828	112.745	-12.320
2100	14.836	89.309	76.883	26.093	156.179	110.580	-11.508
2200	14.844	89.999	77.484	27.577	156.522	108.401	-10.769
2300	14.853	90.659	78.023	29.061	156.858	106.206	-10.092
2400	14.861	91.281	78.563	30.547	157.190	103.999	-9.470
2500	14.870	91.898	79.095	32.034	157.529	101.884	-8.907
2600	14.879	92.481	79.589	33.521	157.867	99.867	-8.395
2700	14.889	93.043	80.047	35.009	158.205	97.840	-7.920
2800	14.899	93.585	80.549	36.497	158.541	95.798	-7.477
2900	14.911	94.108	81.008	37.989	158.874	93.747	-7.065
3000	14.923	94.614	81.453	39.481	159.205	91.680	-6.679
3100	14.936	95.103	81.886	40.974	159.528	89.604	-6.317
3200	14.950	95.577	82.306	42.468	159.847	87.522	-5.977
3300	14.965	96.038	82.715	43.964	160.165	85.429	-5.658
3400	14.981	96.485	83.114	45.461	160.481	83.326	-5.356
3500	14.997	96.919	83.502	46.960	160.796	81.209	-5.071
3600	15.015	97.342	83.881	48.461	161.109	79.081	-4.801
3700	15.033	97.754	84.250	49.963	161.420	76.955	-4.546
3800	15.052	98.155	84.611	51.467	161.728	74.817	-4.303
3900	15.072	98.546	84.963	52.973	162.033	72.668	-4.072
4000	15.092	98.928	85.307	54.482	162.336	70.510	-3.850
4100	15.113	99.301	85.644	55.992	162.636	68.349	-3.622
4200	15.134	99.665	85.974	57.504	162.933	66.187	-3.407
4300	15.156	100.021	86.296	59.019	163.228	64.024	-3.201
4400	15.178	100.370	86.612	60.535	163.521	61.861	-3.001
4500	15.200	100.711	86.927	62.054	163.812	59.698	-2.801
4600	15.222	101.046	87.235	63.575	164.101	57.535	-2.601
4700	15.245	101.373	87.543	65.099	164.388	55.372	-2.401
4800	15.267	101.695	87.851	66.624	164.673	53.209	-2.201
4900	15.290	102.010	88.161	68.152	164.956	51.046	-2.001
5000	15.313	102.319	88.468	69.682	165.237	48.883	-1.801
5100	15.335	102.622	88.769	71.215	165.516	46.720	-1.601
5200	15.358	102.920	89.070	72.749	165.793	44.557	-1.401
5300	15.380	103.213	89.371	74.286	166.068	42.394	-1.201
5400	15.402	103.501	89.673	75.825	166.341	40.232	-1.001
5500	15.424	103.783	89.970	77.367	166.612	38.070	-0.801
5600	15.446	104.062	90.267	78.910	166.881	35.908	-0.601
5700	15.467	104.335	90.560	80.456	167.148	33.746	-0.401
5800	15.488	104.604	90.856	82.003	167.413	31.584	-0.201
5900	15.509	104.869	91.153	83.553	167.676	29.422	-0.001
6000	15.530	105.130	91.453	85.105	167.937	27.260	

June 30, 1968



(IDEAL GAS)

BORON DICHLORIDE UNIPosITIVE ION (BCl₂⁺)

Point Group [D_{∞h}]

S_{298.15} = [61.6 ± 2] gibbs/mol

ΔH_f⁰_{298.15} = 147.4 ± 5 kcal/mol

GFW = 81.71645

Electronic Levels and Quantum Weights

State	ϵ_i , cm ⁻¹	g_i
1 _g ⁺	0	1
1 _g ⁻		
1 _B ²	[16000]	1
1 _A ¹	[35000]	1

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹
[500] (1)
[150] (2)
[800] (1)

Bond Distance: B-Cl = [1.74] Å

Bond Angle: Cl-B-Cl = [180°]

Rotational Constant: B₀ = [0.0785] cm⁻¹

σ = 2

Heat of Formation

The appearance potential (AP) of the positive ion fragment BCl₂⁺ from BCl₃(g) was determined mass spectrometrically by Oberhaus (1), Marriott (2), and Koski (3) as 13.2 ± 0.5, 13.01 ± 0.02, and 11.8 ± 0.2 eV, respectively. From the reaction BCl₃ + e⁻ = BCl₂⁺ + Cl + 2e⁻, the corresponding values of ΔH_f⁰₂₉₈ for BCl₂⁺(g) are derived to be 180.4 ± 11.5, 176.0 ± 0.5, and 148.1 ± 4.6 kcal/mol, using ΔH_f⁰ = -96.078 and 28.520 kcal/mol for BCl₃(g) and Cl(g). The value of ΔH_f⁰ for BCl₂⁺(g) is adopted as 148 ± 5 kcal/mol, since the lowest value is likely to have the least excess kinetic energy in the fragment.

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Waleh (4) predictions for 16 valence electron XY₂ molecules. The electronic states, levels and vibrational frequencies are estimated by comparison with those for CO₂(g). The B-Cl bond distance is estimated using the method of Krasnov (5). The moment of inertia is 3.564 × 10⁻³⁸ g cm². The enthalpy at 0°K is -3.07 kcal/mol.

References

1. O. Oberhaus, Z. Phys. **128**, 366 (1950).
2. J. Marriott and J. D. Cragg, J. Electron. Contr. **1**, 194 (1957).
3. W. S. Koski, J. J. Kaufman, and C. F. Pachucki, J. Am. Chem. Soc. **81**, 1326 (1959).
4. A. D. Waleh, J. Chem. Soc. **1953**, 2266 (1953).
5. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
6. K. S. Krasnov, Zh. Strukt. Khim. **1**, 209 (1960).



BORON DICHLORIDE UNINEGATIVE ION (BCl₂⁻) (IDEAL GAS)

$$GFW = 81.71755$$

Boron Dichloride Uninegative Ion (BCl₂⁻) (Ideal Gas)

$$GFW = 81.71755$$

Point Group C_{2v}BORON DICHLORIDE UNINEGATIVE ION (BCl₂⁻)

(IDEAL GAS)

$$GFW = 81.71755$$

$$\Delta H_f^0 = [-26 \pm 30] \text{ kcal/mol}$$

$$S_{298.15}^0 = [63.5 \pm 2] \text{ gibbs/mol}$$

$$\Delta H_f^0 = [-26 \pm 30] \text{ kcal/mol}$$

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	1
[4000] (1)	3
[20000] (1)	1

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	g
[740] (1)	
[245] (1)	
[990] (1)	

Bond Distance: B-Cl = [1.74] Å

Bond Angle: Cl-B-Cl = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [8.788 \times 10^{-11}] \text{ g}^2 \text{ cm}^6$

$$\sigma = 2$$

Heat of Formation

The electron captured by BCl₂ should go into a non-bonding orbital according to the correlation diagrams of Walsh (1), thus one expects a small electron affinity. In fact one reasonable estimate of the dissociation energy yields a negative electron affinity (EA). Consider the isoelectronic reactions BCl₂⁻ → B⁺ + 2Cl and CCl₂ → C + 2Cl, if we make the assumption that these binding energies are the same then $\Delta H_f^0(\text{BCl}_2^-)$ = -32 kcal. Another possible estimate is obtained from the isoelectronic reactions BCl₂⁻ + BCl → BCl₃ + Cl⁻ and BClAr → BCl + Ar, although the latter reaction is unknown we expect a zero bond strength; applying this to the first reaction yields $\Delta H_f^0(\text{BCl}_2^-)$ = -22 kcal/mol or $\text{EA}(\text{BCl}_2^-)$ = 2 kcal. In consideration of the above arguments we choose $\text{EA}(\text{BCl}_2^-)$ = 6 kcal (2) which gives $\Delta H_f^0(\text{BCl}_2^-)$ = -26 kcal/mol.

Heat Capacity and Entropy

The molecular structure is assumed to be bent using the correlations of A. D. Walsh (1) for 18 valence electron XY₂ molecules. The B-Cl bond distance is estimated using the method of Krasnov (3). The Cl-B-Cl bond angle is taken as 120°. The electronic levels, quantum weights and vibrational frequencies are estimated by comparison with those for CF₂(1) and other related isoelectronic molecules. The three principal moments of inertia are $I_A = 1.179 \times 10^{-39}$, $I_B = 2.873 \times 10^{-38}$ and $I_C = 2.791 \times 10^{-38} \text{ g cm}^2$. The enthalpy at 0°K is -2.76 kcal/mol.

References

1. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
2. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
3. K. S. Krasnov, Zh. Strukt. Khim. 1, 209 (1960).
4. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.

T, °K	C _p ^o	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH _f ^o	ΔG _f ^o	Log K _p
0							
100							
200							
298	10.063	63.549	63.549	.000	-26.000	-27.153	19.904
300	10.080	63.616	63.549	.020	-26.009	-27.161	19.786
400	11.707	66.865	63.986	1.152	-26.526	-27.468	15.008
500	12.296	69.545	64.838	2.354	-27.087	-27.639	12.001
600	12.724	71.826	65.817	3.405	-27.677	-27.694	10.068
700	13.070	73.614	66.820	4.896	-28.276	-27.649	8.632
800	13.369	75.580	67.807	6.219	-28.881	-27.519	7.518
900	13.704	77.176	68.781	7.373	-29.480	-27.313	6.633
1000	14.021	78.636	69.676	8.360	-30.069	-27.040	5.910
1100	14.334	79.987	70.553	10.377	-30.650	-26.710	5.307
1200	14.632	81.247	71.392	11.826	-31.217	-26.327	4.795
1300	14.904	82.429	72.196	13.303	-31.772	-25.896	4.354
1400	15.144	83.583	72.967	14.804	-32.317	-25.423	3.969
1500	15.346	84.595	73.708	16.330	-32.857	-24.914	3.630
1600	15.509	85.591	74.420	17.873	-33.392	-24.365	3.328
1700	15.634	86.535	75.105	19.431	-33.925	-23.784	3.056
1800	15.723	87.431	75.765	20.999	-34.459	-23.173	2.814
1900	15.780	88.283	76.401	22.574	-34.996	-22.531	2.592
2000	15.810	89.093	77.016	24.154	-35.537	-21.861	2.389
2100	15.818	89.865	77.609	25.738	-36.082	-21.163	2.202
2200	15.806	90.600	78.183	27.317	-36.636	-20.440	2.031
2300	15.780	91.302	78.739	28.896	-37.197	-19.690	1.871
2400	15.742	91.973	79.276	30.473	-37.768	-18.917	1.723
2500	15.696	92.615	79.797	32.045	-38.338	-18.010	1.574
2600	15.644	93.229	80.302	33.612	-38.923	-17.070	1.426
2700	15.588	93.819	80.792	35.173	-39.517	-16.107	1.268
2800	15.529	94.385	81.267	36.729	-40.119	-15.122	1.107
2900	15.470	94.929	81.759	38.279	-40.728	-14.113	1.033
3000	15.410	95.452	82.247	39.823	-41.347	-13.086	.917
3100	15.352	95.956	82.614	41.361	-41.975	-12.036	.806
3200	15.294	96.443	83.039	42.893	-42.612	-10.970	.701
3300	15.238	96.913	83.452	44.420	-43.257	-9.897	.601
3400	15.185	97.387	83.855	45.941	-43.909	-8.819	.506
3500	15.133	97.866	84.247	47.457	-44.571	-7.736	.415
3600	15.084	98.232	84.630	48.968	-45.240	-6.649	.327
3700	15.038	98.644	85.003	50.474	-45.917	-5.564	.244
3800	14.994	99.045	85.367	51.976	-46.600	-4.483	.164
3900	14.952	99.434	85.723	53.473	-47.289	-3.406	.086
4000	14.913	99.812	86.070	54.966	-47.984	-2.332	.010
4100	14.876	100.180	86.410	56.456	-48.684	-1.261	.038
4200	14.841	100.538	86.742	57.941	-49.389	-0.201	.073
4300	14.809	100.887	87.067	59.424	-50.099	0.733	.112
4400	14.778	101.227	87.385	60.903	-50.814	1.767	.157
4500	14.750	101.558	87.696	62.380	-51.534	2.801	.207
4600	14.723	101.882	88.001	63.853	-52.259	3.835	.262
4700	14.698	102.199	88.300	65.324	-52.989	4.869	.322
4800	14.674	102.508	88.593	66.793	-53.724	5.903	.387
4900	14.652	102.810	88.880	68.259	-54.464	6.937	.452
5000	14.632	103.106	89.161	69.723	-55.209	7.971	.517
5100	14.613	103.396	89.436	71.186	-55.959	9.005	.582
5200	14.595	103.679	89.709	72.646	-56.714	10.039	.647
5300	14.578	103.957	89.975	74.105	-57.474	11.073	.712
5400	14.562	104.229	90.236	75.562	-58.239	12.107	.777
5500	14.548	104.496	90.493	77.017	-59.009	13.141	.842
5600	14.534	104.758	90.746	78.471	-59.784	14.175	.907
5700	14.521	105.016	90.994	79.924	-60.564	15.209	.972
5800	14.509	105.268	91.238	81.376	-61.349	16.243	1.037
5900	14.498	105.516	91.478	82.826	-62.139	17.277	1.102
6000	14.487	105.760	91.714	84.275	-62.934	18.311	1.167

June 30, 1968; Dec. 31, 1968

Boron Dichloride Fluoride (Ideal Gas) Mol. Wt. = 100.734



MOL. WT. = 100.734

BORON DICHLORIDE FLUORIDE (BCl₂F)

(IDEAL GAS)

Point Group = C_{2v}

$\Delta H_f^\circ 0 = -154 \pm 5 \text{ kcal. mole}^{-1}$

$\Delta H_f^\circ 298.15 = 68.73 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^\circ 298.15 = -154 \pm 5 \text{ kcal. mole}^{-1}$

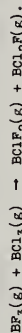
Ground State Quantum Weight = 1

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH_f° kcal. mole ⁻¹	ΔF_f° kcal. mole ⁻¹	Log K _p
0	<0.00	INFINITE	-	-153.630	-153.630	INFINITE
100	9.078	56.280	3.471	-153.630	-153.630	INFINITE
200	16.785	79.785	2.350	-153.664	-153.664	11.0634
300	22.712	94.072	1.800	-153.684	-153.684	11.0634
400	27.417	100.732	1.400	-153.696	-153.696	11.0634
500	31.149	108.819	1.026	-154.001	-154.001	10.9598
600	34.166	117.103	0.745	-154.045	-154.045	10.9099
700	36.651	125.616	0.535	-154.069	-154.069	10.8682
800	38.819	134.306	0.393	-154.082	-154.082	10.8346
900	40.735	143.133	0.295	-154.088	-154.088	10.8055
1000	42.447	152.066	0.226	-154.090	-154.090	10.7805
1100	43.999	161.066	0.176	-154.088	-154.088	10.7598
1200	45.425	170.099	0.140	-154.082	-154.082	10.7425
1300	46.755	179.125	0.112	-154.072	-154.072	10.7278
1400	47.925	188.115	0.090	-154.058	-154.058	10.7155
1500	48.975	197.045	0.072	-154.042	-154.042	10.7052
1600	49.945	205.900	0.058	-154.024	-154.024	10.6965
1700	50.845	214.675	0.047	-154.004	-154.004	10.6892
1800	51.685	223.375	0.038	-153.982	-153.982	10.6830
1900	52.475	232.000	0.031	-153.958	-153.958	10.6778
2000	53.225	240.550	0.026	-153.932	-153.932	10.6735
2100	53.945	249.030	0.022	-153.904	-153.904	10.6700
2200	54.635	257.445	0.019	-153.874	-153.874	10.6672
2300	55.295	265.790	0.017	-153.842	-153.842	10.6650
2400	55.935	274.070	0.015	-153.808	-153.808	10.6633
2500	56.555	282.290	0.014	-153.772	-153.772	10.6620
2600	57.155	290.455	0.013	-153.734	-153.734	10.6610
2700	57.735	298.570	0.012	-153.694	-153.694	10.6602
2800	58.295	306.635	0.011	-153.652	-153.652	10.6596
2900	58.835	314.655	0.010	-153.608	-153.608	10.6592
3000	59.355	322.630	0.010	-153.562	-153.562	10.6589
3100	59.855	330.560	0.009	-153.514	-153.514	10.6587
3200	60.335	338.450	0.009	-153.464	-153.464	10.6586
3300	60.795	346.300	0.008	-153.412	-153.412	10.6586
3400	61.235	354.115	0.008	-153.358	-153.358	10.6587
3500	61.655	361.890	0.007	-153.302	-153.302	10.6589
3600	62.055	369.630	0.007	-153.244	-153.244	10.6592
3700	62.435	377.335	0.006	-153.184	-153.184	10.6596
3800	62.795	385.000	0.006	-153.122	-153.122	10.6600
3900	63.135	392.630	0.005	-153.058	-153.058	10.6604
4000	63.455	400.230	0.005	-152.992	-152.992	10.6608
4100	63.755	407.800	0.004	-152.924	-152.924	10.6612
4200	64.035	415.340	0.004	-152.854	-152.854	10.6616
4300	64.295	422.850	0.003	-152.782	-152.782	10.6620
4400	64.535	430.330	0.003	-152.708	-152.708	10.6624
4500	64.755	437.780	0.002	-152.632	-152.632	10.6628
4600	64.955	445.200	0.002	-152.554	-152.554	10.6632
4700	65.135	452.590	0.002	-152.474	-152.474	10.6636
4800	65.295	459.950	0.001	-152.392	-152.392	10.6640
4900	65.435	467.280	0.001	-152.308	-152.308	10.6644
5000	65.555	474.580	0.001	-152.222	-152.222	10.6648
5100	65.655	481.850	0.000	-152.134	-152.134	10.6652
5200	65.735	489.090	0.000	-152.044	-152.044	10.6656
5300	65.795	496.300	0.000	-151.952	-151.952	10.6660
5400	65.835	503.480	0.000	-151.858	-151.858	10.6664
5500	65.855	510.630	0.000	-151.762	-151.762	10.6668
5600	65.855	517.750	0.000	-151.664	-151.664	10.6672
5700	65.835	524.840	0.000	-151.564	-151.564	10.6676
5800	65.795	531.900	0.000	-151.462	-151.462	10.6680
5900	65.735	538.930	0.000	-151.358	-151.358	10.6684
6000	65.655	545.930	0.000	-151.252	-151.252	10.6688

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Dec. 31, 1964

Heat of Formation.

The values for BCl₂F and BClF₂ of $\Delta H_f^\circ 298.15 = -154$ and $\Delta H_f^\circ 298.15 = -211.6 \text{ kcal. mole}^{-1}$, respectively, are obtained from the average bond energies of BF₃ and BCl₃. The calculated values were each made less negative by about 0.8 kcal. mole⁻¹ in order to make them consistent with the equilibrium measurements of T. H. S. Higgins, E. C. Zeigang, C. J. O. Raw, and A. J. Roseau, J. Chem. Phys. 23, 1544 (1955) and S. R. Oum and R. H. Sanborn, J. Chem. Phys. 33, 955 (1960) for the reaction



Values for the heat of reaction are $\Delta H_{298.15} = +1.68 \text{ kcal. mole}^{-1}$ and $\Delta H_{298.15} = 1.1$ (uncertainty of -0.5 to +0.8) kcal. mole⁻¹, the former calculated from the measured equilibrium constant and the statistical entropy change and the latter obtained from the variation of the equilibrium constant with temperature. Selection of $\Delta H_{298.15} = 1.6 \text{ kcal. mole}^{-1}$ fixes the sum of the heats of formation of BClF₂ and BCl₂F as -365.6 kcal. mole⁻¹, but it does not determine the individual values. Thus, the selected heats of formation are only as accurate as the average bond energy calculations on which they are based. A reasonable estimate of the uncertainty would be ± 5 kcal. mole⁻¹.

Heat Capacity and Entropy.

The spectroscopic constants are based on the work of L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956), who observed ν_1 , ν_2 , and ν_3 and calculated ν_1 , ν_2 , ν_3 , and ν_4 . The frequencies were adjusted to the normal isotopic composition of 61.2% ¹⁰B and 38.8% ¹¹B. The bond angles were taken to be 120° while the bond lengths were assumed to be the same as in the respective trihalides. As a result, the principal moments of inertia are $I_A = 11.8748 \times 10^{-39}$, $I_B = 26.4268 \times 10^{-39}$, and $I_C = 38.3016 \times 10^{-39} \text{ g. cm}^2$.



Boron Monofluoride (BF)

BORON MONOFLUORIDE (BF)

(IDEAL GAS)

MOL. WT. = 29.82

(Ideal Gas) Mol. Wt. = 29.82

Ground State Configuration $1\Sigma^+$ $\Delta H_f^\circ = -28.4 \pm 3.3 \text{ kcal. mole}^{-1}$ $S^\circ_{298.15} = 47.890 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^\circ = -27.7 \pm 3.3 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$E_1, \text{ cm.}^{-1}$	E_1
0	1
$\omega_e = 1410.3 \text{ cm.}^{-1}$	$\omega_e = 11.98 \text{ cm.}^{-1}$
$\omega_e = 1.5286 \text{ cm.}^{-1}$	$\omega_e = 0.0168 \text{ cm.}^{-1}$
$r_e = 1.265 \text{ \AA}$	$r_e = 1.265 \text{ \AA}$

Heat of Formation

The equilibria of the reaction $2/3 \text{ B(c)} + 1/3 \text{ BF}_3(\text{g}) = \text{BF}(\text{g})$ were studied by J. Blauer, M. A. Greenbaum and M. Parber¹, by means of transpiration at pressures below 300μ . The values of $\log K_p$ at 1375 and 1476°K. were reported as -3.99 ± 0.02 and -3.30 ± 0.05 , respectively. By the third law method the value of ΔH_f° 298.15 for the reaction was derived to be $61.38 \text{ kcal. mole}^{-1}$, yielding ΔH_f° 298.15 = $-28.7 \pm 2.6 \text{ kcal. mole}^{-1}$ for $\text{BF}(\text{g})$. The system $\text{B} + \text{CaF}_2$ was studied mass spectrometrically in a graphite Knudsen cell by D. L. Hildenbrand. The equilibria involving $\text{BF}(\text{g})$ were observed. Intensity measurements were made at temperatures, 1583–1734°K. From the third law value, ΔH_f° 298.15 = $12.2 \pm 0.3 \text{ kcal. mole}^{-1}$, for the reaction $\text{BF}_3(\text{g}) + \text{Ca}(\text{g}) = \text{BF}(\text{g}) + \text{CaF}_2(\text{g})$, the value of ΔH_f° 298.15 for $\text{BF}(\text{g})$ was derived as $-26.7 \pm 2 \text{ kcal. mole}^{-1}$. The dissociation energy (D_0°) of $\text{BF}(\text{g})$ molecule has been reported by O. Herzberg², A. G. Gaydon³ and R. F. Barrow⁴, respectively. Hence the corresponding values of ΔH_f° 298.15 for $\text{BF}(\text{g})$ were derived. The results are compared with those obtained from equilibrium data as follows.

Investigator	Reaction	ΔH_f° 298.15, kcal. mole ⁻¹	ΔH_f° 298.15, kcal. mole ⁻¹
Parber, et al. ¹	$2/3 \text{ B(c)} + 1/3 \text{ BF}_3(\text{g}) = \text{BF}(\text{g})$	61.38	-28.7 ± 2.6
Herzberg ²	$\text{BF}(\text{g}) = \text{B(g)} + \text{F(g)}$	100.2	$+51.5$
Gaydon ³	$\text{BF}(\text{g}) = \text{B(g)} + \text{F(g)}$	197.0	-45.3 ± 11.5
Barrow ⁴	$\text{BF}(\text{g}) = \text{B(g)} + \text{F(g)}$	186.0	-34.3
Oross, et al. ⁵	$2/3 \text{ B(c)} + 1/3 \text{ BF}_3(\text{g}) = \text{BF}(\text{g})$	—	-28 ± 3
Hildenbrand ⁶	$\text{BF}_3(\text{g}) + \text{Ca(g)} = \text{BF(g)} + \text{CaF}_2(\text{g})$	12.2	-26.7 ± 2

1 J. Blauer, M. A. Greenbaum and M. Parber, J. Phys. Chem. 58, 2332 (1964).

2 O. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, New York, 1950. ΔH_f° 298.15 was calculated based on $D_0^\circ = 4.3 \text{ e.v.}$

3 A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. ΔH_f° 298.15 was derived from $D_0^\circ = 8.5 \pm 0.5 \text{ e.v.}$

4 R. F. Barrow, Trans. Faraday Soc. 56, 952 (1960). ΔH_f° 298.15 was calculated based on $D_0^\circ = 185 \text{ kcal. mole}^{-1}$.

5 F. Oross, C. Gayman, D. L. Levi and R. H. Lewin, "Stability of Lower Boron Halides", Final Technical Report, August 24, 1963, Fulmer Research Institute Limited, England. The reported value, ΔH_f° 298.15 = $-28 \pm 3 \text{ kcal. mole}^{-1}$, is a preliminary estimated one.

6 D. L. Hildenbrand, "Thermodynamic Properties of Propellant Combustion Products", QLR-65-3, Philco Corporation, California.

The value of ΔH_f° 298.15 adopted is the average of the first and last ΔH_f° 298.15 values listed in the above table.

Heat Capacity and Entropy

The spectroscopic constants used were obtained from R. Onaka, J. Chem. Phys. 21, 374 (1957) and corrected to the average isotopic species. Spectroscopic constants for $\text{BF}(\text{g})$ were also reported by O. Herzberg, loc. cit. The moment of inertia (I) is $1.8321 \times 10^{-39} \text{ g. cm.}^2$

Dec. 31, 1960; Dec. 31, 1964

T, °K.	C_p	$S^\circ - (R^\circ \ln H_{298})/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	INFINITE	-2.076	-28.431	-28.431	INFINITE
100	6.957	40.269	54.108	-1.384	-30.074	65.724
200	6.968	45.093	48.533	-0.688	-32.171	35.153
298	7.073	47.890	-0.000	-27.824	-34.538	25.169
300	7.076	47.934	-0.13	-27.699	-34.379	25.044
400	7.309	50.000	48.171	7.32	-36.610	20.002
500	7.581	51.660	18.708	1.476	-37.759	16.974
600	7.832	53.065	40.320	2.247	-37.879	14.049
700	8.042	54.288	3.841	-28.027	-43.220	13.493
800	8.211	55.374	50.556	3.884	-28.192	12.397
900	8.348	56.349	51.146	4.682	-28.368	11.538
1000	8.457	57.236	51.712	5.523	-28.555	10.847
1100	8.545	58.065	4.373	-28.754	-41.735	10.276
1200	8.620	58.799	7.231	-28.964	-41.814	9.721
1300	8.681	59.484	53.256	8.037	-29.184	9.193
1400	8.732	60.129	53.724	8.967	-29.414	8.641
1500	8.776	60.733	54.171	9.843	-29.655	8.074
1600	8.814	61.301	54.599	10.722	-29.904	7.471
1700	8.848	61.836	55.010	11.605	-30.167	6.843
1800	8.877	62.343	55.403	12.492	-30.436	6.222
1900	8.903	62.824	55.781	13.381	-30.712	5.605
2000	8.927	63.281	56.145	14.272	-30.993	5.000
2100	8.949	63.717	56.495	15.165	-31.270	4.413
2200	8.969	64.134	56.833	16.062	-31.570	3.843
2300	8.987	64.533	57.159	16.960	-31.865	3.287
2400	9.004	64.914	57.474	17.859	-32.164	2.745
2500	9.020	65.283	57.779	18.761	-32.484	2.216
2600	9.035	65.638	58.075	19.663	-32.813	1.700
2700	9.049	65.979	58.361	20.567	-33.153	1.196
2800	9.062	66.308	58.639	21.473	-33.507	0.704
2900	9.075	66.626	58.909	22.380	-33.874	0.224
3000	9.088	66.934	59.172	23.288	-34.246	-0.244
3100	9.100	67.232	59.427	24.197	-34.624	-0.724
3200	9.111	67.521	59.675	25.108	-35.007	-1.204
3300	9.122	67.802	59.917	26.020	-35.394	-1.684
3400	9.133	68.075	60.153	26.932	-35.786	-2.164
3500	9.143	68.339	60.383	27.846	-36.183	-2.644
3600	9.154	68.597	60.608	28.761	-36.584	-3.124
3700	9.164	68.848	60.827	29.677	-36.990	-3.604
3800	9.173	69.093	61.042	30.594	-37.401	-4.084
3900	9.183	69.331	61.251	31.512	-37.817	-4.564
4000	9.192	69.564	61.456	32.430	-38.238	-5.044
4100	9.202	69.791	61.657	33.350	-38.664	-5.524
4200	9.211	70.013	61.853	34.271	-39.094	-6.004
4300	9.220	70.229	62.045	35.192	-39.529	-6.484
4400	9.229	70.441	62.234	36.115	-39.967	-6.964
4500	9.238	70.649	62.418	37.038	-40.407	-7.444
4600	9.246	70.852	62.599	37.962	-40.852	-7.924
4700	9.255	71.051	62.777	38.887	-41.299	-8.404
4800	9.264	71.246	62.952	39.813	-41.749	-8.884
4900	9.272	71.437	63.123	40.740	-42.199	-9.364
5000	9.280	71.624	63.291	41.668	-42.652	-9.844
5100	9.289	71.808	63.456	42.596	-43.104	-10.324
5200	9.297	71.989	63.618	43.525	-43.559	-10.804
5300	9.305	72.166	63.778	44.456	-44.014	-11.284
5400	9.313	72.340	63.935	45.386	-44.471	-11.764
5500	9.322	72.511	64.089	46.318	-44.929	-12.244
5600	9.330	72.679	64.241	47.251	-45.388	-12.724
5700	9.338	72.844	64.391	48.184	-45.848	-13.204
5800	9.346	73.007	64.538	49.116	-46.308	-13.684
5900	9.354	73.166	64.683	50.053	-46.769	-14.164
6000	9.362	73.324	64.826	50.989	-47.229	-14.644

Boron Oxide Fluoride (BOF)

(Ideal Gas) Mol. Wt. = 45.82

BORON OXIDE FLUORIDE (BOF)

(IDEAL GAS)

T, °K.	C _p	S° - (R° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _P
0	4.000	INFINITE	2.374	-143.990	-143.990	INFINITE
100	44.736	41.505	1.677	-144.357	-144.357	315.477
200	8.505	54.562	.901	-144.713	-144.713	156.127
298	9.798	53.705	.000	-145.000	-145.000	106.331
300	9.819	53.766	.018	-145.073	-145.073	105.681
400	10.792	56.730	1.051	-144.930	-145.427	79.454
500	11.540	59.222	2.169	-144.094	-145.770	63.713
600	12.130	61.380	3.354	-144.178	-146.007	53.213
700	12.585	63.268	4.591	-144.271	-146.509	45.709
800	12.935	64.935	5.878	-144.364	-146.806	39.684
900	13.215	66.541	7.184	-144.466	-146.906	35.694
1000	13.515	67.957	8.524	-144.567	-147.270	32.184
1100	13.710	69.250	9.885	-144.675	-147.536	29.311
1200	13.870	70.450	11.274	-144.788	-147.751	26.915
1300	14.000	71.565	12.691	-144.908	-147.923	24.831
1400	14.109	72.607	14.064	-145.035	-148.072	23.145
1500	14.200	73.584	15.479	-145.171	-148.500	21.635
1600	14.277	74.503	16.903	-145.316	-148.716	20.314
1700	14.338	75.368	18.344	-145.470	-148.923	19.164
1800	14.398	76.192	19.774	-145.630	-149.111	18.174
1900	14.446	76.971	21.214	-145.804	-149.311	17.314
2000	14.487	77.713	22.660	-145.980	-149.491	16.535
2100	14.524	78.421	24.111	-146.162	-149.662	15.875
2200	14.558	79.097	25.572	-146.350	-149.826	15.283
2300	14.584	79.745	27.043	-146.544	-149.975	14.753
2400	14.609	80.366	28.482	-146.744	-150.122	14.284
2500	14.631	80.963	29.944	-146.944	-150.266	13.874
2600	14.651	81.537	31.408	-147.154	-150.406	13.524
2700	14.669	82.086	32.844	-147.374	-150.541	13.234
2800	14.685	82.610	34.264	-147.604	-150.671	12.994
2900	14.699	83.110	35.674	-147.844	-150.796	12.794
3000	14.712	83.589	37.071	-148.094	-150.916	12.624
3100	14.724	84.041	38.451	-148.354	-151.031	12.474
3200	14.735	84.466	39.806	-148.624	-151.141	12.344
3300	14.745	84.864	41.136	-148.904	-151.246	12.224
3400	14.752	85.234	42.441	-149.194	-151.346	12.114
3500	14.757	85.574	43.721	-149.494	-151.441	12.014
3600	14.760	85.884	44.976	-149.804	-151.531	11.924
3700	14.762	86.164	46.206	-150.124	-151.616	11.834
3800	14.763	86.414	47.411	-150.454	-151.696	11.754
3900	14.763	86.634	48.591	-150.794	-151.771	11.684
4000	14.763	86.824	49.746	-151.144	-151.841	11.624
4100	14.800	88.249	51.196	-151.504	-151.906	11.574
4200	14.809	88.694	52.621	-151.874	-151.966	11.534
4300	14.819	89.154	54.026	-152.254	-152.021	11.494
4400	14.819	89.524	55.401	-152.644	-152.071	11.454
4500	14.817	89.864	56.746	-153.044	-152.116	11.414
4600	14.821	90.174	58.061	-153.454	-152.156	11.374
4700	14.821	90.454	59.346	-153.874	-152.191	11.334
4800	14.828	90.704	60.601	-154.304	-152.221	11.294
4900	14.834	90.924	61.826	-154.744	-152.246	11.254
5000	14.834	91.124	63.021	-155.194	-152.266	11.214
5100	14.834	91.294	64.186	-155.654	-152.281	11.174
5200	14.834	91.434	65.321	-156.124	-152.291	11.134
5300	14.841	92.054	66.426	-156.604	-152.296	11.094
5400	14.844	92.334	67.491	-157.094	-152.296	11.054
5500	14.846	92.604	68.526	-157.594	-152.291	11.014
5600	14.848	92.874	69.531	-158.104	-152.281	10.974
5700	14.850	93.124	70.506	-158.624	-152.266	10.934
5800	14.852	93.354	71.451	-159.154	-152.246	10.894
5900	14.854	93.564	72.366	-159.694	-152.221	10.854
6000	14.855	93.744	73.241	-160.244	-152.191	10.814

MOL. WT. = 45.82

ΔH_f⁰ = -144 ± 3 kcal. mole⁻¹

ΔF_f⁰ 298.15 = -144 ± 3 kcal. mole⁻¹

Point Group [C_{2v}]

S_{298.15} = [53.7] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹

(1050) (1)

(500) (2)

(1300) (1)

Bond Distance: B-P = [1.30] Å B-O = [1.20] Å

Bond Angle: O-B-P = [180°]

B₀ = [0.30393] cm.⁻¹

σ = 1

Heat of Formation

The equilibrium constants for the reaction B₂O₃(l) + BF₃(g) = 3BOF(g) in the temperature range 1054-1253°K. were determined by M. Parber and J. Blauer, Trans. Faraday Soc. 59, 2080 (1962), using the so-called Molecular Flow Reaction Method. The value of ΔH_f⁰ for this reaction was evaluated by both the second and third law methods, using the equilibrium constants corrected for the trimer and correcting K_p at 1200°K. from 9.6 X 10⁻¹¹ to 9.6 X 10⁻¹⁰.

D. L. Hildenbrand, L. P. Theard and A. M. Saul, J. Chem. Phys. 39, 1973 (1963) analyzed the vapor above mixture of MgP₂ and B₂O₃ contained in a Knudsen cell with a mass spectrometer and found that in the temperature range 980-1230°K. the vapor is composed of BF₃(g), (BOF)₂(g) and BOF(g) species. From the reported temperature dependence of appropriate ion intensities the enthalpy change of the reaction (BOF)₂(g) = 3BOF(g) was derived by the second law method as 127.9 kcal. mole⁻¹ at 1115°K. or 129.75 kcal. mole⁻¹ at 298.15°K. The results obtained are presented as follows, using JANAP free energy functions and auxiliary data.

ΔH_f⁰ 298.15, kcal. mole⁻¹

Second law value Third law value

Kcal. mole⁻¹

Reaction

Parber and Blauer B₂O₃(l) + BF₃(g) = 3BOF(g) 150.2 ± 16.6 149.0 -140.1 ± 6*

Hildenbrand, et al. (BOF)₂(g) = 3BOF(g) 129.8 ± 3 -145.2 ± 1.5

*Calculation based on the third law value and one point rejected due to statistical test.

The adopted value of ΔH_f⁰ 298.15 for BOF(g) is the weighted average of the two ΔH_f⁰ 298.15 values listed above.

Heat Capacity and Entropy

The molecular structure was assumed to be linear. The vibrational frequencies (ω) were estimated from the ω values calculated by the valence force method described by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., 1945, using estimated force constants, k₁ = 10 X 10⁵, k₂ = 25.6 X 10⁵ dynes cm.⁻¹ and k₃ = 0.47 X 10⁻¹¹ dynes cm. rad.⁻¹. The B-O and B-P bond distances were assumed to be the same as those in BO(g) and BP₃(g) molecules.

The moment of inertia is 9.0464 X 10⁻³⁹ g. cm.².

BORON DIFLUORIDE (BF₂)

(IDEAL GAS)

Point Group C_{2v}

S_{298.15} = [58.996] cal. deg.⁻¹ mole⁻¹

ΔH_f⁰ = -130 ± 6 kcal. mole⁻¹

Ground State Quantum Weight = 2

ΔH_f⁰ 298.15 = -130 ± 6 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹
[1120] (1)
[470] (1)
[1450] (1)

Bond Distance: B-F = [1.295] Å

Bond Angle: F-B-F = [120]°

Product of the Moments of Inertia: I_AI_BI_C = 3.96352 X 10⁻¹¹⁶ g.³ cm.⁶

σ = 2

Heat of Formation.

The heat of formation (ΔH_f⁰ 298.15) was obtained from J. L. Margrave, J. Phys. Chem. 66, 1209 (1962), from appearance potentials.

Heat Capacity and Entropy.

The bond distance and angle were assumed to be the same as those in BF₃(g) molecule. The vibrational frequencies were calculated using force constants transferred from those for BF₃(g) given by G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., 1945. The three principal moments of inertia are: I_A = 7.9278 X 10⁻³⁹, I_B = 5.8710 X 10⁻⁴⁰ and I_C = 8.5149 X 10⁻³⁹ g. cm.²

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1964

BF₂

T, °K.	C _p	S ⁰ - (F ⁰ -H ₂₉₈ ⁰)/T	H ⁰ -H ₂₉₈ ⁰	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	- 2.543	- 130.141	- 130.141	INFINITE
100	8.054	49.221	66.991	- 130.046	- 130.050	266.113
200	18.245	124.880	146.880	- 130.000	- 130.000	146.880
298	9.018	58.996	0.000	- 130.000	- 132.777	97.281
300	9.633	59.056	58.997	0.018	- 130.001	96.700
400	10.415	61.936	59.384	1.021	- 130.090	133.666
500	11.101	64.336	60.141	2.068	- 130.233	173.017
600	11.654	66.411	61.017	3.236	- 130.402	194.550
700	12.084	68.241	61.920	4.424	- 130.581	49.303
800	12.415	69.877	62.815	5.650	- 130.766	42.413
900	12.671	71.355	63.683	6.905	- 130.953	37.414
1000	12.870	72.701	64.518	8.182	- 131.146	33.443
1100	13.027	73.935	65.319	9.477	- 131.347	30.260
1200	13.152	75.074	66.085	10.787	- 131.553	27.653
1300	13.254	76.131	66.818	12.107	- 131.770	25.477
1400	13.337	77.116	67.518	13.437	- 131.994	23.632
1500	13.405	78.039	68.189	14.774	- 132.229	22.049
1600	13.463	78.906	68.832	16.117	- 132.474	20.674
1700	13.511	79.723	69.449	17.466	- 132.728	19.469
1800	13.552	80.497	70.042	18.819	- 132.992	18.403
1900	13.587	81.231	70.611	20.176	- 133.262	17.455
2000	13.617	81.928	71.160	21.537	- 133.537	16.604
2100	13.643	82.593	71.689	22.900	- 133.819	15.837
2200	13.666	83.228	72.199	24.265	- 134.107	15.141
2300	13.686	83.836	72.692	25.633	- 134.399	14.507
2400	13.704	84.419	73.168	27.002	- 134.698	13.928
2500	13.720	84.979	73.630	28.374	- 140.388	13.395
2600	13.734	85.517	74.077	29.746	- 140.689	12.894
2700	13.747	86.036	74.510	31.120	- 140.990	12.422
2800	13.758	86.536	74.931	32.496	- 141.291	11.983
2900	13.768	87.019	75.339	33.872	- 141.595	11.575
3000	13.777	87.486	75.736	35.249	- 141.901	11.194
3100	13.785	87.938	76.123	36.627	- 142.207	10.839
3200	13.793	88.376	76.499	38.006	- 142.515	10.505
3300	13.800	88.800	76.865	39.386	- 142.824	10.191
3400	13.806	89.212	77.222	40.766	- 143.135	9.896
3500	13.812	89.613	77.577	42.147	- 143.448	9.617
3600	13.817	90.002	77.921	43.529	- 143.761	9.354
3700	13.822	90.380	78.262	44.911	- 144.077	9.105
3800	13.827	90.749	78.597	46.293	- 144.395	8.869
3900	13.831	91.108	78.884	47.676	- 144.715	8.645
4000	13.835	91.459	79.194	49.059	- 145.040	8.432
4100	13.839	91.800	79.497	50.443	- 145.367	8.225
4200	13.842	92.134	79.794	51.827	- 145.696	8.025
4300	13.845	92.459	80.085	53.211	- 146.027	7.831
4400	13.848	92.778	80.370	54.596	- 146.359	7.645
4500	13.851	93.089	80.649	55.981	- 146.694	7.468
4600	13.853	93.393	80.923	57.366	- 147.026	7.296
4700	13.856	93.691	81.191	58.752	- 147.359	7.129
4800	13.858	93.983	81.455	60.137	- 147.693	6.966
4900	13.860	94.269	81.713	61.523	- 148.028	6.806
5000	13.862	94.549	81.967	62.909	- 148.364	6.649
5100	13.864	94.823	82.217	64.296	- 148.691	6.494
5200	13.866	95.093	82.462	65.682	- 149.018	6.341
5300	13.867	95.357	82.702	67.069	- 149.346	6.189
5400	13.869	95.616	82.939	68.456	- 149.675	6.038
5500	13.871	95.871	83.172	69.842	- 150.004	5.887
5600	13.872	96.121	83.401	71.230	- 150.333	5.736
5700	13.873	96.366	83.626	72.617	- 150.662	5.584
5800	13.875	96.607	83.848	74.004	- 151.000	5.432
5900	13.876	96.845	84.066	75.392	- 151.338	5.280
6000	13.877	97.078	84.281	76.779	- 151.676	5.128

Boron Difluoride Unipositive Ion (BF₂⁺)
(Ideal Gas) GFW = 48.80725

T, °K	C _p ^o	$\frac{\text{gibbs/mol}}{S^o - (G^o - H^o_{298})/T}$	H ^o - H ^o ₂₉₈	$\frac{\text{kcal/mol}}{\Delta H^o}$	ΔG^o	Log K _p
0						
100						
200						
298	10.586	53.785	53.785	.000	61.340	- 59.624
300						
400	10.405	53.850	53.785	.070	81.322	- 59.243
500	11.513	57.032	54.213	1.118	80.349	- 43.501
600	12.211	59.675	55.048	2.315	79.250	- 34.640
700	12.747	61.955	56.014	3.564	78.062	- 28.434
800	13.176	63.752	57.598	4.850	76.788	- 23.420
900	13.513	65.173	58.840	6.132	75.458	- 18.420
1000	13.762	66.786	59.853	7.522	74.105	- 17.995
1100	14.052	70.119	60.727	10.331	72.685	- 15.885
1200	14.266	73.485	61.358	13.155	71.225	- 14.151
1300	14.426	76.785	61.785	15.980	69.725	- 12.466
1400	14.549	79.985	63.120	18.745	68.201	- 10.404
1500	14.614	83.138	63.848	21.456	66.664	- 9.479
1600	14.670	86.246	64.546	24.118	65.106	- 8.667
1700	14.716	89.304	65.216	26.736	63.532	- 7.906
1800	14.756	92.319	65.856	29.304	61.951	- 7.200
1900	14.789	95.289	66.473	31.829	60.359	- 6.546
2000	14.819	98.216	67.067	34.309	58.755	- 5.942
2100	14.844	101.099	67.639	36.736	57.141	- 5.386
2200	14.866	103.939	68.189	39.113	55.518	- 4.875
2300	14.886	106.739	68.723	41.440	53.885	- 4.400
2400	14.703	81.390	69.238	43.715	52.245	- 3.960
2500	14.718	81.990	69.736	46.013	50.599	- 3.557
2600	14.732	82.568	70.218	48.240	48.945	- 3.182
2700	14.746	83.126	70.684	50.497	47.278	- 2.835
2800	14.756	83.660	71.140	52.682	45.600	- 2.516
2900	14.766	84.178	71.581	54.800	43.903	- 2.223
3000	14.775	84.679	72.009	56.851	42.195	- 1.955
3100	14.784	85.164	72.426	58.839	40.478	- 1.710
3200	14.790	85.634	72.831	60.763	38.753	- 1.485
3300	14.800	86.089	73.226	62.627	37.019	- 1.279
3400	14.808	86.531	73.611	64.436	35.276	- 1.091
3500	14.815	86.960	73.986	66.189	33.525	- 0.920
3600	14.822	87.377	74.352	67.890	31.765	- 0.765
3700	14.829	87.784	74.710	69.540	29.996	- 0.625
3800	14.833	88.169	75.059	71.140	28.218	- 0.500
3900	14.843	88.565	75.400	72.691	26.432	- 0.389
4000	14.850	88.941	75.734	74.185	24.638	- 0.299
4100	14.857	89.307	76.061	75.621	22.835	- 0.228
4200	14.862	89.659	76.381	76.999	21.023	- 0.173
4300	14.872	90.015	76.691	78.268	19.202	- 0.131
4400	14.880	90.357	77.000	79.529	17.373	- 0.099
4500	14.888	90.692	77.301	80.782	15.537	- 0.076
4600	14.897	91.019	77.595	82.028	13.693	- 0.060
4700	14.914	91.453	77.888	83.261	11.840	- 0.050
4800	14.924	91.861	78.171	84.486	9.978	- 0.044
4900	14.933	92.263	78.446	85.706	8.113	- 0.040
5000	14.943	92.658	78.698	86.920	6.245	- 0.037
5100	14.943	92.658	78.698	86.920	4.377	- 0.036
5200	14.965	92.113	79.512	87.738	2.509	- 0.036
5300	14.965	92.113	79.512	87.738	0.641	- 0.036
5400	14.976	93.413	79.766	88.441	- 1.288	- 0.036
5500	14.987	93.688	80.017	89.133	- 3.218	- 0.036
5600	14.999	93.959	80.263	89.813	- 5.148	- 0.036
5700	15.009	94.226	80.506	90.486	- 7.078	- 0.036
5800	15.023	94.485	80.745	91.155	- 9.008	- 0.036
5900	15.035	94.742	80.980	91.818	- 10.938	- 0.036
6000	15.048	94.995	81.211	92.477	- 12.868	- 0.036

June 30, 1968

BORON DIFLUORIDE UNIPOSITIVE ION (BF₂⁺)
Point Group [D_{∞h}]
S^o_{298.15} = [53.8 ± 2] gibbs/mol
ΔH_f^o = 83.9 ± 2 kcal/mol
ΔH_f^o_{298.15} = 84.0 ± 2 kcal/mol
(IDEAL GAS)

Electronic Levels and Quantum Weights

State	$\frac{e_i \text{ cm}^{-1}}{g_i}$	$\frac{g_i}{g_1}$
1 _g ⁺	0	1
1 _{B₂}	[25000]	1

Vibrational Frequencies and Degeneracies

$\frac{g_i \text{ cm}^{-1}}{g_1}$
[900] (1)
[370] (2)
[1550] (1)

Bond Distance: B-F = [1.31] Å
Bond Angle: F-B-F = [180°]
Rotational Constant: B₀ = [0.2885] cm⁻¹
σ = 2

Heat of Formation

The electron impact reaction at low pressure in BF₃(g) has been studied with a mass spectrometer by Osberghaus (1), Law (2), and Harriott (3). From the reported appearance potentials 17.0 ± 0.5, 16.2 ± 0.2, and 16.7 ± 0.05 eV and assumed process BF₂⁺ + e = BF₂⁺ + F + 2e, we calculate the corresponding values of ΔH_f^o₂₉₈ (BF₂⁺, g) as 102.8 ± 11.5, 84.4 ± 4.6, and 83.7 ± 1.2 kcal/mol, using ΔH_f^o = 270.977 and 18.357 kcal/mol for BF₃(g) and F(g). The adopted value of ΔH_f^o for BF₂⁺(g) is 84 ± 2 kcal/mol, since the lower values are likely to have the least excess kinetic energy in the fragments.

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh (4) prediction for 16 valence electron XY₂ molecules. The electronic states and levels, and vibrational frequencies are estimated by comparison with those for CO₂(3). The B-F bond distance is calculated by the method recommended by Krasnov (5). The moment of inertia is 1.083 × 10⁻³⁸ g cm². The enthalpy at 0°K is -2.54 kcal/mol.

References

1. O. Osberghaus, Z. Phys. **128**, 366 (1950).
2. R. W. Law and J. L. Margrave, J. Chem. Phys. **25**, 1086 (1956).
3. J. Harriott and J. D. Craggs, J. Electron. Contr. **3**, 134 (1957).
4. A. D. Walsh, J. Chem. Soc. **1953**, 2266 (1953).
5. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, 1966.
6. K. S. Krasnov, Zh. Strukt. Khim. **1**, 209 (1960).

BF₂⁺

BF₂⁺

BORON DIFLUORIDE UNINEGATIVE ION (BF₂⁻) (IDEAL GAS) GFW = 48.60835Point Group [C_{2v}]Boron Difluoride Uninegative Ion (BF₂⁻)

(Ideal Gas) GFW = 48.60835

S_{298.15} = [57.5 ± 2] gibbs/mol

Electronic Levels and Quantum Heights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	1
[6000]	3
[24000]	1

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	g_i
[1000] (1)	1
[5701] (1)	1
[11000] (1)	1

Bond Distance: B-F = [1.30] Å

Bond Angle: F-B-F = [120°]

Product of the Moments of Inertia: I_AI_BI_C = [4.05 × 10⁻¹¹⁶] g³ cm⁶

σ = 2

Heat of Formation

The electron captured by BF₂ should go into a non-bonding orbital according to the correlation diagrams of Walsh (1), thus we would expect a small electron affinity. Two estimates of the dissociation energy of BF₂⁻ indicate a negative electron affinity (EA); consider the isoelectronic reactions BF₂⁻ → B⁻ + 2F and CF₂ → C + 2F if we make the reasonable assumption that the atomization energies are the same then ΔH_{f298}(BF₂⁻, g) = -86 kcal/mol, or EA(BF₂⁻) = -44 kcal. Another approach is to consider the isoelectronic reactions BF₂⁻ → BF + F⁻ and BFHe → BF + He, although the latter reaction is unknown we would expect zero bond strength, and if used in the first reaction this yields ΔH_{f298}(BF₂⁻, g) = -90 kcal/mol, or EA(BF₂⁻) = -40 kcal.

In consideration of the above we choose EA(BF₂⁻) = EA(B, g) = 6 kcal (2), which gives ΔH_{f298}(BF₂⁻, g) = -136 kcal/mol.

Heat Capacity and Entropy

The molecular structure and B-F bond distance are assumed to be the same as those for the BF₂(g) molecule. The electronic levels, quantum heights and vibrational frequencies are estimated by comparison with those for CF₂(g) which is isoelectronic with BF₂⁻. The three principal moments of inertia are: I_A = 5.904 × 10⁻⁴⁰, I_B = 7.997 × 10⁻³⁹ and I_C = 8.587 × 10⁻³⁹ g cm². The enthalpy at 0°K is -2.52 kcal/mol.

References

1. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
2. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
3. G. Herzberg, "Electronic Spectra of Polyatomic Molecules", D. Van Nostrand Co., Inc., New York, 1966.

T, °K	C _p ^o	S ^o	-(C _p ^o - H ₂₉₈)/T	H ^o - H ₂₉₈	kcal/mol ΔH _f ^o	ΔG _f ^o	Log K _p
0							
100							
200							
298	9.702	57.489	57.489	.000	-136.000	-136.790	100.270
300	9.722	57.549	57.489	.018	-136.010	-136.796	99.655
400	10.728	60.489	57.483	1.042	-136.575	-136.973	74.638
500	11.500	62.970	58.659	2.156	-137.178	-137.604	59.884
600	12.058	65.119	59.561	3.335	-137.803	-138.910	49.869
700	12.461	67.010	60.492	4.562	-138.439	-139.710	42.683
800	12.762	68.694	61.414	5.824	-139.085	-139.420	37.268
900	13.000	70.211	62.309	7.112	-139.736	-139.049	33.037
1000	13.204	71.592	63.169	8.423	-140.392	-135.603	29.636
1100	13.393	72.859	63.993	9.753	-141.055	-135.094	26.841
1200	13.579	74.033	64.781	11.101	-141.720	-134.522	24.250
1300	13.767	75.127	65.536	12.466	-142.386	-133.894	22.510
1400	13.959	76.154	66.258	13.855	-143.050	-133.215	20.796
1500	14.155	77.124	66.950	15.260	-143.714	-132.490	19.104
1600	14.351	78.044	67.616	16.686	-144.373	-131.720	17.492
1700	14.543	78.919	68.254	18.130	-145.029	-130.909	16.029
1800	14.729	79.756	68.870	19.594	-145.678	-130.061	14.792
1900	14.905	80.557	69.464	21.076	-146.320	-129.176	13.659
2000	15.069	81.326	70.038	22.575	-146.954	-128.256	12.615
2100	15.216	82.065	70.594	24.089	-147.582	-127.306	11.749
2200	15.351	82.776	71.131	25.616	-148.203	-126.324	11.049
2300	15.467	83.461	71.653	27.159	-148.816	-125.316	11.008
2400	15.567	84.121	72.158	28.711	-149.431	-124.282	11.317
2500	15.650	84.759	72.650	30.272	-150.049	-123.113	10.763
2600	15.717	85.374	73.127	31.840	-150.631	-121.809	10.239
2700	15.769	85.968	73.592	33.415	-151.202	-120.480	9.752
2800	15.808	86.542	74.044	34.994	-151.763	-119.132	9.299
2900	15.834	87.097	74.485	36.576	-152.317	-117.787	8.874
3000	15.848	87.634	74.914	38.160	-152.841	-116.439	8.477
3100	15.853	88.154	75.333	39.745	-153.359	-115.056	8.105
3200	15.849	88.657	75.742	41.330	-153.860	-113.529	7.754
3300	15.838	89.145	76.140	42.915	-154.349	-112.078	7.423
3400	15.820	89.618	76.530	44.498	-154.823	-110.611	7.110
3500	15.797	90.076	76.910	46.079	-155.289	-109.126	6.814
3600	15.770	90.520	77.282	47.657	-155.747	-107.621	6.533
3700	15.739	90.952	77.646	49.233	-156.196	-106.099	6.267
3800	15.705	91.371	78.002	50.805	-156.636	-104.561	6.014
3900	15.669	91.779	78.350	52.373	-157.063	-103.013	5.773
4000	15.631	92.175	78.690	53.938	-157.477	-101.455	5.542
4100	15.592	92.561	79.024	55.500	-157.880	-99.887	5.304
4200	15.552	92.936	79.351	57.057	-158.275	-98.310	5.064
4300	15.512	93.301	79.671	58.610	-158.663	-96.725	4.821
4400	15.472	93.658	79.985	60.159	-159.044	-95.132	4.574
4500	15.432	94.005	80.293	61.705	-159.418	-93.530	4.322
4600	15.393	94.344	80.594	63.246	-159.786	-91.916	4.064
4700	15.354	94.674	80.890	64.783	-160.149	-90.291	3.800
4800	15.316	94.997	81.181	66.317	-160.507	-88.655	3.530
4900	15.278	95.312	81.466	67.846	-160.860	-87.008	3.254
5000	15.242	95.621	81.746	69.372	-161.209	-85.356	2.972
5100	15.207	95.922	82.021	70.895	-161.554	-83.700	2.684
5200	15.172	96.217	82.291	72.414	-161.895	-82.040	2.390
5300	15.139	96.506	82.557	73.929	-162.232	-80.376	2.090
5400	15.107	96.789	82.818	75.442	-162.566	-78.708	1.784
5500	15.076	97.065	83.074	76.951	-162.896	-77.036	1.472
5600	15.046	97.337	83.327	78.457	-163.222	-75.360	1.154
5700	15.017	97.603	83.575	79.960	-163.545	-73.680	0.830
5800	14.989	97.864	83.819	81.460	-163.865	-71.996	0.500
5900	14.963	98.120	84.059	82.956	-164.182	-70.308	0.164
6000	14.937	98.371	84.296	84.453	-164.496	-68.616	-0.174

June 30, 1968; Dec. 31, 1968

Point Group C_{2v}

$\Delta H_f^\circ = [-257 \pm 5] \text{ kcal. mole}^{-1}$

$\Delta H_f^\circ 298.15 = [-259 \pm 5] \text{ kcal. mole}^{-1}$

$S^\circ 298.15 = [64.31] \text{ cal. deg}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}
[3680](1)	[888](1)
[1463](1)	[698](1)
[1420](1)	[480](1)
[1250](1)	[480](1)

Bond Distance: B-F = [1.30] Å B-O = [1.36] Å O-H = [0.96] Å

Bond Angle: F-B-F = [120]° F-B-O = [120]° B-O-H = [105]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.05094 \times 10^{-114}] \text{ g}^3 \text{ cm}^6$

$\sigma^- = 1$

Heat of Formation: $\Delta H_f^\circ 298.15$ was calculated based on an assumption that $\Delta H_f^\circ 298.15 = 0$ for the reaction $2/3 \text{ BF}_3(\text{g}) + 1/3 \text{ B(OH)}_3(\text{g}) = \text{BOHF}_2(\text{g})$.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from J. S. Gorden, Astrocyetene International, Inc., private communication, November 2, 1982. The B-F and O-H bond distances were assumed to be the same as those in $\text{BF}_3(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ molecules, respectively. The B-O bond distance and the bond angles were estimated from related molecules. The three principal moments of inertia are: $I_A = 7.8114 \times 10^{-39}$, $I_B = 8.3333 \times 10^{-39}$ and $I_C = 1.61447 \times 10^{-38} \text{ g. cm}^2$.

Boron Oxide Difluoride (BOF₂)
(Ideal Gas) GFW = 64.8072

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	.0000	INFINITE	-	2.757	-	199.317	INFINITE
100	8.114	53.574	73.172	1.960	-	199.568	438.430
200	9.843	59.653	65.017	1.073	-	199.809	216.246
298	11.998	63.989	63.989	.000	-	200.000	144.339
300	12.036	64.063	63.989	.022	-	200.003	143.435
400	13.900	67.792	64.485	1.323	-	200.150	106.997
500	15.307	71.053	65.479	2.787	-	200.272	85.119
600	16.330	73.039	66.653	4.371	-	200.372	70.526
700	17.070	74.515	67.844	6.054	-	200.452	60.446
800	17.618	75.632	69.106	7.779	-	200.510	52.273
900	18.026	80.432	70.307	9.563	-	200.555	46.165
1000	18.337	82.848	71.467	11.381	-	200.600	41.313
1100	18.577	84.808	72.582	13.238	-	200.700	37.326
1200	18.767	86.292	73.657	15.132	-	200.800	34.042
1300	18.919	87.411	74.679	16.980	-	200.883	31.188
1400	19.042	88.148	75.663	18.878	-	200.970	28.775
1500	19.143	89.607	76.607	20.787	-	201.069	26.683
1600	19.227	91.203	77.512	22.706	-	201.176	24.852
1700	19.298	92.876	78.381	24.642	-	201.268	23.237
1800	19.358	93.976	79.217	26.595	-	201.423	21.797
1900	19.409	95.024	80.022	28.504	-	201.559	20.509
2000	19.453	96.020	80.797	30.447	-	201.702	19.349
2100	19.492	96.971	81.545	32.384	-	201.832	18.300
2200	19.527	97.877	82.268	34.298	-	201.948	17.374
2300	19.557	98.747	82.964	36.259	-	202.178	16.471
2400	19.585	99.580	83.640	38.257	-	202.345	15.671
2500	19.611	100.380	84.293	40.216	-	202.512	14.924
2600	19.635	101.149	84.927	42.170	-	202.688	14.224
2700	19.658	101.887	85.542	44.113	-	202.868	13.574
2800	19.680	102.606	86.138	46.110	-	203.049	12.974
2900	19.701	103.297	86.718	48.079	-	203.234	12.412
3000	19.723	103.965	87.282	50.050	-	203.424	11.888
3100	19.744	104.612	87.831	52.034	-	203.612	11.397
3200	19.766	105.240	88.365	54.039	-	203.806	10.937
3300	19.788	105.848	88.886	55.977	-	203.999	10.503
3400	19.810	106.439	89.393	57.957	-	204.195	10.095
3500	19.834	107.014	89.888	59.939	-	204.394	9.710
3600	19.858	107.573	90.372	61.924	-	204.593	9.346
3700	19.882	108.117	90.842	63.915	-	204.795	8.999
3800	19.908	108.648	91.306	65.900	-	204.998	8.674
3900	19.935	109.165	91.757	67.882	-	205.203	8.364
4000	19.962	109.670	92.199	69.867	-	205.409	8.066
4100	19.990	110.164	92.631	71.885	-	205.616	7.782
4200	20.019	110.646	93.051	73.888	-	205.824	7.510
4300	20.049	111.117	93.469	75.888	-	206.034	7.256
4400	20.079	111.578	93.875	77.895	-	206.245	7.007
4500	20.110	112.030	94.273	79.904	-	206.457	6.763
4600	20.142	112.472	94.664	81.917	-	206.670	6.523
4700	20.174	112.906	95.048	83.933	-	206.884	6.286
4800	20.206	113.331	95.424	85.952	-	207.099	6.051
4900	20.239	113.748	95.794	87.974	-	207.315	5.816
5000	20.273	114.157	96.157	89.999	-	207.532	5.586
5100	20.306	114.559	96.518	92.028	-	207.750	5.356
5200	20.340	114.953	96.865	94.061	-	207.968	5.126
5300	20.374	115.341	97.210	96.096	-	208.187	4.896
5400	20.407	115.722	97.549	98.135	-	208.406	4.666
5500	20.441	116.097	97.883	100.178	-	208.625	4.436
5600	20.475	116.466	98.212	102.224	-	208.844	4.206
5700	20.508	116.828	98.535	104.273	-	209.063	3.976
5800	20.541	117.185	98.853	106.325	-	209.282	3.746
5900	20.574	117.537	99.167	108.381	-	209.501	3.516
6000	20.606	117.883	99.476	110.440	-	209.720	3.286

Dec. 31, 1965; Dec. 31, 1966

BORON OXIDE DIFLUORIDE (BOF₂)
(IDEAL GAS)

Point Group C_{2v} ΔH_f⁰ = [-199 ± 15] kcal/mol

S_{298.15}⁰ = [64] gibbs/mol ΔH_f⁰_{298.15} = [-200 ± 15] kcal/mol

Electronic Levels and Quantum Weights

$\frac{E, \text{ cm}^{-1}}{0}$	$\frac{g_i}{[2]}$
17171	[2]
22390	[2]

Vibrational Frequencies and Degeneracies

$\frac{\omega_e, \text{ cm}^{-1}}{1377 (1)}$	$\frac{\omega_e, \text{ cm}^{-1}}{(850) (1)}$
856 (1)	[1100] (1)
491 (1)	[500] (1)

Bond Distance : B-F = 1.30 ± 0.05 Å

Bond Angle : F-B-O = 117 ± 5°

Product of the Moments of Inertia: I_AI_BI_C = 9.9464 × 10⁻¹¹⁵ g³ cm⁶

Heat of Formation

The molecule BF₂O(g) is similar to BO₂(g) in that both have an extra electron. Based on an assumption that D₀(F₂B-O) = D₀(OB-O) = 10 = 134.3 kcal/mol, where the quantity -10 kcal/mol is estimated as the resonance stabilization energy in BO₂(g), the heat of formation (ΔH_f⁰_{298.15}) for BF₂O(g) is calculated to be -208 kcal/mol.

Assuming D₀(F₂BO-H) = D₀(HO-H) = 118 kcal/mol, the value of ΔH_f⁰_{298.15}(F₂BO,g) is evaluated as -191.6 kcal/mol, using ΔH_f⁰ = 51.63 and -257.35 kcal/mol for H(g) and F₂BOH(g), respectively.

The value of ΔH_f⁰_{298.15} for BOF₂(g) is tentatively adopted as -200 ± 15 kcal/mol.

Heat Capacity and Entropy

The 4465-Å emission spectrum was observed in a discharge through BF₃ and O₂ by C. W. Mathews, J. Mol. Spectry, **19**, 203 (1966). The emitter of the discharge was shown to be either the planar BOF₂ molecule or molecule-ion BOF₂⁺. No experimental evidence has been found to distinguish between them. The molecular structure, bond distances and angles were reported by Mathews, based on a rotational analysis of the emission spectrum. These values are adopted here.

Three vibrational frequencies for both 11P₁BOF₂ and 10P₁BOF₂ molecules (or ions) were determined by vibrational analysis of the 5800 - Å bands of the emission spectrum by C. W. Mathews and K. K. Innes, J. Mol. Spectry, **15**, 199 (1965). These values are corrected to the average isotopic species and adopted. The last three frequencies are estimated from values calculated by the valence-force method, using force constants transferred from COF₂(g).

The ground state quantum weight is taken as 2 because of the extra electron. The other two electronic levels are estimated from the band systems at 5800 and 4465 Å, assuming that the two systems have a common lower state, i.e. the ground state.

The three principal moments of inertia are: I_A = 8.4647 × 10⁻³⁹, I_B = 7.4045 × 10⁻³⁹ and I_C = 1.5869 × 10⁻³⁸ g cm².

BORON TRIFLUORIDE (BF₃) (IDEAL GAS) GFW = 67.8062

Boron Trifluoride (BF₃) (Ideal Gas) GFW = 67.8062

Point Group D_{3h}
S_{298.15} = 60.77 ± 0.01 gibbs/mol
Ground State Quantum Weight = 1
ΔH_{f,0}⁰ = -270.7 ± 0.4 kcal/mol
ΔH_{f,298.15}⁰ = -271.42 ± 0.4 kcal/mol

T, °K	C _p ⁰	S ⁰ - (C _p ⁰ - H _{298.15} ⁰)/T	gibbs/mol	H _f ⁰ - H _{298.15} ⁰	ΔH _f ⁰	Log K _p
0	∞	∞	∞	270.747	270.747	INFINITE
100	6.147	50.215	-1.986	270.998	269.907	589.680
200	10.030	56.372	-1.087	271.228	269.146	793.646
298	12.057	60.766	-0.000	271.420	268.722	196.046
300	12.092	60.841	0.022	271.424	267.428	194.621
400	13.753	64.556	1.318	271.605	266.068	145.373
500	15.044	67.770	2.761	271.786	264.664	115.684
600	16.430	70.405	4.317	271.953	263.223	95.879
700	17.733	72.533	5.959	272.103	261.755	81.723
800	17.344	75.413	7.666	272.240	260.269	71.102
900	17.779	77.483	9.423	272.363	258.765	62.637
1000	18.117	79.374	11.219	272.480	257.247	56.221
1100	18.383	81.118	13.044	272.594	255.719	50.807
1200	18.593	82.723	14.893	272.712	254.178	46.292
1300	18.766	84.218	16.762	272.832	252.629	42.471
1400	18.905	85.611	18.646	272.955	251.070	39.194
1500	19.021	86.922	20.542	273.066	249.502	36.352
1600	19.117	88.153	22.440	273.125	247.926	33.645
1700	19.199	89.315	24.365	273.171	246.339	31.649
1800	19.268	90.414	26.288	273.226	244.744	29.716
1900	19.327	91.457	28.218	273.285	243.144	27.968
2000	19.378	92.450	30.153	273.349	241.530	26.393
2100	19.422	93.396	32.093	273.419	239.912	24.968
2200	19.460	94.301	34.038	273.494	238.246	23.671
2300	19.494	95.167	35.985	273.574	236.546	22.487
2400	19.524	95.997	37.936	273.660	234.820	21.400
2500	19.551	96.795	39.890	273.750	233.081	20.390
2600	19.575	97.542	41.846	273.827	231.362	19.448
2700	19.598	98.247	43.805	273.916	229.672	18.574
2800	19.614	99.014	45.765	274.006	227.981	17.764
2900	19.631	99.703	47.728	274.099	226.267	17.007
3000	19.647	100.368	49.691	274.194	224.530	16.302
3100	19.661	101.013	51.657	274.290	222.741	15.641
3200	19.671	101.643	53.624	274.389	220.924	15.021
3300	19.685	102.243	55.597	274.489	219.091	14.438
3400	19.696	102.831	57.561	274.592	217.242	13.889
3500	19.706	103.402	59.531	274.699	215.374	13.371
3600	19.715	103.957	61.502	274.804	213.492	12.882
3700	19.724	104.504	63.474	274.914	211.594	12.419
3800	19.730	105.023	65.446	275.024	209.684	11.979
3900	19.738	105.536	67.420	275.134	207.758	11.562
4000	19.744	106.036	69.394	275.244	205.813	11.168
4100	19.750	106.523	71.368	275.359	203.859	10.810
4200	19.756	107.000	73.320	275.474	201.896	10.479
4300	19.766	107.491	75.256	275.594	199.924	10.170
4400	19.771	107.963	77.179	275.714	197.942	9.884
4500	19.774	108.423	79.097	275.834	195.952	9.620
4600	19.775	108.877	81.016	275.954	193.952	9.377
4700	19.780	109.323	82.934	276.074	191.942	9.154
4800	19.783	109.759	84.852	276.194	189.924	8.950
4900	19.786	110.187	86.769	276.314	187.896	8.766
5000	19.790	110.607	88.687	276.434	185.859	8.603
5100	19.793	111.019	90.597	276.554	183.813	8.458
5200	19.796	111.423	92.507	276.674	181.758	8.323
5300	19.801	111.823	94.417	276.794	179.694	8.197
5400	19.804	112.219	96.327	276.914	177.620	8.080
5500	19.806	112.611	98.237	277.034	175.536	7.972
5600	19.806	112.991	100.147	277.154	173.442	7.873
5700	19.811	113.366	102.057	277.274	171.338	7.782
5800	19.813	113.728	103.967	277.394	169.224	7.699
5900	19.815	114.087	105.877	277.514	167.100	7.623
6000	19.815	114.437	107.787	277.634	164.966	7.554

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1964; Sept. 30, 1965; June 30, 1969

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
888 (1)
696.7 (1)
1463.3 (2)
480.7 (2)

Bond Distance: B-F = 1.307 ± 0.002 Å
Bond Angle: F-B-F = 120°
Products of the Moments of Inertia: I_AI_BI_C = 1.0563 × 10⁻¹¹⁴ g³ cm⁶ σ = 6

Heat of Formation

The adopted heat of formation was selected by a simultaneous adjustment of several interrelated pieces of data relating to the heat of formation of HF (see HF, § table 11-11-60). The data which were considered relating directly to BF₃ were as follows.
A. NF₃(g) + B(c, β) + BF₃(g) + 0.5 H₂ ΔH₂₉₈⁰ = -231.46 ± 1.2 kcal/mol
Ludwig and Cooper (1) report the above value after correction for 0.44 percent impurities in the boron. As much as 5 percent unburned boron was determined by analysis.

B. 1.5 F₂(g) + B(c, β) + BF₃(g)
Wise et al. (2) originally reported ΔH₂₉₈⁰ = -270.1 ± 0.24 kcal/mol but later reanalysis (3) of the impurities and due allowance for their effect changed this to -271.6 ± 0.9 kcal/mol. Johnson et al. (3) using zone refined boron obtained ΔH₂₉₈⁰ = -271.65 ± 0.22 kcal/mol after correction for 0.12 percent impurities. Domalski and Armstrong (4) obtained ΔH₂₉₈⁰ = -271.03 ± 0.51 kcal/mol from a combustion in the presence of Teflon, the boron contained 0.32 percent impurities and corrections were included. The above reaction constituted about 0.35 of the total energy measured. The measurements of Gross et al. (5), although on a zone refined sample, did not include a complete purity analysis and their data were not included since probable impurities could introduce serious errors.

C. 3HF(50 H₂O) + B(c, β) + 0.75 O₂(g) + BF₃(g) + 1.5 H₂O(l)
From the measurements of Gunn (6) on the reaction of BF₃(g) + 15.67 HF(3.747 H₂O) + [solution] and Good and Månsson (7) for the reaction B(c, β) + 0.75 O₂(g) + 18.57 HF(3.085 H₂O) + [solution] + 1.5 H₂O(l), where this resulting solutions have the same composition, we obtain ΔH₂₉₈⁰ = -142.77 ± 0.5 kcal/mol. Further details of the simultaneous solution are given by Syverud (8).

Heat Capacity and Entropy

The fundamental frequencies were selected from the measurements of Lindeman and Wilson (9), McKean (10), Nielsen (11), Anderson et al. (12) and Yost et al. (13). The bond lengths and structure are those reported by Gin et al. (14) which are in agreement with those of Kuchitsu and Konaka (15) from gas phase electron diffraction. These measurements disagree with the earlier determinations of Nielson (11) and Levy and Brockway (16) but are considerably more precise and are adopted.
The individual moments of inertia are I_A = I_B = 8.083 × 10⁻³⁹ g cm² and I_C = 16.186 × 10⁻³⁹ g cm².

References

1. J. R. Ludwig and W. J. Cooper, J. Chem. Eng. Data **8**, 76 (1963).
2. S. S. Wise, J. L. Hargrave, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. **65**, 2157 (1961).
3. G. K. Johnson, H. M. Feder and W. N. Hubbard, J. Phys. Chem. **70**, 1 (1966).
4. E. S. Domalski and G. T. Armstrong, J. Res. Natl. Bur. Std. **71A**, 195 (1967).
5. P. Gross, C. Hayman, D. L. Levi and M. C. Stuart, Fulmer Research Institute Report R.146/4/23 Nov. 1960.
6. S. R. Gunn, J. Phys. Chem. **62**, 1010 (1958).
7. M. D. Good and M. Månsson, J. Phys. Chem. **70**, 97 (1966).
8. A. N. Syverud, AFPL-TR-69-70, January 1969.
9. L. F. Lindeman and M. K. Wilson, J. Chem. Phys. **24**, 1002 (1956).
10. D. C. McKean, J. Chem. Phys. **24**, 242 (1956).
11. A. H. Nielsen, J. Chem. Phys. **22**, 659 (1954).
12. T. F. Anderson, E. N. Lessetts and D. M. Yost, J. Chem. Phys. **44**, 703 (1966).
13. D. M. Yost, D. DeVault, T. F. Anderson, and E. N. Lessetts, J. Chem. Phys. **38**, 424 (1963).
14. S. G. W. Gln, J. K. Kenney and J. Overend, J. Chem. Phys. **45**, 442 (1966).
15. K. Kuchitsu and S. Konaka, J. Chem. Phys. **45**, 442 (1966).
16. H. Levy and L. O. Brockway, J. Amer. Chem. Soc. **59**, 2085 (1937).

GFW = 125.907

(CRYSTAL)

POTASSIUM TETRAFLUOROBORATE (KBF₄)

Potassium Tetrafluoroborate (KBF₄) (Crystal)

GFW = 125.907

T, °K	Cp	$\frac{\text{Btu}}{\text{lb-mol}} \cdot \frac{1}{^\circ\text{F}}$	$\frac{\text{cal}}{\text{mol}} \cdot \frac{1}{^\circ\text{K}}$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log Kp
0							
100							
200							
298	27.362	12.000	32.000	.000	-451.000	-424.625	312.774
300	27.433	32.170	32.001	.051	-450.995	-426.474	310.646
400	31.266	40.585	33.122	2.985	-451.237	-414.237	228.514
500	35.125	47.977	35.367	6.305	-450.687	-410.047	179.231
600	37.962	50.430	38.469	13.176	-446.681	-402.250	146.519
700	39.019	51.748	41.094	16.626	-444.165	-394.884	123.244
800	39.075	52.040	43.265	20.180	-442.600	-387.509	105.667
900	39.131	52.310	45.000	23.841	-441.969	-380.385	92.370
1000	39.188	52.567	47.466	27.606	-441.280	-373.246	81.573
1100	39.244	52.806	50.640	31.478	-440.543	-366.155	72.550
1200	40.301	55.916	56.370	35.455	-441.366	-356.356	64.901
1300	41.357	59.183	58.749	39.538	-440.220	-347.652	58.446
1400	42.413	62.287	61.054	43.727	-438.989	-339.037	52.926
1500	43.470	65.249	63.235	48.021	-437.674	-330.514	48.156

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1965; Dec. 31, 1969

 ΔH°_0 = Unknown $\Delta H^\circ_{298.15} = -451.0 \pm 1 \text{ kcal/mol}$ $\Delta H^\circ = 3.36 \pm 0.04 \text{ kcal/mol}$ $\Delta H_m^\circ = 4.22 \pm 0.04 \text{ kcal/mol}$ $\Delta H^\circ_{298.15} = [80] \text{ kcal/mol}$

Heat of Formation

Bills and Cotton (1) measured the enthalpies of several reactions at 25°C which led to the following result:

$$\text{H}_3\text{BO}_3(\text{c}) + 4(\text{HF} \cdot 23 \text{ H}_2\text{O}) + \text{KNO}_3(\text{c}) \rightarrow \text{KBF}_4(\text{c}) + \text{HNO}_3 \cdot 92 \text{ H}_2\text{O} + 3\text{H}_2\text{O}$$
 $\Delta H^\circ = -19.26 \pm 0.6 \text{ kcal/mol}$

Combining this result with the following heat of formation data,

 $\Delta H^\circ(\text{H}_3\text{BO}_3, \text{c}) = -261.47 \pm 0.2 \text{ kcal/mol (2)}$ $\Delta H^\circ(\text{HF} \cdot 23 \text{ H}_2\text{O}) = -76.75 \pm 0.1 \text{ kcal/mol (3)}$ $\Delta H^\circ(\text{KNO}_3, \text{c}) = -118.22 \text{ kcal/mol (4)}$ $\Delta H^\circ(\text{HNO}_3 \cdot 92 \text{ H}_2\text{O}) = -49.44 \text{ kcal/mol (5)}$ $\Delta H^\circ(\text{H}_2\text{O}, \text{l}) = -68.315 \text{ kcal/mol (5)}$

We derive, $\Delta H^\circ(\text{KBF}_4, \text{c}) = -451.6 \pm 1.2 \text{ kcal/mol}$.

Gross, Hayman, and Joël (6) recently measured the following heats of reaction:

 $\text{NaF}(\text{c}) + \text{BF}_3(\text{g}) \rightarrow \text{NaBF}_4(\text{c})$ $\Delta H^\circ = -32.04 \pm 0.12 \text{ kcal/mol}$ $\text{NaF}(\text{c}) + \text{HF}(\text{aq.}) \rightarrow \text{Solin A}$ $\Delta H^\circ = +8.14 \pm 0.18 \text{ kcal/mol}$ $\text{NaBF}_4(\text{c}) + \text{HF}(\text{aq.}) \rightarrow \text{Solin A}$ $\Delta H^\circ = -2.94 \pm 0.13 \text{ kcal/mol}$

These data combine to give, $\Delta H^\circ = -43.13 \pm 0.22 \text{ kcal/mol}$, for the reaction

 $\text{KF}(\text{c}) + \text{BF}_3(\text{g}) \rightarrow \text{KBF}_4(\text{c})$

Combining this result with the following heats of formation,

 $\Delta H^\circ(\text{KF}, \text{c}) = -135.9 \pm 0.1 \text{ kcal/mol (7)}$ $\Delta H^\circ(\text{BF}_3, \text{g}) = -271.42 \pm 0.4 \text{ kcal/mol (7)}$

We derive, $\Delta H^\circ(\text{KBF}_4, \text{c}) = -450.5 \pm 0.7 \text{ kcal/mol}$. An average value, $\Delta H^\circ(\text{KBF}_4, \text{c}) = -451.0 \pm 1 \text{ kcal/mol}$, of these two results is adopted here.

Heat Capacity and Entropy

The heat capacity data are calculated from the high temperature enthalpy data of Dworin and Bredig (8). S°_{298} is chosen such that a third-law analysis of the equilibrium data for the reaction

 $\text{KBF}_4(\text{c}, \text{l}) \rightleftharpoons \text{KF}(\text{c}, \text{l}) + \text{BF}_3(\text{g})$

reported by de Boer and van Liempt (9) gives the experimentally determined heat of reaction at 25°C (8).

Transition Data

It is from the high temperature studies of Dworin and Bredig (8). ΔH° is calculated from their high temperature enthalpy data.

Melting Data

T_m has been reported as 803°K by de Boer and van Liempt (9) and 843°K by Dworin and Bredig (8). Dworin and Bredig's value is adopted here. ΔH_m° is calculated from their high temperature enthalpy data.

Sublimation Data

ΔH°_{298} is estimated by comparison with data for LiAlF₄(c) reported by Hildenbrand and Theard (10).

References

1. J. L. Bills and F. A. Cotton, J. Phys. Chem., **64**, 1477 (1960).
2. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, Dec. 31, 1964.
3. Ref. 2, Dec. 31, 1968 and Ref. 2, MSRPD-MS2, 1965 and Ref. 5.
4. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
5. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
6. P. Gross, C. Hayman, and H. A. Joël, Trans. Faraday Soc., **64**, 317 (1968).
7. Ref. 2, June 30, 1969.
8. A. S. Dworin and M. A. Bredig, private communication, Oak Ridge Natl. Lab., Sept. 23, 1969.
9. J. H. de Boer and J. A. M. van Liempt, Rec. Trav. Chim., **146**, 124 (1977).
10. D. L. Hildenbrand and L. F. Theard, Aeronautic, Division of Ford Motor Company, Publication No. U-2174, June 15, 1961.

POTASSIUM TETRAFLUOROBORATE (KBF₄) (LIQUID)

GFW = 125.907

Potassium Tetrafluoroborate (KBF₄)

GFW = 125.907

 $\Delta H_f^\circ = \text{Unknown}$ $S_{298.15}^\circ = 35.88 \pm 4.0 \text{ gibbs/mol}$ $\Delta H_f^\circ = -446.8 \pm 1.5 \text{ kcal/mol}$ $T_m = 843^\circ\text{K}$ $\Delta H_m^\circ = 4.22 \pm 0.04 \text{ kcal/mol}$

Heat of Formation

$\Delta H_f^\circ(l)$ is calculated from $\Delta H_f^\circ(c)$ by adding the heat of melting and the difference in $H_{843} - H_{298}$ between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity data are calculated from the high temperature enthalpy data of Dworkin and Bredig (1). S_{298}° is calculated in a manner analogous to the heat of formation.

Melting Data

T_m has been reported as 803°K by de Boer and van Liempt (2) and 843°K by Dworkin and Bredig (1). Dworkin and Bredig's value is adopted here. ΔH_m° is calculated from their high temperature enthalpy data.

References

1. A. S. Dworkin and M. A. Bredig, private communication, Oak Ridge Natl. Lab., Sept. 23, 1969.
2. J. H. de Boer and J. A. M. van Liempt, Rec. Trav. Chim., 46, 124 (1927).

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
298	39.942	35.882	35.882	0.000	-446.801	-423.584	310.495
300	39.942	36.129	35.883	0.074	-446.773	-423.440	308.476
400	39.942	47.620	35.449	4.063	-445.955	-423.768	277.855
500	39.942	58.532	40.408	6.082	-444.731	-406.309	176.496
600	39.942	63.815	43.720	12.056	-443.602	-401.202	146.136
700	39.942	69.972	47.042	16.051	-442.542	-394.219	123.041
800	39.942	75.305	50.249	20.095	-441.536	-387.309	105.689
900	39.942	80.116	53.360	24.187	-440.584	-380.461	87.751
1000	39.942	84.218	56.105	28.033	-439.654	-374.072	81.753
1100	39.942	86.025	56.909	32.027	-437.685	-366.533	72.623
1200	39.942	91.508	61.482	36.022	-435.601	-358.292	65.254
1300	39.942	94.637	63.916	40.016	-435.543	-350.144	56.864
1400	39.942	96.222	66.222	44.010	-434.507	-342.078	53.400
1500	39.942	100.413	68.410	48.004	-433.493	-334.078	48.675

Dec. 31, 1969

GFW = 125.907

(IDEAL GAS)

POTASSIUM TETRAFLUOROBORATE (KBF₄)Potassium Tetrafluoroborate (KBF₄)

(Ideal Gas)

GFW = 125.907

 $\Delta H_f^\circ = [-369.0 \pm 5] \text{ kcal/mol}$ $\Delta H_f^\circ = [-371.0 \pm 5] \text{ kcal/mol}$ Point Group [C_{3v}]S_{298.15} = [75.35 ± 3] gibbs/mol

Ground State Quantum Weight = [1]

T, °K	Cp ^a	S ^b	-(C ^a -H ^b)/T	H ^a -H ^b /T	ΔH ^c	ΔG ^d	Log Kp
0	0.000	INFINITE	INFINITE	4.206	-	-369.001	INFINITE
100	10.833	57.949	91.403	3.345	-	-369.950	801.525
200	17.379	67.628	77.182	1.911	-	-363.249	396.940
298	21.257	75.350	77.852	0.000	-	-359.550	263.557
300	21.315	75.481	75.350	0.39	-	-359.479	261.880
400	23.922	81.993	74.220	2.309	-	-355.476	194.223
500	25.768	87.541	77.843	4.799	-	-352.193	153.568
600	27.097	92.363	79.954	7.484	-	-347.151	126.864
700	28.044	96.134	82.034	10.204	-	-342.914	107.042
800	28.780	100.113	84.100	13.050	-	-338.668	92.520
900	29.318	103.836	86.106	15.956	-	-334.402	81.204
1000	29.730	106.947	88.037	18.910	-	-330.123	72.148
1100	30.050	109.796	89.887	21.899	-	-324.808	64.533
1200	30.297	112.452	91.589	24.917	-	-318.452	58.161
1300	30.472	114.923	93.149	27.956	-	-312.606	52.554
1400	30.578	117.233	94.587	31.018	-	-306.517	47.649
1500	30.608	119.444	96.516	34.092	-	-300.435	43.773
1600	30.621	121.516	97.939	37.178	-	-294.360	40.208
1700	30.619	123.469	99.822	40.275	-	-288.301	36.945
1800	30.607	125.313	102.268	43.371	-	-282.259	34.267
1900	30.586	127.057	105.101	46.494	-	-276.166	31.766
2000	30.556	128.712	107.365	49.614	-	-270.104	29.516
2100	30.517	129.287	109.583	52.739	-	-264.050	27.680
2200	30.471	129.783	111.764	55.869	-	-258.096	26.130
2300	30.419	130.246	113.902	59.003	-	-252.143	24.830
2400	30.363	130.681	115.999	62.141	-	-246.192	23.792
2500	30.304	131.133	118.051	65.282	-	-240.244	22.958
2600	30.243	131.597	120.070	68.426	-	-234.298	22.302
2700	30.181	132.084	122.073	71.572	-	-228.356	21.800
2800	30.119	132.592	124.043	74.721	-	-222.417	21.444
2900	30.056	133.129	125.982	77.872	-	-216.482	21.176
3000	30.000	133.694	127.895	81.025	-	-210.552	21.000
3100	30.553	134.287	129.783	84.179	-	-204.623	20.920
3200	30.667	134.900	131.648	87.335	-	-198.696	20.930
3300	30.841	135.532	133.472	90.493	-	-192.772	21.000
3400	31.074	136.185	135.359	93.651	-	-186.850	21.176
3500	31.404	136.871	137.200	96.811	-	-180.928	21.400
3600	31.814	137.594	139.000	99.972	-	-175.000	21.676
3700	32.307	138.357	140.761	103.136	-	-169.072	22.000
3800	32.884	139.169	142.493	106.300	-	-163.144	22.376
3900	33.547	140.032	144.200	109.464	-	-157.216	22.800
4000	34.294	140.954	145.894	112.625	-	-151.288	23.276
4100	35.125	141.932	147.574	115.790	-	-145.360	23.800
4200	36.042	142.975	149.243	118.956	-	-139.432	24.376
4300	37.047	143.994	150.900	122.123	-	-133.504	25.000
4400	38.141	145.000	152.543	125.290	-	-127.576	25.676
4500	39.324	146.000	154.177	128.457	-	-121.648	26.400
4600	40.597	147.000	155.800	131.625	-	-115.720	27.176
4700	41.964	148.000	157.417	134.793	-	-109.792	28.000
4800	43.424	149.000	159.024	137.961	-	-103.864	28.876
4900	44.977	150.000	160.624	141.133	-	-97.936	29.800
5000	46.624	151.000	162.217	144.303	-	-92.008	30.776
5100	48.364	152.000	163.800	147.473	-	-86.080	31.800
5200	50.197	153.000	165.376	150.643	-	-80.152	32.876
5300	52.124	154.000	166.943	153.813	-	-74.224	34.000
5400	54.141	155.000	168.500	156.983	-	-68.296	35.176
5500	56.247	156.000	170.050	160.153	-	-62.368	36.400
5600	58.444	157.000	171.594	163.323	-	-56.440	37.676
5700	60.731	158.000	173.127	166.493	-	-50.512	39.000
5800	63.204	159.000	174.650	169.663	-	-44.584	40.376
5900	65.861	160.000	176.167	172.833	-	-38.656	41.800
6000	68.694	161.000	177.674	176.003	-	-32.728	43.276

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1965; Dec. 31, 1969

Raman spectra of BF₄ in various phases have been reported by (1, 2, 3, 4). The molecular structure is assumed to be the same as for LiAlF₄ as discussed by Porter and Zeller (5). The B-F and K-F bond lengths and F-B-F bond angle are average values of the crystallographic data recently reported by Clark and Lynton (6). The B-K bond length is calculated from the above structural data according to the assumed molecular model. The individual moments of inertia are $I_A = I_B = 5.292 \times 10^{-38} \text{ g cm}^2$ and $I_C = 1.617 \times 10^{-38} \text{ g cm}^2$.

References

1. G. L. Coté and H. W. Thompson, Proc. Royal Soc. (London), **210A**, 217 (1951).
2. J. O. Edwards, G. C. Morrison, V. F. Ross, and J. W. Schultz, J. Amer. Chem. Soc., **77**, 266 (1955).
3. J. Leconte, C. Duval, and C. Wadler, Compt. Rend., **249**, 1891 (1959).
4. J. A. A. Ketelaar and R. L. Fulton, Z. Elektrochem., **64**, 641 (1960).
5. R. F. Porter and E. E. Zeller, J. Chem. Phys., **33**, 858 (1960).
6. M. J. R. Clark and H. Lynton, Can. J. Chem., **47**, 2579 (1969).

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	Log K _p
0	0.000	0.000	INFINITE	- 2.065	105.039	INFINITE
100	6.962	33.438	47.242	- 1.380	103.222	- 225.580
200	6.966	38.265	41.685	- 0.684	105.638	- 110.329
298	6.975	41.047	41.047	0.000	105.800	- 72.296
300	6.975	41.060	41.047	0.013	105.801	- 71.818
400	7.111	43.701	41.047	0.013	105.801	- 42.585
500	7.108	44.576	41.860	1.418	105.775	- 40.683
600	7.252	45.984	42.425	2.135	105.667	- 33.282
700	7.422	47.114	43.016	2.869	105.534	- 27.787
800	7.569	48.027	43.592	3.520	105.387	- 23.671
900	7.695	48.735	44.155	4.094	105.230	- 20.314
1000	7.826	49.288	44.675	5.173	105.074	- 17.921
1100	8.067	50.611	45.181	5.973	104.907	- 15.835
1200	8.193	51.318	45.663	6.766	104.734	- 14.100
1300	8.265	51.826	46.124	7.501	104.553	- 12.684
1400	8.301	52.189	46.561	8.186	104.368	- 11.452
1500	8.492	53.180	46.986	9.262	104.166	- 10.294
1600	8.571	53.731	47.300	10.145	103.957	- 9.347
1700	8.641	54.253	47.779	11.005	103.739	- 8.512
1800	8.701	54.748	48.172	11.846	103.513	- 7.781
1900	8.761	55.221	48.512	12.746	103.280	- 7.111
2000	8.814	55.671	48.855	13.625	103.042	- 6.518
2100	8.861	56.103	49.104	14.509	102.799	- 5.983
2200	8.905	56.516	49.517	15.397	102.552	- 5.497
2300	8.946	56.910	49.830	16.280	102.300	- 5.054
2400	8.986	57.290	50.146	17.158	102.043	- 4.648
2500	9.019	57.662	50.427	18.086	96.394	- 4.288
2600	9.053	58.016	50.712	18.960	96.138	- 3.965
2700	9.084	58.358	50.989	19.807	95.881	- 3.666
2800	9.114	58.690	51.250	20.625	95.625	- 3.393
2900	9.143	59.009	51.520	21.420	95.370	- 3.150
3000	9.169	59.320	51.775	22.635	95.112	- 2.933
3100	9.195	59.621	52.023	23.593	94.856	- 2.669
3200	9.220	59.913	52.265	24.474	94.600	- 2.461
3300	9.246	60.197	52.500	25.290	94.344	- 2.266
3400	9.269	60.473	52.731	26.048	94.088	- 2.086
3500	9.290	60.743	52.957	27.251	93.831	- 1.908
3600	9.312	61.005	53.177	28.161	93.575	- 1.747
3700	9.333	61.260	53.392	29.113	93.318	- 1.593
3800	9.353	61.510	53.602	29.961	93.061	- 1.446
3900	9.375	61.753	53.808	30.984	92.804	- 1.311
4000	9.394	61.990	54.010	31.923	92.547	- 1.186
4100	9.414	62.222	54.207	32.863	92.290	- 1.071
4200	9.433	62.449	54.401	33.805	92.033	- 0.964
4300	9.451	62.672	54.592	34.748	91.776	- 0.865
4400	9.470	62.886	54.779	35.696	91.519	- 0.772
4500	9.489	63.102	54.959	36.644	91.262	- 0.685
4600	9.507	63.311	55.138	37.593	91.005	- 0.604
4700	9.524	63.516	55.315	38.545	90.748	- 0.528
4800	9.541	63.718	55.489	39.497	90.491	- 0.457
4900	9.559	63.916	55.657	40.453	90.234	- 0.390
5000	9.576	64.106	55.824	41.410	90.000	- 0.326
5100	9.593	64.296	55.989	42.369	89.753	- 0.266
5200	9.610	64.483	56.150	43.329	89.506	- 0.210
5300	9.626	64.666	56.309	44.284	89.259	- 0.158
5400	9.643	64.846	56.460	45.234	89.012	- 0.110
5500	9.660	65.023	56.620	46.219	88.765	- 0.064
5600	9.676	65.197	56.771	47.186	88.518	- 0.021
5700	9.692	65.369	56.921	48.154	88.271	- 0.021
5800	9.708	65.537	57.068	49.124	88.024	- 0.021
5900	9.725	65.700	57.215	50.094	87.777	- 0.021
6000	9.740	65.867	57.356	51.069	87.530	- 0.021

Dec. 31, 1980; Mar. 31, 1983; Dec. 31, 1984

Ground State Configuration $1\Sigma^+$
 $\Delta H_f^\circ 0 = 105.0 \pm 2.0 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [41.047] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ 298.15 = 105.8 \pm 2.0 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$\frac{\epsilon_i, \text{ cm.}^{-1}}{0} \frac{g_i}{1}$
 $\omega_e = [2368] \text{ cm.}^{-1}$
 $\omega_e x_e = [49] \text{ cm.}^{-1}$
 $\sigma = 1$
 $B_e = 12.036 \text{ cm.}^{-1}$
 $\alpha_e = .413 \text{ cm.}^{-1}$
 $r_e = 1.2325 \text{ \AA}$

Heat of Formation.

$\Delta H_f^\circ 298.15$ was calculated from D_0 (BH) = 3.39 ± 0.04 e.v. reported by A. C. Hurley, Proc. Royal Soc. (London), A281, 237 (1961). Hurley stated "by combining an analysis of the spectroscopic data with theoretical calculations we obtain a greatly improved estimate of D_0 (BH)". This value and the other D_0 (BH) values which are tabulated below are based on the same spectroscopic data but differ due to different methods of analysis.

D_0 (BH)	Method	Reference
3.0 ± 0.4 e.v.	Birge-Sponner extrapolations	A. G. Heydon "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, Ltd., London, 1955.
3.5 e.v.	Observed predissociation by rotation in BH, A ¹ Π and deduced D_0 (BH).	G. M. Alley and R. B. Horsfall Jr., Phys. Rev., 51, 491 (1937).

< 3.51 e.v.

Pre-dissociation limit. This is only an upper limit due to a maximum in the potential curve of the A¹Π state.

3.38 ± 0.04 e.v.

The potential energy curve of the A¹Π state was determined and was found to have a maximum and a minimum in agreement with Herzberg and Mundle (loc. cit.)

Heat Capacity and Entropy.

The molecular constants from G. Herzberg (loc. cit.) were adjusted for the natural abundance of B^{10} and B^{11} . Because the constants ω_e and $\omega_e x_e$ could not be determined directly from the spectrum, Alley and Horsfall (loc. cit.) obtained estimates for the ground state $X\ 1\Sigma^+$ from the rotational contents for this state and the relations $D_e = 4 B_e^2 / \omega_e^2$ and $\omega_e x_e / \omega_e = 0.6 \alpha_e / B_e$.

Boron Oxide Hydride (HBO)

(Ideal Gas) Mol. Wt. = 27.828

BORON OXIDE HYDRIDE (HBO)

(IDEAL GAS)

MOL. WT. = 27.828

Point Group C_{2v}
 $S_{298.15}^\circ = [50.256] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Round State Quantum Weight = 1

$\Delta H_f^\circ 0 = [-20 \pm 20] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [-20 \pm 20] \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

(cm.^{-1})
 [1900](1)
 [700](2)
 [2300](1)

Bond Distance: H-B = $[1.23] \text{ \AA}$ B-O = $[1.20] \text{ \AA}$
 Bond Angle: H-B-O = $[180]^\circ$
 Rotational Constants: $B_0 = [1.3011] \text{ cm.}^{-1}$

 $\sigma = 1$

Heat of Formation

The heat of formation of the hypothetical species HBO(g) is controversial. Using $\Delta H_f^\circ 298.15 = [255] \text{ kcal. mole}^{-1}$ for the reaction $\text{HBO(g)} = \text{H(g)} + \text{O(g)}$, the value of $\Delta H_f^\circ 298.15$ for HBO(g) is calculated as $[-13] \text{ kcal. mole}^{-1}$. The value of $\Delta H_f^\circ 298.15$ is the sum of the constituent bond energies, i.e. $D(\text{H-B}) = 87$ and $D(\text{B-O}) = 168 \text{ kcal. mole}^{-1}$. The $D(\text{H-B})$ value is derived from the dissociation of $\text{BH}_3(\text{g})$ and $D(\text{B-O})$ value is calculated as the average value of the B-O bond energies, 175 and 161 kcal. mole^{-1} , in BO(g) and $\text{BO}_2(\text{g})$ molecules, respectively.

However, by comparison with the following dissociation reactions:

$(\text{FBO})_3(\text{g}) \rightarrow 3 \text{ FBO(g)}$ $\Delta H_f^\circ 298.15 = 135 \text{ kcal. mole}^{-1}$ or 45 kcal. mole^{-1} per mole of FBO(g)
 $(\text{HBO})_3(\text{g}) \rightarrow 3 \text{ HBO(g)}$ $\Delta H_f^\circ 298.15 = 141.8 \text{ kcal. mole}^{-1}$ or 47 kcal. mole^{-1} per mole of HBO(g)
 $(\text{ClBO})_3(\text{g}) \rightarrow 3 \text{ ClBO(g)}$ $\Delta H_f^\circ 298.15 = 170.6 \text{ kcal. mole}^{-1}$ or 57 kcal. mole^{-1} per mole of ClBO(g)

It is estimated $\Delta H_f^\circ 298.15 = [70] \text{ kcal. mole}^{-1}$ for the reaction $1/3(\text{HBO})_3(\text{g}) \rightarrow \text{HBO(g)}$, based on the electronegativity difference among the F, Cl and H atoms. Hence the value of $\Delta H_f^\circ 298.15$ for HBO(g) is calculated to be $-27 \text{ kcal. mole}^{-1}$. The adopted value of $\Delta H_f^\circ 298.15$ for HBO(g) is $1/2(-13-27) = -20 \text{ kcal. mole}^{-1}$. The uncertainty is given as $\pm 20 \text{ kcal. mole}^{-1}$. Other methods of estimation have been tried such as the comparison of the difference in $\Delta H_f^\circ 298.15$ between H-CH_3 and HO-CH_3 with the corresponding difference between H-BO and HO-BO , etc. They lead to very large negative values for $\Delta H_f^\circ 298.15(\text{HBO, g})$. However, a value of $260 \pm 15 \text{ kcal. mole}^{-1}$ for the atomization of HBO(g) was used by L. V. Ourvech, et al., "Thermodynamic Properties of Individual Substances," Vol. I, Academy of Science, USSR, Moscow, 1962, which was obtained by comparison with the dissociation energies for BO, BH, CH and HCN molecules.

Heat Capacity and Entropy

The vibrational frequencies and molecular structure were obtained from W. H. Evans, private communication, October 6, 1960. The bond lengths of H-B and B-O in the HBO(g) molecule were assumed to be the same as those in the BH(g) and BO(g) molecules, respectively. The moment of inertia (I) is calculated as $2.1561 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C_p°	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	INFINITE	2.215	19.873	19.873	INFINITE
100	6.972	40.373	5.574	19.021	20.654	45.138
200	7.620	45.349	4.342	19.021	21.387	23.381
298	8.635	48.584	4.484	20.000	22.109	16.206
300	8.652	48.637	4.494	20.002	22.123	16.116
400	9.694	51.246	4.934	20.118	22.813	12.466
500	10.190	53.442	4.922	20.261	23.471	10.259
600	10.802	55.355	5.021	20.413	24.089	8.277
700	11.345	56.968	5.127	20.579	24.677	6.597
800	11.819	58.308	5.207	20.699	25.283	5.207
900	12.225	60.024	5.280	20.825	25.868	4.077
1000	12.571	61.331	5.361	20.943	26.400	3.169
1100	12.863	62.243	5.414	21.057	26.940	2.532
1200	13.118	62.735	5.456	21.168	27.491	2.070
1300	13.348	63.036	5.492	21.261	27.991	1.749
1400	13.556	63.264	5.523	21.346	28.451	1.449
1500	13.746	63.434	5.550	21.421	28.871	1.169
1600	13.916	63.556	5.574	21.488	29.261	0.909
1700	14.068	63.634	5.595	21.548	29.631	0.669
1800	14.204	63.674	5.613	21.604	29.981	0.449
1900	14.326	63.688	5.628	21.654	30.311	0.249
2000	14.436	63.688	5.640	21.699	30.621	0.069
2100	14.534	63.668	5.648	21.739	30.911	-0.111
2200	14.622	63.624	5.653	21.774	31.181	-0.311
2300	14.698	63.560	5.656	21.804	31.431	-0.511
2400	14.764	63.478	5.656	21.829	31.661	-0.711
2500	14.822	63.380	5.653	21.849	31.871	-0.911
2600	14.874	63.268	5.648	21.864	32.061	-1.111
2700	14.922	63.144	5.640	21.874	32.231	-1.311
2800	14.966	63.008	5.628	21.879	32.381	-1.511
2900	15.006	62.864	5.613	21.879	32.511	-1.711
3000	15.042	62.704	5.595	21.864	32.621	-1.911
3100	15.074	62.528	5.574	21.839	32.711	-2.111
3200	15.102	62.336	5.548	21.804	32.781	-2.311
3300	15.126	62.132	5.517	21.759	32.831	-2.511
3400	15.146	61.908	5.481	21.704	32.861	-2.711
3500	15.162	61.664	5.440	21.639	32.871	-2.911
3600	15.174	61.400	5.385	21.564	32.861	-3.111
3700	15.182	61.116	5.316	21.479	32.821	-3.311
3800	15.186	60.812	5.232	21.384	32.751	-3.511
3900	15.186	60.488	5.136	21.279	32.651	-3.711
4000	15.182	60.144	5.028	21.164	32.521	-3.911
4100	15.174	59.780	4.908	21.039	32.371	-4.111
4200	15.162	59.396	4.776	20.904	32.201	-4.311
4300	15.146	58.992	4.632	20.759	32.011	-4.511
4400	15.126	58.568	4.476	20.604	31.801	-4.711
4500	15.102	58.124	4.308	20.439	31.571	-4.911
4600	15.074	57.660	4.128	20.264	31.321	-5.111
4700	15.042	57.176	3.936	20.079	31.051	-5.311
4800	15.006	56.672	3.732	19.884	30.761	-5.511
4900	14.966	56.148	3.516	19.679	30.451	-5.711
5000	14.922	55.604	3.288	19.464	30.121	-5.911
5100	14.874	55.040	3.048	19.239	29.771	-6.111
5200	14.822	54.456	2.796	18.994	29.401	-6.311
5300	14.764	53.852	2.532	18.729	28.991	-6.511
5400	14.698	53.228	2.256	18.444	28.541	-6.711
5500	14.622	52.584	1.968	18.139	28.051	-6.911
5600	14.534	51.920	1.668	17.814	27.521	-7.111
5700	14.436	51.236	1.356	17.469	26.951	-7.311
5800	14.326	50.532	1.032	17.104	26.341	-7.511
5900	14.204	49.808	0.696	16.719	25.681	-7.711
6000	14.068	49.064	0.348	16.314	25.071	-7.911

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o)/T	H ^o -H ^o 298	kcal/mol ΔH ^o	ΔG ^o	Log Kp
100							
200							
298	9.067	51.774	51.774	.000	335.000	330.452	- 242.228
300	9.085	51.831	51.775	.017	335.008	330.423	- 240.713
400	9.931	54.256	52.182	.067	335.015	329.814	- 235.242
500	10.656	56.659	52.762	1.999	335.031	327.134	- 142.690
600	11.273	58.657	53.698	3.095	336.222	325.358	- 118.511
700	11.615	60.636	54.564	4.251	336.618	323.515	- 101.006
800	12.022	62.245	55.425	5.456	337.023	321.616	- 97.661
900	12.452	63.613	56.256	6.704	337.458	319.659	- 94.275
1000	12.906	65.003	57.059	7.984	337.926	317.669	- 69.426
1100	13.226	66.311	57.862	9.294	338.429	315.629	- 62.710
1200	13.441	67.471	58.615	10.627	338.959	313.553	- 57.106
1300	13.620	68.534	59.338	11.981	339.514	311.439	- 52.358
1400	13.769	69.524	60.033	13.356	340.094	309.284	- 48.474
1500	13.897	70.454	60.701	14.734	340.700	307.121	- 44.747
1600	14.004	71.424	61.344	16.129	340.921	304.921	- 41.650
1700	14.096	72.276	61.962	17.534	340.700	302.658	- 38.914
1800	14.175	73.084	62.557	18.948	341.072	300.430	- 36.269
1900	14.243	73.852	63.132	20.366	341.434	298.240	- 33.705
2000	14.302	74.586	63.686	21.796	341.784	296.099	- 31.234
2100	14.354	75.284	64.222	23.229	342.144	293.996	- 28.855
2200	14.400	75.952	64.740	24.667	342.487	291.926	- 26.536
2300	14.441	76.593	65.242	26.109	342.823	289.895	- 24.265
2400	14.476	77.209	65.724	27.554	343.146	287.900	- 22.042
2500	14.506	77.800	66.199	29.004	343.465	285.945	- 19.867
2600	14.538	78.370	66.656	30.456	343.780	284.020	- 17.741
2700	14.564	78.919	67.100	31.912	344.082	282.180	- 15.666
2800	14.588	79.449	67.532	33.366	344.374	280.013	- 13.646
2900	14.610	79.960	67.956	34.818	344.658	277.830	- 11.686
3000	14.631	80.457	68.366	36.269	344.934	275.636	- 9.790
3100	14.649	80.937	68.758	37.755	345.197	273.436	- 7.920
3200	14.667	81.403	69.146	39.221	345.452	271.222	- 6.121
3300	14.684	81.854	69.524	40.689	345.694	269.003	- 4.372
3400	14.699	82.291	69.894	42.149	345.924	266.782	- 2.686
3500	14.715	82.719	70.254	43.629	346.146	264.552	- 1.052
3600	14.729	83.134	70.606	45.101	346.362	262.279	- 0.437
3700	14.743	83.538	70.950	46.574	346.572	260.022	- 0.185
3800	14.756	83.931	71.286	48.049	346.776	257.753	- 0.125
3900	14.769	84.314	71.614	49.524	346.974	255.482	- 0.166
4000	14.779	84.686	71.936	51.003	347.166	253.212	- 0.207
4100	14.795	85.054	72.253	52.482	347.352	250.942	- 0.248
4200	14.808	85.410	72.562	53.962	347.534	248.672	- 0.289
4300	14.820	85.759	72.865	55.444	347.712	246.402	- 0.330
4400	14.831	86.103	73.165	56.929	347.886	244.132	- 0.371
4500	14.855	86.433	73.455	58.410	348.056	241.862	- 0.412
4600	14.857	86.760	73.739	59.895	348.222	239.592	- 0.453
4700	14.865	87.079	74.019	61.382	348.384	237.322	- 0.494
4800	14.881	87.393	74.295	62.869	348.542	235.052	- 0.535
4900	14.894	87.703	74.569	64.356	348.696	232.782	- 0.576
5000	14.905	88.001	74.831	65.848	348.846	230.512	- 0.617
5100	14.916	88.296	75.092	67.339	348.992	228.242	- 0.658
5200	14.928	88.586	75.349	68.831	349.134	225.972	- 0.699
5300	14.940	88.870	75.601	70.324	349.272	223.702	- 0.740
5400	14.951	89.149	75.849	71.815	349.406	221.432	- 0.781
5500	14.963	89.424	76.094	73.315	349.536	219.162	- 0.822
5600	14.974	89.694	76.334	74.811	349.662	216.892	- 0.863
5700	14.986	89.959	76.571	76.309	349.784	214.622	- 0.904
5800	14.997	90.219	76.804	77.809	349.902	212.352	- 0.945
5900	15.008	90.476	77.034	79.306	350.016	210.082	- 0.986
6000	15.019	90.728	77.260	80.810	350.126	207.812	- 1.027

June 30, 1968

(IDEAL GAS)

BORON OXIDE HYDRIDE UNIPosITIVE ION (HBO⁺)

GFW = 27.81782

Point Group [C_{∞v}]
S_{298.15} = [51.8 ± 1.5] gibbs/mol
ΔH^o_f = [335 ± 20] kcal/mol
ΔH^o_f = [335 ± 20] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[4]
[20000]	[2]

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	g_i
[1700] (1)	[600] (2)
[2000] (1)	[2000] (1)

Bond Distance: B-H = [1.25] Å
Bond Angle: H-B-O = [180°]
Rotational Constant: B₀ = [1.208] cm⁻¹
σ = 1

Heat of Formation

Using the correlations developed by A. D. Walsh, J. Chem. Soc. 2288 (1933) for HAO molecules the electron removed by ionization ought to be a bonding electron. This indicates a high ionization potential and also the bond dissociation energy of BO-H⁺ should be significantly less than BO-H. Assuming a decrease of 40 kcal we obtain ΔH^o_f(HBO⁺, g) = 335 ± 20 kcal/mol, which corresponds to an ionization potential of 355 kcal or 15.4 ± 1 eV. This is in accord with the ionization potential of BO, 12.8 eV, from National Bureau of Standards Report 8628, Jan. 1, 1965, which should be less than HBO since this electron in BO is unpaired.

Heat Capacity and Entropy

According to the correlations of Walsh loc.cit., the molecule should be linear and since the unpaired electron is in a pi orbital, the ground state should be ²Π. A first excited state is estimated at 20000 cm⁻¹ to be ²Σ by analogy with the isoelectronic molecule CO⁺. Since HBO⁺ is lacking a bonding electron compared to HBO, we assume that the bond lengths will be slightly longer than in HBO. The vibrational frequencies are also estimated from those in HBO by assuming all values to be 10 per cent lower due to the weaker bonding.

The enthalpy at 0°K is -2.275 kcal/mol.

BHO⁺

Metaboric Acid (HBO₂)

(Crystal) Mol. Wt. = 43.828

T. °K.	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0							
100							
200							
298	13.000	11.700	11.700	0.000	-191.870	-175.677	128.769
300	13.100	11.781	11.781	0.024	-191.870	-175.677	127.902
400	14.700	15.778	12.234	1.417	-191.857	-170.147	92.959
500	15.900	19.187	13.292	2.947	-191.821	-164.723	71.997
600	17.100	22.188	14.529	4.295	-191.773	-159.293	56.051
700	18.300	24.681	15.773	5.490	-191.709	-153.912	48.051
800	19.500	26.757	17.131	6.457	-191.632	-148.547	40.579
900	20.700	28.429	18.429	10.446	-190.979	-143.219	34.777
1000	22.000	32.337	19.706	12.630	-190.566	-137.933	30.144
1100	22.480	34.456	20.923	14.865	-189.137	-132.401	26.362
1200	22.960	36.256	22.131	17.043	-187.117	-127.686	23.217
1300	22.800	38.256	23.331	19.403	-185.296	-122.819	20.563
1400	22.960	39.954	24.458	21.694	-183.893	-117.181	18.292
1500	23.000	41.540	25.545	23.993	-182.509	-112.074	16.328

METABORIC ACID (HBO₂)

(CRYSTAL)

MOL. WT. = 43.828

ΔH_f° O = Unknown

ΔH_f° 298.15 = -191.87 ± 0.20 kcal. mole⁻¹

ΔH_m° = Unknown

ΔH_s° 298.15 = 57.9 ± 1.0 kcal. mole⁻¹

S° 298.15 = [11.7 ± 1.0] cal. deg.⁻¹ mole⁻¹

T_m = 509 ± 1°K

Heat of Formation.

The enthalpy change (ΔH_f°) of the reaction HBO₂ (c, I) + H₂O(l) = H₃BO₃(c) has been determined by M. V. Kilday and E. J. Prosen, J. Am. Chem. Soc. 82, 5508 (1960). From the value, ΔH_f° 298.15 = -1.28 kcal. mole⁻¹, the heat of formation (ΔH_f° 298.15) for HBO₂ (c, I) is derived to be -191.87 ± 0.20 kcal. mole⁻¹ which is adopted. The heats of solution of HBO₂ (c, I) in H₂O(l) was measured by N. D. Sokolova, S. M. Skuratov, A. M. Shemonaeva and Y. M. Yuldasheva, Russ. J. Inorg. Chem. 6, 395 (1961). Based on the reported value, ΔH_f° 298.15 = 1.76 ± 0.01 kcal. mole⁻¹ for the reaction HBO₂(c, I) + 501 H₂O(l) = H₃BO₃·500 H₂O(sol.), the heat of formation for HBO₂(c, I) was derived as -189.46 ± 0.20 kcal. mole⁻¹, using ΔH_f° 298.15(H₂O, l) = -68.317 and ΔH_f° 298.15(H₃BO₃·500 H₂O, sol.) = -286.02 ± 0.20 kcal. mole⁻¹.

Heat Capacity and Entropy.

The values of heat capacity for HBO₂(c, I) were estimated by comparison with those of its constituent oxides. S° 298.15 was calculated as the sum of the entropy contributions from H⁺ and BO₂⁻ in HBO₂(c) suggested by K. K. Kelley, private communication, June 1960, and O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York, 1958.

Melting Data.

P. C. Kreczek, O. M. Morey and H. E. Merwin, Am. J. Sci. (5) 35A, 143 (1938) reported the existence of three crystal forms of HBO₂(c), namely HBO₂(c, I), m.p. 503 ± 1°K; HBO₂(c, II), m.p. 474.1 ± 0.5°K; and HBO₂(c, III), m.p. 449.2 ± 0.2°K. However, there was no solid phase equilibrium found among these three crystals. N. D. Sokolova, S. M. Skuratov, A. M. Shemonaeva and Y. M. Yuldasheva, loc. cit., measured the heats of solution in water of HBO₂(c, I) and HBO₂(c, II) and derived the heat of transition as ΔH_t° 298.15(II → I) = 1.29 kcal. mole⁻¹.

Heat of Sublimation.

The value of ΔH_s° 298.15 was calculated as the difference between the ΔH_f° 298.15 values for HBO₂(g) and HBO₂(c).

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	<0.00	INFINITE	2.544	-133.175	-133.175	INFINITE	
100	7.6816	57.273	1.094	-130.457	-130.457	71.275	
200	8.616	53.517	1.028	-133.709	-133.709	144.430	
300	9.404	52.273	1.000	-134.000	-134.000	196.310	
400	10.118	57.273	0.910	-134.006	-134.006	95.705	
500	11.366	60.420	1.094	-134.311	-134.311	71.275	
600	12.466	58.504	2.287	-129.459	-129.459	56.584	
700	13.402	65.436	3.382	-134.896	-128.401	46.768	
800	14.189	67.562	4.262	-135.161	-127.297	39.742	
900	14.851	69.502	6.483	-135.404	-126.159	34.463	
1000	15.434	71.284	6.247	-135.626	-124.989	30.350	
1100	15.895	72.934	9.495	-135.831	-123.795	27.054	
1200	16.311	74.469	64.372	-136.026	-122.583	24.354	
1300	16.671	75.904	65.274	-136.210	-121.351	22.100	
1400	16.986	77.251	66.144	-136.390	-120.106	20.181	
1500	17.260	78.520	66.983	-136.566	-118.847	18.552	
1600	17.501	79.719	67.793	-136.742	-117.575	17.150	
1700	17.713	80.856	68.574	-136.920	-116.292	15.884	
1800	17.901	81.935	69.328	-137.100	-115.006	14.783	
1900	18.066	82.963	70.057	-137.284	-113.761	13.803	
2000	18.214	83.944	70.763	-137.471	-112.556	12.926	
2100	18.345	84.882	71.445	-137.659	-111.381	12.155	
2200	18.462	85.779	72.107	-137.851	-109.713	11.417	
2300	18.567	86.641	72.748	-138.047	-108.370	10.765	
2400	18.661	87.468	73.370	-138.246	-107.017	10.168	
2500	18.746	88.264	73.974	-138.451	-105.652	9.620	
2600	18.822	89.031	74.561	-138.664	-104.276	9.107	
2700	18.892	89.771	75.132	-138.880	-102.896	8.622	
2800	18.955	90.485	75.688	-139.100	-101.516	8.172	
2900	19.012	91.175	76.228	-139.324	-100.136	7.755	
3000	19.063	91.843	76.755	-139.552	-98.756	7.364	
3100	19.113	92.490	77.269	-139.784	-97.376	6.999	
3200	19.156	93.118	77.770	-140.020	-95.996	6.659	
3300	19.197	93.727	78.260	-140.260	-94.616	6.339	
3400	19.234	94.318	78.737	-140.504	-93.236	6.037	
3500	19.268	94.893	79.204	-140.752	-91.856	5.753	
3600	19.300	95.452	79.660	-141.004	-90.476	5.485	
3700	19.336	95.996	80.107	-141.260	-89.096	5.231	
3800	19.371	96.526	80.543	-141.520	-87.716	4.991	
3900	19.404	97.042	80.971	-141.784	-86.336	4.762	
4000	19.436	97.546	81.389	-142.052	-84.956	4.546	
4100	19.467	98.038	81.799	-142.324	-83.576	4.342	
4200	19.496	98.518	82.201	-142.600	-82.196	4.148	
4300	19.524	98.986	82.595	-142.880	-80.816	3.964	
4400	19.550	99.445	82.982	-143.164	-79.436	3.792	
4500	19.574	99.893	83.361	-143.452	-78.056	3.632	
4600	19.597	100.331	83.733	-143.744	-76.676	3.484	
4700	19.619	100.760	84.099	-144.040	-75.296	3.348	
4800	19.639	101.180	84.468	-144.340	-73.916	3.224	
4900	19.657	101.592	84.831	-144.644	-72.536	3.112	
5000	19.673	101.995	85.187	-144.952	-71.156	3.010	
5100	19.688	102.391	85.538	-145.264	-69.776	2.918	
5200	19.702	102.779	85.884	-145.580	-68.396	2.836	
5300	19.715	103.159	86.162	-145.900	-67.016	2.764	
5400	19.727	103.533	86.487	-146.224	-65.636	2.702	
5500	19.738	103.903	86.806	-146.552	-64.256	2.650	
5600	19.748	104.269	87.120	-146.884	-62.876	2.608	
5700	19.757	104.631	87.429	-147.220	-61.496	2.576	
5800	19.765	104.991	87.734	-147.560	-60.116	2.554	
5900	19.772	105.343	88.034	-147.904	-58.736	2.542	
6000	19.778	105.695	88.329	-148.252	-57.356	2.540	
6100	19.783	106.047	88.620	-148.604	-55.976	2.548	

Dec. 31, 1960; Mar. 31, 1961; June 30, 1963; Dec. 31, 1964

METABORIC ACID (HBO₂)

(IDEAL GAS)

ΔH_f^o = -133.2 ± 1.0 kcal. mole⁻¹ΔH_f^o 298.15 = -134.0 ± 1.0 kcal. mole⁻¹ΔH_f^o 298.15 = -134.0 ± 1.0 kcal. mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹k, cm.⁻¹

[1250](1)

[600](1)

[700](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

[1420](1)

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

σ = 1

Bond Distances: H-O = [1.0] Å

Bond Angles: H-O-B = [120]°

Product of the Moments of Inertia: I_AI_BI_C = 9.6851 X 10⁻¹¹⁷ g.³ cm.⁶

Heat of Formation.

The equilibrium pressures of the reaction 1/2 B₂O₃(l) + 1/2 H₂O(g) = HBO₂(g) have been measured by several investigators. Using the equilibrium data reported, the heats of reaction (ΔH_f^o 298.15) were evaluated by both the second and third law methods. The corresponding heats of formation for HBO₂(g) were derived based on the ΔH_f^o 298.15 values obtained by the third law method. The results obtained are presented as follows.

Investigator

Temperature, °K.

Second Law Value

Third Law Value

ΔH_f^o 298.15, kcal. mole⁻¹ΔH_f

Boron Dihydride (BH₂)

(Ideal Gas) Mol. Wt. = 12.836

BORON DIHYDRIDE (BH₂) (IDEAL GAS)

MOL. WT. = 12.836

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	(H° - H° ₂₉₈)/T	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	35.000	35.000	35.000	2.153	48.163	48.163	48.163	INFINITE
200	7.332	43.045	43.045	1.575	48.088	48.088	48.088	- 102.769
298	8.133	43.045	43.045	1.000	48.000	48.000	48.000	- 32.903
300	8.149	43.046	43.046	0.915	47.997	47.997	47.997	- 32.686
400	8.597	45.553	45.553	0.771	47.837	47.837	47.837	- 23.998
500	9.597	47.682	47.682	1.199	47.653	47.653	47.653	- 18.759
600	10.160	49.422	49.422	2.188	47.467	47.467	47.467	- 15.274
700	10.671	51.027	51.027	3.930	47.291	47.291	47.291	- 12.809
800	11.136	52.483	52.483	4.920	47.130	47.130	47.130	- 10.907
900	11.556	53.819	53.819	6.055	46.987	46.987	46.987	- 9.538
1000	11.930	55.037	55.037	7.487	46.859	46.859	46.859	- 8.399
1100	12.258	56.210	56.210	8.440	46.739	46.739	46.739	- 7.469
1200	12.545	57.289	57.289	9.680	46.626	46.626	46.626	- 6.656
1300	12.795	58.303	58.303	10.948	46.510	46.510	46.510	- 6.044
1400	13.012	59.259	59.259	12.238	46.405	46.405	46.405	- 5.606
1500	13.200	60.164	60.164	13.549	46.289	46.289	46.289	- 5.003
1600	13.365	61.021	61.021	14.877	46.166	46.166	46.166	- 4.582
1700	13.508	61.835	61.835	16.221	46.038	46.038	46.038	- 4.212
1800	13.634	62.611	62.611	17.579	45.905	45.905	45.905	- 3.884
1900	13.745	63.351	63.351	18.951	45.768	45.768	45.768	- 3.598
2000	13.842	64.059	64.059	20.327	45.619	45.619	45.619	- 3.338
2100	13.928	64.736	64.736	21.716	45.469	45.469	45.469	- 3.091
2200	14.005	65.386	65.386	23.112	45.313	45.313	45.313	- 2.876
2300	14.074	66.010	66.010	24.516	45.153	45.153	45.153	- 2.681
2400	14.138	66.614	66.614	25.926	44.989	44.989	44.989	- 2.504
2500	14.198	67.189	67.189	27.343	44.827	44.827	44.827	- 2.348
2600	14.239	67.746	67.746	28.764	44.664	44.664	44.664	- 2.216
2700	14.283	68.284	68.284	30.190	44.508	44.508	44.508	- 2.094
2800	14.323	68.805	68.805	31.621	44.351	44.351	44.351	- 1.981
2900	14.360	69.309	69.309	33.055	44.191	44.191	44.191	- 1.877
3000	14.393	69.795	69.795	34.493	44.035	44.035	44.035	- 1.780
3100	14.424	70.268	70.268	35.934	43.883	43.883	43.883	- 1.689
3200	14.452	70.726	70.726	37.377	43.737	43.737	43.737	- 1.605
3300	14.477	71.171	71.171	38.824	43.596	43.596	43.596	- 1.526
3400	14.500	71.603	71.603	39.275	43.461	43.461	43.461	- 1.452
3500	14.522	72.024	72.024	40.724	43.331	43.331	43.331	- 1.383
3600	14.542	72.434	72.434	42.171	43.206	43.206	43.206	- 1.318
3700	14.561	72.832	72.832	43.617	43.086	43.086	43.086	- 1.257
3800	14.578	73.221	73.221	45.069	42.974	42.974	42.974	- 1.199
3900	14.593	73.600	73.600	46.528	42.868	42.868	42.868	- 1.144
4000	14.609	73.970	73.970	47.988	42.764	42.764	42.764	- 1.091
4100	14.622	74.330	74.330	49.450	42.661	42.661	42.661	- 1.039
4200	14.635	74.683	74.683	50.913	42.560	42.560	42.560	- 0.989
4300	14.647	75.027	75.027	52.377	42.461	42.461	42.461	- 0.940
4400	14.658	75.369	75.369	53.842	42.364	42.364	42.364	- 0.892
4500	14.669	75.694	75.694	55.308	42.269	42.269	42.269	- 0.845
4600	14.679	76.016	76.016	56.775	42.176	42.176	42.176	- 0.799
4700	14.688	76.332	76.332	58.242	42.084	42.084	42.084	- 0.754
4800	14.697	76.645	76.645	59.709	41.993	41.993	41.993	- 0.709
4900	14.705	76.955	76.955	61.176	41.903	41.903	41.903	- 0.664
5000	14.713	77.262	77.262	62.642	41.814	41.814	41.814	- 0.619
5100	14.720	77.553	77.553	64.108	41.726	41.726	41.726	- 0.574
5200	14.727	77.819	77.819	65.574	41.640	41.640	41.640	- 0.529
5300	14.733	78.100	78.100	67.039	41.555	41.555	41.555	- 0.484
5400	14.739	78.375	78.375	68.504	41.471	41.471	41.471	- 0.439
5500	14.745	78.646	78.646	69.972	41.388	41.388	41.388	- 0.394
5600	14.751	78.911	78.911	71.439	41.305	41.305	41.305	- 0.349
5700	14.756	79.172	79.172	72.895	41.223	41.223	41.223	- 0.304
5800	14.761	79.429	79.429	74.346	41.141	41.141	41.141	- 0.259
5900	14.766	79.681	79.681	75.792	41.060	41.060	41.060	- 0.214
6000	14.770	79.930	79.930	77.234	40.980	40.980	40.980	- 0.169

Dec. 31, 1960; Dec. 31, 1964

Point Group [D_{∞h}]ΔH_f⁰ = 48 ± 15 kcal. mole⁻¹S_{298.15} = [43.045] cal. deg.⁻¹ mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω_j, cm.⁻¹ [ω_j, cm.⁻¹] [g_j, cm.⁻¹] [2g_j]

[2430](1) [840](2) [2650](1)

Bond Distance: B-H = [1.20 Å]

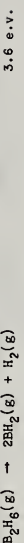
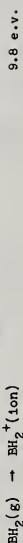
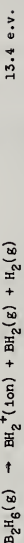
Bond Angle: H-B-H = [180°]

Rotational Constant: B₀ = 5.80683 cm.⁻¹

σ = 2

Heat of Formation.

ΔH_f⁰ 298.15 was calculated from appearance potentials reported by T. P. Fehlner and W. S. Koski, J. Am. Chem. Soc. **86**, 2733 (1964) and the JANAF (B₂H₆(g)) ΔH_f⁰ 298.15 = +9.8 kcal. mole⁻¹. For example

The ΔH_f⁰ data is summarized below.

Investigator	Method	ΔH _f ⁰ 298.15 kcal. mole ⁻¹
T. P. Fehlner and W. S. Koski (loc. cit.)	Appearance Potentials	48
C. J. Olmstead and J. R. Perrin, Marquardt Corp., Van Nuys, Calif., and J. Ferrier, Oilin Matheson Chemical Corp., New York 22, N.Y., "Estimation of the Heats of Formation of Gaseous Combustion Product Molecules", October 1959.	Estimate	66
P. C. H. Jordan and H. C. Longuet-Higgins, Mol. Phys. 5 , 121 (1962).	Estimate	93

The bond distance B-H = 1.20 Å was estimated from a consideration of BH(g), BH₂(g) and other molecules. The bond angle H-B-H = 180° and the electronic configuration of the ground state [2_g] were estimated by P. C. H. Jordan and H. C. Longuet-Higgins (loc. cit.). The frequencies were estimated assuming valence forces [G. Herzberg, "Molecular Spectra and Molecular Structure II Infrared and Raman Spectra of Polyatomic Molecules" D. Van Nostrand Co. Inc., N. Y. (1945) pgs 172] and using force constants, k₁ = 3.5 × 10⁵ dynes cm.⁻¹ and k_f = 0.35 × 10⁵ dynes cm.⁻¹, estimated from BH₃, (see A. Shepp and S. H. Bauer, J. Am. Chem. Soc. **76**, 265 (1954)).

Heat Capacity and Entropy.

The bond distance B-H = 1.20 Å was estimated from a consideration of BH(g), BH₂(g) and other molecules. The bond angle H-B-H = 180° and the electronic configuration of the ground state [2_g] were estimated by P. C. H. Jordan and H. C. Longuet-Higgins (loc. cit.). The frequencies were estimated assuming valence forces [G. Herzberg, "Molecular Spectra and Molecular Structure II Infrared and Raman Spectra of Polyatomic Molecules" D. Van Nostrand Co. Inc., N. Y. (1945) pgs 172] and using force constants, k₁ = 3.5 × 10⁵ dynes cm.⁻¹ and k_f = 0.35 × 10⁵ dynes cm.⁻¹, estimated from BH₃, (see A. Shepp and S. H. Bauer, J. Am. Chem. Soc. **76**, 265 (1954)).

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	.000	.000	INFINITE	2.814	-112.423	-112.423	INFINITE
100	8.200	47.428	67.576	-2.015	-113.102	-113.246	245.115
200	10.129	53.643	59.178	-1.107	-113.557	-109.217	119.342
298	12.432	58.116	.000	.000	-114.000	-106.994	78.425
300	12.475	58.193	58.116	.023	-114.008	-106.951	77.910
400	14.625	62.085	58.632	1.381	-114.377	-104.540	57.115
500	16.377	65.544	59.675	2.934	-114.667	-102.046	44.602
600	17.769	68.658	60.917	4.644	-114.887	-99.500	36.241
700	18.813	71.469	62.249	6.416	-115.031	-96.326	28.767
800	19.581	74.069	63.549	8.146	-115.120	-93.176	22.271
900	20.580	76.448	64.852	10.437	-115.231	-89.100	16.472
1000	21.226	78.651	66.123	12.528	-115.270	-84.440	11.115
1100	21.771	80.700	67.356	14.679	-115.288	-79.483	7.182
1200	22.230	82.610	68.543	16.828	-115.280	-74.245	3.658
1300	22.610	84.410	69.700	19.123	-115.260	-68.726	0.574
1400	22.970	86.100	70.814	21.404	-115.244	-62.974	11.074
1500	23.262	87.695	71.885	23.716	-115.250	-56.910	10.025
1600	23.514	89.205	72.921	26.035	-115.239	-50.366	8.276
1700	23.731	90.637	73.937	28.267	-115.229	-43.366	6.877
1800	23.925	91.999	74.888	30.500	-115.220	-35.810	5.732
1900	24.092	93.297	75.823	32.701	-115.232	-27.704	4.777
2000	24.240	94.537	76.728	35.618	-115.239	-19.048	4.067
2100	24.370	95.723	77.604	38.049	-115.252	-9.760	3.542
2200	24.489	96.855	78.450	40.066	-115.252	0.000	3.142
2300	24.589	97.950	79.278	42.584	-115.269	5.234	2.816
2400	24.681	99.008	80.078	45.409	-115.335	10.464	2.557
2500	24.763	100.008	80.855	48.437	-120.767	15.742	2.360
2600	24.837	100.980	81.611	50.361	-120.809	16.894	2.216
2700	24.904	101.916	82.346	52.184	-120.809	17.952	2.100
2800	24.965	102.826	83.051	53.942	-120.909	18.916	2.000
2900	25.019	103.703	83.757	55.641	-120.966	19.800	1.916
3000	25.069	104.552	84.437	57.284	-121.028	20.616	1.848
3100	25.115	105.375	85.099	58.865	-121.094	21.360	1.794
3200	25.157	106.171	85.747	60.386	-121.164	22.036	1.750
3300	25.195	106.947	86.376	61.806	-121.244	22.650	1.717
3400	25.230	107.700	86.992	63.126	-121.326	23.200	1.684
3500	25.263	108.432	87.594	64.346	-121.415	23.696	1.656
3600	25.293	109.144	88.183	65.466	-121.508	24.136	1.634
3700	25.320	109.831	88.757	66.486	-121.606	24.520	1.615
3800	25.346	110.513	89.322	67.406	-121.712	24.856	1.597
3900	25.370	111.172	89.874	68.226	-121.822	25.144	1.580
4000	25.392	111.814	90.415	68.946	-121.936	25.384	1.564
4100	25.412	112.441	90.944	69.566	-122.054	25.576	1.549
4200	25.430	113.055	91.463	70.086	-122.176	25.720	1.534
4300	25.449	113.653	91.973	70.506	-122.302	25.824	1.519
4400	25.466	114.238	92.472	70.826	-122.432	25.896	1.504
4500	25.482	114.810	92.962	71.146	-122.566	25.936	1.489
4600	25.497	115.371	93.443	71.466	-122.704	25.944	1.474
4700	25.510	115.919	93.916	71.786	-122.846	25.916	1.459
4800	25.522	116.455	94.381	72.006	-122.992	25.856	1.444
4900	25.536	116.983	94.835	72.226	-123.142	25.764	1.429
5000	25.547	117.499	95.284	72.446	-123.296	25.636	1.414
5100	25.558	118.005	95.724	72.666	-123.454	25.474	1.399
5200	25.570	118.501	96.149	72.886	-123.616	25.284	1.384
5300	25.578	118.988	96.564	73.006	-123.782	25.064	1.369
5400	25.587	119.466	96.970	73.126	-123.952	24.816	1.354
5500	25.596	119.936	97.366	73.246	-124.126	24.544	1.339
5600	25.604	120.397	97.744	73.366	-124.304	24.244	1.324
5700	25.612	120.849	98.116	73.486	-124.486	23.916	1.309
5800	25.620	121.296	98.476	73.606	-124.672	23.564	1.294
5900	25.627	121.734	98.824	73.726	-124.862	23.184	1.279
6000	25.634	122.165	99.161	73.846	-125.056	22.784	1.264

Dec. 31, 1960; Dec. 31, 1964.

Point Group [C_{2h}]
 $\Delta H_f^\circ 0 = [-112 \pm 15] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [-114 \pm 15] \text{ kcal. mole}^{-1}$

S° 298.15 = [58.116] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
[2500](1)	[750](1)	[1300](1)
[1150](1)	[460](1)	[1000](1)
[1100](1)	[3000](1)	[450](1)

Bond Distance: B-O = [1.27] Å O-H = [0.97] Å

Bond Angle: H-O-B = [105]° O-B-O = [180]°

Product of the Moments of Inertia: $I_A I_B I_C = [2.42627 \times 10^{-116}] \text{ g.}^3 \text{ cm.}^6$

σ = 2

Heat of Formation.

The value of $\Delta H_f^\circ 298.15$ for B(OH)₂(g) was calculated by using the bond energy, D°(B-OH) = 132.7 kcal. mole⁻¹, and the heats of formation for B(g) and OH(g) as 132.80 and 9.33 kcal. mole⁻¹, respectively.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for B(OH)₃(g) and other related molecules. The bond distances and angles were estimated by comparison with those for B(OH)₃(g) and H₂O₂(g) molecules. The molecular configuration is assumed to be trans which is considered as more stable than the cis-form. The three principal moments of inertia are: $I_A = 2.6870 \times 10^{-40}$, $I_B = 9.3682 \times 10^{-39}$ and $I_C = 9.6369 \times 10^{-39} \text{ g. cm.}^2$

Boron Trihydride (BH₃)

(Ideal Gas) Mol. Wt. = 13.844

T, °K.	C _p	S°	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	7.952	INFIMITE	2.421	26.407	26.407	INFIMITE	INFIMITE
100	7.983	35.983	1.626	26.057	26.057	-57.004	-57.004
200	8.159	45.855	.824	25.874	25.874	-28.674	-28.674
298	8.657	48.680	.000	25.800	25.800	-19.420	-19.420
300	8.666	48.934	.016	25.492	26.500	-19.304	-19.304
400	9.304	47.512	.514	25.027	26.905	-14.700	-14.700
500	10.048	49.666	1.881	24.532	27.432	-11.990	-11.990
600	10.863	51.569	2.926	24.052	28.037	-10.210	-10.210
700	11.658	53.207	4.054	23.581	28.741	-8.979	-8.979
800	12.439	54.622	5.264	23.117	29.523	-8.065	-8.065
900	13.207	56.440	6.554	22.673	30.333	-7.365	-7.365
1000	13.957	57.874	8.058	22.253	31.179	-6.814	-6.814
1100	14.576	59.234	9.700	21.867	32.052	-6.388	-6.388
1200	15.122	60.524	10.323	21.512	32.952	-6.001	-6.001
1300	15.603	61.756	11.924	21.185	33.883	-5.653	-5.653
1400	16.026	62.926	13.497	20.883	34.849	-5.342	-5.342
1500	16.396	64.046	15.048	20.602	35.841	-5.070	-5.070
1600	16.721	65.115	16.580	20.340	36.866	-4.833	-4.833
1700	17.007	66.138	18.111	20.112	37.924	-4.622	-4.622
1800	17.258	67.117	19.635	20.035	39.013	-4.430	-4.430
1900	17.460	68.056	21.152	20.060	40.133	-4.255	-4.255
2000	17.627	68.958	22.658	20.187	41.287	-4.100	-4.100
2100	17.762	69.825	24.152	20.412	42.467	-3.961	-3.961
2200	17.868	70.659	25.633	20.637	43.673	-3.837	-3.837
2300	17.947	71.462	27.100	20.862	44.906	-3.726	-3.726
2400	18.002	72.237	28.552	21.087	46.167	-3.626	-3.626
2500	18.038	72.986	29.988	21.312	47.455	-3.536	-3.536
2600	18.058	73.700	31.409	21.537	48.770	-3.455	-3.455
2700	18.067	74.384	32.818	21.762	50.113	-3.381	-3.381
2800	18.067	75.043	34.218	21.987	51.484	-3.314	-3.314
2900	18.058	75.673	35.609	22.212	52.884	-3.254	-3.254
3000	18.038	76.278	36.992	22.437	54.313	-3.200	-3.200
3100	18.008	76.855	38.368	22.662	55.772	-3.151	-3.151
3200	17.968	77.400	39.738	22.887	57.261	-3.107	-3.107
3300	17.919	77.919	41.103	23.112	58.780	-3.068	-3.068
3400	17.862	78.400	42.463	23.337	60.329	-3.033	-3.033
3500	17.798	78.850	43.818	23.562	61.908	-3.002	-3.002
3600	17.728	79.268	45.168	23.787	63.517	-2.974	-2.974
3700	17.653	79.650	46.513	24.012	65.156	-2.949	-2.949
3800	17.573	80.000	47.853	24.237	66.825	-2.926	-2.926
3900	17.488	80.318	49.188	24.462	68.524	-2.904	-2.904
4000	17.398	80.600	50.518	24.687	70.253	-2.883	-2.883
4100	17.303	80.850	51.843	24.912	72.012	-2.863	-2.863
4200	17.203	81.075	53.163	25.137	73.801	-2.843	-2.843
4300	17.098	81.275	54.478	25.362	75.620	-2.823	-2.823
4400	16.988	81.450	55.788	25.587	77.469	-2.803	-2.803
4500	16.873	81.600	57.093	25.812	79.348	-2.783	-2.783
4600	16.753	81.725	58.393	26.037	81.257	-2.763	-2.763
4700	16.628	81.825	59.688	26.262	83.196	-2.743	-2.743
4800	16.498	81.900	60.978	26.487	85.165	-2.723	-2.723
4900	16.363	81.950	62.263	26.712	87.164	-2.703	-2.703
5000	16.223	81.975	63.543	26.937	89.193	-2.683	-2.683
5100	16.078	81.975	64.818	27.162	91.252	-2.663	-2.663
5200	15.928	81.950	66.088	27.387	93.341	-2.643	-2.643
5300	15.773	81.900	67.353	27.612	95.460	-2.623	-2.623
5400	15.613	81.825	68.613	27.837	97.609	-2.603	-2.603
5500	15.448	81.725	69.868	28.062	99.788	-2.583	-2.583
5600	15.278	81.600	71.118	28.287	101.997	-2.563	-2.563
5700	15.103	81.450	72.363	28.512	104.236	-2.543	-2.543
5800	14.923	81.275	73.598	28.737	106.505	-2.523	-2.523
5900	14.738	81.075	74.823	28.962	108.804	-2.503	-2.503
6000	14.548	80.850	76.043	29.187	111.133	-2.483	-2.483

Dec. 31, 1960; Dec. 31, 1964

BORON TRIHYDRIDE (BH₃)

(IDEAL GAS)

BH₃

MOL. WT. = 13.844

Point Group [D_{3h}]

ΔH_f⁰ = 26.4 ± 10 kcal. mole⁻¹

S_{298.15}⁰ = [44.680] cal. deg.⁻¹ mole⁻¹

ΔH_f⁰ 298.15 = 25.5 ± 10 kcal. mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[2384](1)	[602](1)
[1765](2)	[2976](2)

Bond Distances: B-H = [1.16 Å]

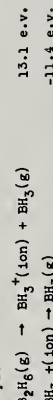
Bond Angle: H-B-H = [120°]

Product of the Moments of Inertia: I_AI_BI_C = [7.71 X 10⁻¹¹g.³ cm.⁶]

σ = 6

Heat of Formation

ΔH_f⁰ 298.15 was calculated from appearance potentials reported by T. P. Fehlner and W. S. Koski J. Am. Chem. Soc. 86, 2733 (1964). For example



The heat of formation data is summarized below.

Reaction: B₂H₆(g) → 2BH₃(g)*

*The auxiliary ΔH_f⁰ 298.15(B₂H₆) was from the JANAP Table dated Dec. 31, 1964

Investigator	Method	ΔH _f ⁰
P. C. H. Jordan and H. C. Longuet-Higgins	Bond energy parameters obtained by linear extrapolation from NH and CH bonds	59.9 kcal. mole ⁻¹
Bayley, and P. E. Stafford, J. Chem. Phys. 41, 2207(1964)	Apparent equilibrium constants	55 ± 8 kcal. mole ⁻¹
E. J. Sinke, et al. (loc. cit.)	A recalculation by JANAP and P = 10 ⁻¹⁶ atm (ΔG = degree of dissociation)	49 ± 8 kcal. mole ⁻¹
W. C. Price, T. R. Passmore and D. M. Roessler, Discussions Faraday Soc. 35, 201 (1963)	Correlations of ionization and dissociation energies of hydrides and fluorides in relation to electronic structure.	41.5 kcal. mole ⁻¹
T. P. Fehlner and W. S. Koski (loc. cit.)	Appearance Potentials	39.2 kcal. mole ⁻¹
M. E. Garabedian and S. H. Benson, J. Am. Chem. Soc. 86, 176 (1964).	From kinetic data for the decomposition of BH ₃ CO	32-38 kcal. mole ⁻¹
R. E. McCoy and S. H. Bauer J. Am. Chem. Soc. 78, 2061 (1956)	From calorimetric measurements of analogous compounds	28.4 ± 2 kcal. mole ⁻¹
L. Pauling, "The Nature of the Chemical Bond" Cornell University Press, Ithaca, N.Y. (1960) 3rd Ed.	From electronegativities	23.9 kcal. mole ⁻¹
		18 kcal. mole ⁻¹

Heat Capacity and Entropy

The molecular configuration, [planar, H-B-H angle = 120°], was estimated by A. Shepp and S. H. Bauer, J. Am. Chem. Soc. 76, 265 (1954) as well as by P. C. H. Jordan and H. C. Longuet-Higgins, (loc. cit.). In addition Shepp and Bauer estimated the bond distance and the vibrational frequencies. Jordan and Longuet-Higgins estimated the electronic configuration [A₁]. The principal moments of inertia calculated from these molecular constants are, I_A = I_B = 3.378 X 10⁻⁴⁰ and I_C = 6.756 X 10⁻⁴⁰ gm.²

BH₃

Mol. Wt. = 61.844

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	0.000	0.000	0.000	-258.231	-258.231	19.714
100	6.958	18.616	1.681	-256.549	-256.549	20.532
200	14.018	22.615	0.000	-251.567	-251.567	21.532
298	19.440	21.210	0.000	-251.567	-251.567	16.968
300	19.540	21.331	-0.036	-251.567	-251.567	16.968
400	25.830	23.613	2.316	-251.567	-251.567	16.968
500	27.400	23.302	4.790	-251.567	-251.567	16.968
600	30.400	23.764	7.683	-251.567	-251.567	16.968
700	32.260	24.032	10.534	-251.567	-251.567	16.968
800	33.820	24.172	13.342	-251.567	-251.567	16.968
900	35.080	24.248	16.109	-251.567	-251.567	16.968
1000	36.100	24.249	18.841	-251.567	-251.567	16.968
1100	40.147	24.273	23.612	-251.567	-251.567	16.968
1200	41.400	24.273	28.691	-251.567	-251.567	16.968
1300	43.327	24.273	34.036	-251.567	-251.567	16.968
1400	43.327	24.273	39.577	-251.567	-251.567	16.968
1500	44.000	24.273	45.345	-251.567	-251.567	16.968

Heat of Formation (ΔH_f⁰) of H₃BO₃(c) was taken from W. D. Good, M. Mansson and J. P. McCullough, Quarterly Technical Report No. 9, Nov. 4, 1963, U. S. Bur. Mines, Bartlesville, Oklahoma. The value was derived based on the following measurements

B(c) + 0.75 O₂(g) + 18.674 HF-57.219 H₂O(l) = HBF₄·14.674 HF-58.719 H₂O(l)
 H₃BO₃(c) + 18.674 HF-55.719 H₂O(l) = HBF₄·14.675 HF-58.719 H₂O(l)
 The heats of solution of H₃BO₃(c) in water have been measured by many investigators. L. G. Fasolino, "Heat of Formation of B₂O₃(c) and B₂O₃(am.)" NONR-3608 (OO), June 2, 1964, National Research Corporation, Massachusetts, obtained the value, ΔH_f⁰ 298.15 = 5.45 ± 0.01 kcal mole⁻¹ for the reaction H₃BO₃(c) + 504 H₂O(l) = H₃BO₃·504 H₂O(sol.) which leads to ΔH_f⁰ 298.15 (H₃BO₃·504 H₂O, sol.) = -256.02 kcal mole⁻¹. The ΔH_f⁰ 298.15 value is in reasonable agreement with the value reported by J. Smieko and L. S. Mason, J. Am. Chem. Soc. 72, 3679 (1950) in which the heats of solution and dilution of H₃BO₃(c) were given. The heats of solution of H₃BO₃(c) in water measured by other previous investigators were reviewed by L. G. Fasolino, loc. cit.

Heat Capacity and Entropy

The low temperature (16-295°K) heat capacities were reported by H. L. Johnston and E. C. Kerr, J. Am. Chem. Soc. 72, 4733 (1950). The heat capacities above 300°K were estimated by comparison with those of its constituent oxides. S_{298.15} was obtained from H. L. Johnston and E. C. Kerr, loc. cit., using S₁₇ = 0.18 cal deg⁻¹ mole⁻¹.

Melting Data

The value of T_m was taken from F. C. Krack, G. W. Morey and H. E. Merwin, Am. J. Sci. [5] 35A, 143 (1938). However, H₃BO₃(c) is in a metastable state at T_m. Measurements of the decomposition pressure of H₃BO₃(c) to form HBO₂(c, II or III) and H₂O(g) have been made by H. Menzel, H. Schulz and H. Deckert, Z. anorg. allgem. Chem. 220, 49 (1934); A. Thiel and H. Siebenack, Z. anorg. allgem. Chem. 220, 236 (1934); M. V. Stachelberg, F. Outram and J. Dussel, Z. Elektrochem. 43, 14 (1937); S. Bezzi, Gazz. chim. ital. 65, 766 (1935); and H. Tazaki, J. Sci. Hiroshima Univ. Ser. A 10, 37, 55, 63, 109, 113 (1939). The decomposition pressures of the system H₃BO₃(c) = H₂O(g) + HBO₂(c, I), at the temperatures of 312 to 352°K, have been reported by E. D. West, "The properties of Boron Compounds", ARL Technical Report 60-278, May 1960, National Bureau of Standards.

Temperature of Decomposition

The decomposition temperature (T_d) is calculated as the temperature at which the free energy change of the reaction H₃BO₃(c) + HBO₂(c) + H₂O(g) approaches zero.

Heat of Sublimation

The heat of sublimation (ΔH_s⁰ 298.15) is derived as the difference between the ΔH_f⁰ 298.15 values for H₃BO₃(g) and H₃BO₃(c).



MOL. WT. = 61.844

(IDEAL GAS)

BORIC ACID (H_3BO_3)

Boric Acid (H_3BO_3) Mol. Wt. = 61.844

T. °K.	C_p	$S^\circ - (H^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _f
0	11.043	56.791	-235.509	-231.294	505.469
100	12.873	64.896	-236.334	-226.770	247.791
200	15.616	70.539	-237.160	-221.900	162.649
300	15.659	70.636	-237.175	-221.806	161.378
400	16.371	75.522	-237.187	-221.570	118.323
500	20.640	79.874	-236.503	-211.166	92.296
600	22.471	83.805	-236.002	-205.450	74.004
700	23.946	86.468	-235.431	-200.055	64.457
800	25.215	90.468	-234.734	-194.411	53.108
900	26.280	93.701	-234.033	-188.726	45.827
1000	27.199	96.519	-233.260	-183.011	39.995
1100	27.994	99.150	-232.451	-177.270	35.250
1200	28.693	101.717	-231.600	-171.529	31.238
1300	29.300	103.917	-230.743	-165.765	27.666
1400	29.832	106.129	-229.860	-159.975	24.975
1500	30.298	108.203	-228.969	-154.212	22.466
1600	30.708	110.172	-228.074	-148.427	20.273
1700	31.061	112.050	-227.177	-142.633	18.413
1800	31.367	113.830	-226.273	-136.834	16.813
1900	31.639	115.534	-225.369	-131.026	15.471
2000	31.880	117.165	-224.477	-125.217	13.662
2100	32.143	118.728	-223.582	-119.400	12.426
2200	32.422	120.227	-222.686	-113.586	11.350
2300	32.722	121.670	-221.790	-107.775	10.239
2400	33.043	123.056	-220.894	-101.961	9.291
2500	33.387	124.395	-219.998	-96.147	8.390
2600	33.758	125.685	-219.102	-90.332	7.559
2700	34.157	126.931	-218.206	-84.517	6.788
2800	34.585	128.136	-217.310	-78.702	6.071
2900	35.043	129.302	-216.414	-72.887	5.403
3000	35.531	130.432	-215.518	-67.072	4.760
3100	36.049	131.528	-214.622	-61.257	4.197
3200	36.597	132.590	-213.726	-55.442	3.650
3300	37.175	133.624	-212.830	-49.627	3.135
3400	37.783	134.628	-211.934	-43.812	2.651
3500	38.421	135.604	-211.038	-37.997	2.194
3600	39.089	136.555	-210.142	-32.182	1.762
3700	39.787	137.481	-209.246	-26.367	1.342
3800	40.515	138.381	-208.350	-20.552	0.932
3900	41.273	139.254	-207.454	-14.737	0.532
4000	42.061	140.102	-206.558	-8.922	0.142
4100	42.879	140.925	-205.662	-3.107	-0.248
4200	43.727	141.725	-204.766	2.708	-0.638
4300	44.605	142.502	-203.870	6.854	-1.028
4400	45.513	143.257	-202.974	10.900	-1.418
4500	46.451	143.991	-202.078	14.946	-1.808
4600	47.419	144.695	-201.182	18.992	-2.198
4700	48.417	145.369	-200.286	23.038	-2.588
4800	49.445	146.013	-199.390	27.084	-2.978
4900	50.503	146.627	-198.494	31.130	-3.368
5000	51.591	147.211	-197.598	35.176	-3.758
5100	52.709	147.765	-196.702	39.222	-4.148
5200	53.857	148.289	-195.806	43.268	-4.538
5300	55.035	148.783	-194.910	47.314	-4.928
5400	56.243	149.247	-194.014	51.360	-5.318
5500	57.481	149.681	-193.118	55.406	-5.708
5600	58.749	150.085	-192.222	59.452	-6.098
5700	60.047	150.459	-191.326	63.498	-6.488
5800	61.375	150.803	-190.430	67.544	-6.878
5900	62.733	151.117	-189.534	71.590	-7.268
6000	64.121	151.401	-188.638	75.636	-7.658

Mar. 31, 1961; Dec. 31, 1964

Point Group C_{3h}

$S_{298.15}^\circ = [70.539] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = 1

$\Delta H_f^\circ = \text{Unknown}$

$\Delta H_f^\circ 298.15 = -237.16 \pm 0.60 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies		
ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
3250(1)	Rotation	1185(2)
1060(1)	3150(2)	Rotation
881(1)	1440(2)	Rotation
652(1)	544(2)	

Bond Distances: B-O = $[1.36] \text{ \AA}$ O-H = $[0.96] \text{ \AA}$

Bond Angle: H-O-B = $[114]^\circ$ O-B-O = $[120]^\circ$

Product of the Moments of Inertia: $I_{AB}I_C = [1.15684 \times 10^{-114}] \text{ g.}^3 \text{ cm.}^6$

$\sigma^- = 3$

Heat of Formation.

The vapor pressures of $\text{H}_3\text{BO}_3(\text{c})$, 109 - 140°C, were measured by M. V. Stackelberg, F. Quatram and J. Dressel, Z. Elektrochem. 53, 14 (1957). Using the vapor pressures reported, the heats of sublimation of $\text{H}_3\text{BO}_3(\text{c})$ were evaluated to be 24.4 ± 0.6 and $24.22 \text{ kcal. mole}^{-1}$ by the second and third law methods, respectively. The heat of formation ($\Delta H_f^\circ 298.15$) for $\text{H}_3\text{BO}_3(\text{c})$ was calculated from the $\Delta H_f^\circ 298.15$ and $\Delta H^\circ 298.15$ for $\text{H}_3\text{BO}_3(\text{c})$. The $\Delta H^\circ 298.15$ value adopted is the average of the second and third law values mentioned previously.

Heat Capacity and Entropy.

The molecular structure and constants were taken from O. W. F. T. Pistorius, J. Chem. Phys. 21, 1454 (1959) based on an X-ray diffraction study on $\text{H}_3\text{BO}_3(\text{c})$ by W. H. Zachariasen, Acta Cryst. 1, 305 (1954). The O-H bond distance was reestimated as 0.96 Å instead of 0.88 Å reported. From the existing infrared and Raman spectra data on $\text{H}_3\text{BO}_3(\text{c})$ and its aqueous solution C. W. F. T. Pistorius, loc. cit., carried out a normal coordinate treatment by means of Wilson's F-O matrix method and calculated the fifteen fundamental frequencies for $\text{H}_3\text{BO}_3(\text{c})$. For $\text{H}_3\text{BO}_3(\text{g})$ twelve reported frequencies were used and corrected to the average isotopic species. The three torsional frequencies, 824(1) and 209(2) cm.⁻¹, were not used based on an assumption that there are three internal rotations, i.e. three OH groups, each rotates about its own B-O bond. Employing the model of having three free rotating OH tops, the value of S_{400} was evaluated statistically as 75.522 cal. deg.⁻¹ mole.⁻¹. The corresponding value obtained by using the second law value of ΔS_{400}° , $48.39 \pm 1.42 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, for the reaction $\text{H}_3\text{BO}_3(\text{c}) = \text{H}_3\text{BO}_3(\text{g})$, is $75.97 \pm 1.42 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ which is in good agreement with the S_{400}° value based on a model having three free rotating groups. Thus the assumed model is adopted to evaluate the thermodynamic functions. The three principal moments of inertia are: $I_A = I_C = 8.3320 \times 10^{-2} \text{ g. cm.}^2$ and $I_B = 1.6664 \times 10^{-35} \text{ g. cm.}^2$. The reduced moment of inertia for OH top is $I_r = 1.15321 \times 10^{-40} \text{ g. cm.}^2$. The infrared absorption spectrum of $\text{H}_3\text{BO}_3(\text{g})$ was observed under conditions where one atmosphere of water vapor with a path length of approximately one meter as background, by F. T. Greene, O. E. Leroy, S. P. Randall, J. R. Soulen, L. H. Spinar and J. L. Margrave, "Spectra and Thermodynamic Properties of Light-Element Oxides and Hydroxides", Proceedings of the Conference on Propellant Thermodynamics and Handling, Columbus, Ohio, July, 1959. The following fundamentals were obtained: 3220 cm.⁻¹ S., 1490 cm.⁻¹ S., 1199 cm.⁻¹ S., 881 cm.⁻¹ W., and 669 cm.⁻¹ W.



T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	10.370	7.782	3.949	52.146	52.146	INFINITE
200	17.566	17.335	3.441	48.618	48.618	106.249
298	23.081	25.480	2.021	54.062	43.446	47.474
300	23.120	25.423	2.000	54.230	36.191	27.093
400	24.120	32.456	0.043	54.231	38.002	27.748
500	24.410	37.866	2.420	54.678	32.594	17.608
600	25.343	42.383	4.845	55.007	27.010	11.806
700	26.500	45.160	7.324	55.129	21.308	7.704
800	27.500	47.223	9.524	55.129	17.772	4.924
900	28.430	48.534	11.510	55.006	15.159	2.775
1000	29.240	49.594	13.514	54.850	13.016	1.108
1100	29.900	50.393	15.431	54.688	1.016	.222
1200	30.450	50.962	17.269	73.444	7.603	1.511
1300	30.900	51.362	19.031	72.708	14.997	2.724
1400	31.290	51.632	20.723	72.708	22.4274	3.744
1500	31.620	51.817	22.352	72.368	29.570	4.616
1600	31.900	51.938	23.922	72.052	36.861	5.367
1700	32.150	52.002	25.437	71.749	44.089	6.022
1800	32.380	52.038	26.906	71.454	51.323	6.596
1900	32.590	52.056	28.327	71.169	58.559	7.107
2000	32.780	52.067	29.700	70.894	65.742	7.562
2100	32.950	52.071	31.025	70.627	72.934	7.969

POTASSIUM TETRAHYDROBORATE (KBH₄) (CRYSTAL)

MOL. WT. = 53.952

$\Delta H_f^0 = -52.15 \pm .55 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 298.15 = -54.23 \pm .55 \text{ kcal. mole}^{-1}$
 $T_d = [770]^{\circ}\text{K}$

$S_{298.15} = 25.48 \text{ cal. deg.}^{-1} \text{ mole}$

Heat of Formation.

The heat of reaction of KBH₄(c) with hydrochloric acid has been measured by solution calorimetry and reported by W. H. Johnson, R. H. Schumm, I. H. Wilson, and E. J. Prosen, J. Res. Nat'l. Bur. Std. 65A, 97 (1961)

$\text{KBH}_4(\text{c}) + \text{HCl}(\text{g}) + 3\text{H}_2\text{O}(\text{liq}) \rightarrow \text{KCl}(\text{c}) + \text{H}_3\text{BO}_3(\text{c}) + 4\text{H}_2(\text{g}) \quad \Delta H_r = -84.82 \pm .44 \text{ kcal. mole}$
The ΔH_f 298.15 value for HCl(g) and H₃BO₃(c) were obtained from the JANAP Tables. The ΔH_f 298.15 value for KCl(c) was calculated from ΔH_f 298.15 K° = -60.52 kcal. mole⁻¹, ΔH_f 298.15 Cl° = -39.952 kcal. mole⁻¹ and ΔH dilution = 4.12 kcal. mole⁻¹ obtained from NES. Rept. 8504, 1 July 1964 - Appendix III by W. H. Evans. ΔH_f 298.15 for H₂O(liq) was obtained from W. H. Evans, loc. cit. Unpublished data of The Dow Chemical Company Thermal Laboratory give a value of ΔH_f 298.15 = -55.0 ± 1.0 kcal. mole⁻¹ by solution calorimetry.

Heat Capacity and Entropy.

C_p and S° at temperatures below 298.15°K were reported by G. T. Furukawa, M. L. Reilly, and J. H. Piciorelli, J. Res. Nat'l. Bur. Std. 68A, 651 (1964). The values of C_p in the range from 298.15 to 700°K were obtained from T. B. Douglas and A. W. Harman, J. Res. Nat'l. Bur. Std. 69, 117 (1965). These two sets of C_p data were plotted and joined smoothly at 298.15°K. The values of C_p above 700°K were estimated by graphical extrapolation.

Temperature of Decomposition.

The temperature of decomposition (into constituent elements) was estimated according to a report by T. B. Douglas and A. W. Harman, loc. cit.



Lithium Tetrahydroborate (LiBH_4)
(Crystal) Mol. Wt. = 21.792

LITHIUM TETRAHYDROBORATE (LiBH_4) (CRYSTAL)

MOL. WT. = 21.792

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹ S° - (F° - H ₂₉₈)/T	cal. mole ⁻¹ H° - H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	∞.000	INFINITE	3.028	-43.105	-	INFINITE
100	7.175	4.084	31.660	-44.033	-	87.033
200	14.239	11.470	19.727	-45.097	-34.917	38.154
298	19.777	18.120	∞.000	-45.522	-29.824	21.860
300	19.835	18.242	∞.037	-45.527	-29.727	21.455
400	21.750	20.231	18.924	-45.772	-24.422	13.343
500	23.440	29.273	20.502	-46.739	-18.983	8.297
600	25.130	33.708	22.341	-46.821	-13.415	4.866
700	26.270	37.672	24.253	-46.938	-7.830	2.444
800	27.000	41.171	26.155	-46.959	-3.537	0.810
900	27.435	44.635	28.150	-46.883	3.537	0.810
1000	27.570	47.327	29.802	-46.848	8.915	1.948
1100	27.818	49.967	31.517	-46.822	14.490	2.879
1200	28.040	52.397	33.157	-46.804	20.064	3.654
1300	28.240	54.688	34.729	-46.800	25.638	4.304
1400	28.410	56.794	36.223	-46.811	31.208	4.872
1500	28.517	58.704	37.657	-46.843	36.782	5.359
1600	28.600	60.551	39.031	-46.894	42.357	5.785
1700	28.795	62.293	40.348	-47.105	47.927	6.333
1800	28.980	63.984	41.614	-47.380	53.497	6.841
1900	29.040	65.509	42.830	-47.718	59.067	7.312
2000	29.130	67.001	44.002	-48.114	64.637	7.742

$S_{298.15}^0 = 18.120 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = [750^\circ \text{K.}]$

Heat of Formation.

The heat of formation of $\text{LiBH}_4(\text{c})$ was calculated from the solution calorimetry of W. D. Davis, L. S. Mason, and G. Stegeman J. Am. Chem. Soc. **71**, 2775 (1949). The heats of reaction were measured for the following reactions:

$\text{LiBH}_4(\text{c}) + 1.25(\text{HCl} \cdot 200 \text{ H}_2\text{O}) + 3 \text{ H}_2\text{O}(l) \rightarrow (\text{NaCl} + \text{H}_3\text{BO}_3 + 0.25 \text{ HCl}) \cdot 247 \text{ H}_2\text{O} + 4 \text{ H}_2(\text{g})$ $\Delta H_{298.15}^0 = -72.14 \text{ kcal.}$

$\text{LiCl} \cdot 60 \text{ H}_2\text{O} + \text{H}_3\text{BO}_3 \cdot 60 \text{ H}_2\text{O} + 0.25(\text{HCl} \cdot 508 \text{ H}_2\text{O}) \rightarrow (\text{LiCl} + \text{H}_3\text{BO}_3 + 0.25 \text{ HCl}) \cdot 247 \text{ H}_2\text{O}$ $\Delta H_{298.15}^0 = 0.00 \text{ kcal.}$

$\text{H}_3\text{BO}_3 \cdot 60 \text{ H}_2\text{O} + \infty \text{ H}_2\text{O} \rightarrow \text{H}_3\text{BO}_3 \cdot \infty \text{ H}_2\text{O}$ $\Delta H_{298.15}^0 = 0.200 \text{ kcal.}$

The summation of the above reactions yields:

$\text{LiBH}_4(\text{c}) + 1.25(\text{HCl} \cdot 200 \text{ H}_2\text{O}) + 3 \text{ H}_2\text{O}(l) + \infty \text{ H}_2\text{O} \rightarrow \text{LiCl} \cdot 60 \text{ H}_2\text{O} + \text{H}_3\text{BO}_3 \cdot \infty \text{ H}_2\text{O} + 0.25(\text{HCl} \cdot 508 \text{ H}_2\text{O}) + 4 \text{ H}_2(\text{g})$

The heat of formation of Lithium Borohydride crystal was calculated to be -45.522 kcal. mole⁻¹ with the following auxiliary data:

Reference

HCl(g) JANAF; Dilution data from NBS. Rept. 8504, 1 July 1964 Appendix III by W. H. Evans

HCl(g) JANAF; Dilution data from W. H. Evans, loc. cit.

Li⁺ see NaBH_4 tables; Cl⁻ and dilution data W. H. Evans, loc. cit.

JANAF $\text{H}_3\text{BO}_3(\text{c})$ and dilution data from J. Smisko and L. S. Mason J. of Am. Chem. Soc. **72**, 3879 (1950)

*This ΔH_f^0 298.15 value was obtained from J. Smisko and L. S. Mason loc. cit.

Compound Heat of Formation at 298.15

HCl (508 H ₂ O)	-39.815
HCl (200 H ₂ O)	-39.696
LiCl (60 H ₂ O)	-106.023
H ₃ BO ₃ (∞H ₂ O)	-256.05

Heat Capacity and Entropy.

The low temperature heat capacities, 15-72 - 302.88 °K were obtained from the measurements by N.C. Hallett and H. L. Johnston, J. Am. Chem. Soc., **75**, 1496 (1953). The C_p values above 298.15°K were estimated by comparison with the C_p 's for NaBH_4 .

The entropy was based on S_{15}^0 (extrap) = 0.0874 reported by N. C. Hallett and H. L. Johnston loc. cit.

Melting Data.

T_m was estimated by comparison with the T_m for NaBH_4 .



Sodium Tetrahydroborate (NaBH₄)

(Crystal) Mol. Wt. = 37.84

SODIUM TETRAHYDROBORATE (NaBH₄)

(CRYSTAL)

MOL. WT. = 37.84

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	0.000	INFINITE	-3.693	-43.862	-43.862	INFINITE
100	17.076	11.123	11.123	-43.862	-43.862	-43.862	88.446
200	17.076	16.656	24.232	-43.862	-43.862	-43.862	85.446
298	20.670	24.232	24.232	4.000	-45.855	-30.380	22.208
300	20.708	24.360	24.232	4.038	-45.855	-30.284	22.061
400	22.600	30.583	25.068	2.206	-46.741	-25.007	15.662
500	24.330	35.814	26.707	4.553	-46.946	-19.548	8.544
600	25.960	40.395	28.614	7.068	-47.027	-14.036	5.120
700	27.550	44.517	30.526	9.744	-46.977	-8.565	2.674
800	28.750	48.276	32.575	12.561	-46.812	-3.069	-0.854
900	29.700	51.720	34.513	15.486	-46.567	2.363	-5.574
1000	30.400	54.869	36.395	18.494	-46.270	7.784	-1.701
1100	31.080	57.821	38.211	21.571	-45.945	13.172	-2.617
1200	31.490	60.544	39.960	24.700	-45.643	18.600	-3.458
1300	31.710	63.074	41.642	27.862	-45.300	24.067	-4.219
1400	31.820	65.429	43.298	31.039	-44.925	29.563	-4.936
1500	31.860	67.626	44.810	34.223	-44.521	35.083	-5.619
1600	31.890	69.683	46.301	37.411	-44.089	40.629	-6.269
1700	31.910	71.617	47.734	40.601	-43.634	46.192	-6.885
1800	31.920	73.441	49.112	43.792	-43.157	51.765	-7.467
1900	31.930	75.167	50.438	46.986	-42.660	57.348	-8.015
2000	31.930	76.807	51.716	50.183	-42.143	62.931	-8.534

Dec. 31, 1960; Dec. 31, 1964

$$S_{298}^{o} = 24.232 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 189.9^{\circ}\text{K}$$

$$T_m = 770^{\circ}\text{K}$$

$$\Delta H_f^o = -43.86 \pm .07 \text{ kcal. mole}^{-1}$$

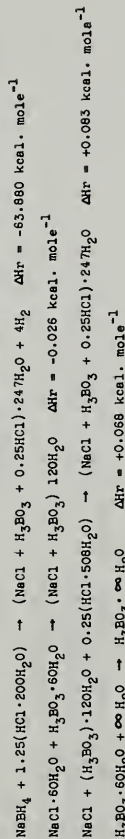
$$\Delta H_f^o 298.15 = -45.85 \pm .07 \text{ kcal. mole}^{-1}$$

$$\Delta H_{f,1}^o = 0.2388 \text{ kcal. mole}^{-1}$$

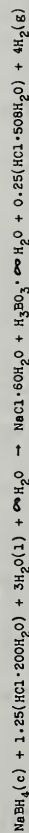
$$\Delta H_m^o = \text{Unknown}$$

Heat of Formation.

The heat of formation was calculated from the solution calorimetry of W. D. Davis, L. S. Mason and G. Stegeman, J. Am. Chem. Soc. **71**, 2775 (1949). The heats of reaction and mixing were measured for the following reactions:



The summation of the above equations yields:



$$\Delta H_r = -63.889 \text{ kcal. mole}^{-1}$$

The ΔH_f 298.15 values for HCl were obtained from JANAF values for HCl(g) and heat of dilution data of NBS. Rept. 8504, 1 July 1964 - Appendix III by W. H. Evans. The ΔH_f 298.15 $\text{H}_2\text{O}(l)$ value was obtained from W. H. Evans loc. cit. The ΔH_f 298.15 value for NaCl was obtained from JANAF value of NaCl(c) together with dilution data from W. H. Evans, loc. cit. The ΔH_f 298.15 value for H_3BO_3 was obtained from JANAF value for $\text{H}_3\text{BO}_3(c)$ together with dilution data of J. Smisko and L. S. Mason, J. of Am. Chem. Soc. **72**, 3679 (1950).

Heat Capacity and Entropy.

The low temperature heat capacity (15.76 - 301.26) was obtained from H. L. Johnston and N. C. Hallett, J. Am. Chem. Soc. **75**, 1467 (1953). In the area of transition (169-193.5°K) the average $\Delta H = 635.3$ cal./mole and the average $\Delta S = 3.35$ cal./mole °K were adopted from H. L. Johnston and N. C. Hallett, loc. cit. Using the present base line these ΔH and ΔS values yield a heat of transition of 0.2388 kcal. mole⁻¹. The low temperature heat capacity was fitted with the smoothed heat capacity data (288.15 - 700°K) of T. B. Douglas and A. W. Harman, J. Research Natl. Bur. Standards **60**, 117 (1956). The heat capacity above 700°K was extrapolated from the plot of both sets of data.

Transition Data.

The temperature and heat of transition were obtained from H. L. Johnston and N. C. Hallett loc. cit.

Melting Data.

The melting data was obtained from T. B. Douglas and A. W. Harman loc. cit.

Boron Iodide (BI)

(Ideal Gas) Mol. Wt. = 137.73

BORON MONOIODIDE (BI)

(IDEAL GAS)

MOL. WT. = 137.73

T, °K. C_p S° - (F° - H₂₉₈°)/T (kcal. mole⁻¹) ΔH_f° ΔF° Log K_p

0	0.000	INFINITE	-2.178	72.691	72.691	INFINITE	
100	0.986	47.539	-1.482	68.999	68.999	-150.791	
200	2.485	52.508	-0.763	73.067	73.067	-70.973	
298	3.021	53.604	-0.000	73.000	73.000	-44.696	
300	3.029	53.653	0.015	72.998	72.998	-44.366	
400	3.366	58.013	0.836	70.911	70.911	-31.121	
500	3.568	59.904	1.684	65.584	65.584	-23.593	
600	3.696	61.478	2.567	65.524	65.524	-18.618	
700	3.782	62.825	3.421	65.433	65.433	-15.411	
800	3.844	64.002	4.303	65.310	65.310	-12.859	
900	3.891	65.047	5.190	65.188	65.188	-10.878	
1000	3.927	65.985	6.081	65.061	65.061	-9.297	
1100	3.958	66.838	6.975	64.938	64.938	-8.006	
1200	3.983	67.618	7.872	64.812	64.812	-6.929	
1300	4.006	68.338	8.771	64.691	64.691	-6.020	
1400	4.026	69.006	9.673	64.571	64.571	-5.255	
1500	4.044	69.630	10.577	64.457	64.457	-4.587	
1600	4.061	70.214	11.482	64.348	64.348	-4.004	
1700	4.076	70.764	12.389	64.243	64.243	-3.492	
1800	4.091	71.283	13.297	64.143	64.143	-3.038	
1900	4.105	71.775	14.207	64.047	64.047	-2.634	
2000	4.119	72.242	15.118	63.954	63.954	-2.272	
2100	4.132	72.687	16.031	63.863	63.863	-1.945	
2200	4.145	73.113	16.945	63.774	63.774	-1.650	
2300	4.158	73.519	17.860	63.687	63.687	-1.381	
2400	4.170	73.900	18.776	63.602	63.602	-1.136	
2500	4.182	74.284	19.694	63.519	63.519	-0.921	
2600	4.194	74.644	20.612	63.437	63.437	-0.732	
2700	4.205	74.992	21.532	63.356	63.356	-0.559	
2800	4.217	75.326	22.453	63.276	63.276	-0.399	
2900	4.228	75.650	23.376	63.197	63.197	-0.250	
3000	4.239	75.963	24.299	63.119	63.119	-0.112	
3100	4.251	76.266	25.224	63.043	63.043	-0.016	
3200	4.262	76.560	26.149	62.968	62.968	0.136	
3300	4.273	76.845	27.076	62.894	62.894	0.248	
3400	4.284	77.122	28.004	62.821	62.821	0.353	
3500	4.295	77.392	28.933	62.749	62.749	0.451	
3600	4.306	77.654	29.863	62.678	62.678	0.543	
3700	4.317	77.909	30.794	62.608	62.608	0.630	
3800	4.327	78.157	31.726	62.539	62.539	0.712	
3900	4.338	78.400	32.659	62.471	62.471	0.790	
4000	4.349	78.636	33.594	62.404	62.404	0.866	
4100	4.360	78.867	34.529	62.338	62.338	0.943	
4200	4.370	79.093	35.466	62.273	62.273	1.020	
4300	4.381	79.314	36.403	62.208	62.208	1.097	
4400	4.392	79.529	37.342	62.143	62.143	1.174	
4500	4.402	79.741	38.281	62.078	62.078	1.251	
4600	4.413	79.947	39.222	62.013	62.013	1.328	
4700	4.423	80.150	40.164	61.948	61.948	1.405	
4800	4.434	80.348	41.107	61.883	61.883	1.482	
4900	4.445	80.543	42.051	61.818	61.818	1.559	
5000	4.455	80.734	42.996	61.753	61.753	1.636	
5100	4.466	80.921	43.942	61.688	61.688	1.713	
5200	4.476	81.105	44.889	61.623	61.623	1.790	
5300	4.487	81.286	45.837	61.558	61.558	1.867	
5400	4.497	81.463	46.786	61.493	61.493	1.944	
5500	4.508	81.638	47.737	61.428	61.428	2.021	
5600	4.518	81.809	48.688	61.363	61.363	2.098	
5700	4.529	81.977	49.640	61.298	61.298	2.175	
5800	4.539	82.143	50.594	61.233	61.233	2.252	
5900	4.550	82.306	51.548	61.168	61.168	2.329	
6000	4.560	82.467	52.503	61.103	61.103	2.406	

Ground State Configuration [1Σ⁺]

S_{298.15}° = [55.604] cal. deg.⁻¹ mole⁻¹

ΔH_f° 298.15 = [73.0 ± 10] kcal. mole⁻¹

Electronic Levels and Quantum Weight

E _i	E _i
0	[1]

ω_e = [600] cm.⁻¹

σ = 1

α_e = [0.3912] cm.⁻¹

r_e = [2.08] Å

Heat of Formation.

The ratio D(BI) / (ΔH_f(BI₃)/3) = 1.177, where ΔH_f signifies the heat of atomization, was applied to BI₃ giving D(BI) = 84.4 kcal. mole⁻¹ and ΔH_f 298 = 75 ± 10 kcal. mole⁻¹.

Heat Capacity and Entropy.

The bond length was first estimated by comparison with the ratio of the bond lengths in the other boron trihalides and monohalides. The vibrational frequency was then calculated using Guggenheim's Relation [Proc. Phys. Soc. (London) 58, 456 (1946)] which was checked using BBr and shown to give an excellent fit. The quantity X_eμ^{1/2}, where μ is the reduced mass, has been shown to be constant for similar molecules and its value was transferred from BBr to give X_e and ω_e for BI. α_e was then calculated using the Morse potential function and E_e was determined from the bond length. The ground state configuration was assumed to be the same as that in BBr.

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈ °)/T	H ^o -H ₂₉₈ °	cal. mole ⁻¹	ΔH _f ^o	Log K _p
0	-0.00	INFINITE	-	2.903	58.453	INFINITE	58.453	INFINITE
100	9.116	42.311	2.114	2.903	58.453	58.453	58.453	58.453
200	10.696	68.490	73.005	-1.103	58.453	58.453	58.453	58.453
298	11.731	73.964	73.964	-0.000	58.000	58.000	44.642	32.722
300	11.748	74.037	73.964	+0.022	57.993	57.993	44.560	32.460
400	12.447	77.320	78.434	1.234	53.711	53.711	40.280	22.007
500	12.880	80.348	79.343	2.302	43.043	43.043	37.937	16.361
600	13.155	82.722	78.480	3.805	42.974	42.974	36.921	13.448
700	13.336	84.765	77.435	5.130	42.884	42.884	35.920	11.214
800	13.461	86.554	76.466	6.430	42.778	42.778	34.932	9.542
900	13.549	88.145	75.454	7.621	42.659	42.659	33.957	8.245
1000	13.615	89.576	80.396	8.519	42.527	42.527	32.999	7.211
1100	13.664	90.876	81.290	10.543	42.380	42.380	32.052	6.368
1200	13.702	92.067	82.140	11.912	42.221	42.221	31.120	5.607
1300	13.732	93.165	82.946	13.284	42.050	42.050	30.202	5.077
1400	13.756	94.183	83.713	14.658	41.865	41.865	29.298	4.573
1500	13.776	95.153	84.443	16.035	41.668	41.668	28.405	4.136
1600	13.792	96.022	85.139	17.413	41.459	41.459	27.530	3.760
1700	13.805	96.859	85.804	18.793	41.238	41.238	26.666	3.428
1800	13.816	97.648	86.440	20.174	41.007	41.007	25.814	3.134
1900	13.826	98.396	87.050	21.556	40.767	40.767	24.971	2.873
2000	13.834	99.103	87.633	22.939	40.521	40.521	24.130	2.639
2100	13.841	99.780	88.197	24.323	40.269	40.269	23.339	2.429
2200	13.847	100.424	88.739	25.707	40.010	40.010	22.538	2.239
2300	13.853	101.040	89.260	27.092	39.746	39.746	21.752	2.067
2400	13.857	101.630	89.768	28.478	39.477	39.477	20.976	1.910
2500	13.861	102.195	90.249	29.864	39.203	39.203	20.216	1.776
2600	13.865	102.739	90.719	31.250	38.923	38.923	19.462	1.663
2700	13.868	103.262	91.174	32.637	38.637	38.637	18.717	1.559
2800	13.871	103.767	91.615	34.024	38.346	38.346	17.984	1.463
2900	13.874	104.254	92.042	35.411	38.051	38.051	17.253	1.375
3000	13.876	104.724	92.457	36.799	37.753	37.753	16.523	1.293
3100	13.879	105.179	92.860	38.186	37.451	37.451	15.793	1.217
3200	13.881	105.620	93.253	39.574	37.145	37.145	15.063	1.146
3300	13.882	106.047	93.633	40.962	36.835	36.835	14.333	1.081
3400	13.884	106.461	94.005	42.350	36.521	36.521	13.603	1.019
3500	13.886	106.864	94.368	43.739	36.203	36.203	12.873	0.962
3600	13.887	107.255	94.719	45.128	35.884	35.884	12.143	0.909
3700	13.888	107.635	95.063	46.517	35.561	35.561	11.413	0.858
3800	13.889	108.006	95.399	47.906	35.235	35.235	10.683	0.811
3900	13.890	108.368	95.726	49.295	34.906	34.906	9.953	0.767
4000	13.891	108.718	96.047	50.684	34.574	34.574	9.223	0.722
4100	13.892	109.061	96.360	52.073	34.241	34.241	8.493	0.678
4200	13.893	109.396	96.667	53.462	33.906	33.906	7.763	0.634
4300	13.894	109.723	96.966	54.851	33.571	33.571	7.033	0.591
4400	13.895	110.042	97.258	56.240	33.235	33.235	6.303	0.548
4500	13.895	110.353	97.548	57.630	32.900	32.900	5.573	0.505
4600	13.896	110.660	97.829	59.020	32.564	32.564	4.843	0.462
4700	13.897	110.959	98.105	60.410	32.229	32.229	4.113	0.419
4800	13.897	111.252	98.376	61.799	31.894	31.894	3.383	0.376
4900	13.898	111.538	98.642	63.188	31.559	31.559	2.653	0.333
5000	13.898	111.818	98.903	64.579	31.224	31.224	1.923	0.290
5100	13.899	112.094	99.159	65.969	30.889	30.889	1.193	0.247
5200	13.899	112.364	99.410	67.359	30.554	30.554	0.463	0.204
5300	13.900	112.629	99.657	68.749	30.219	30.219	-0.267	0.161
5400	13.900	112.890	99.900	70.139	29.884	29.884	-0.997	0.118
5500	13.901	113.144	100.138	71.529	29.549	29.549	-1.727	0.075
5600	13.901	113.394	100.372	72.919	29.214	29.214	-2.457	0.032
5700	13.901	113.640	100.603	74.309	28.879	28.879	-3.187	-0.011
5800	13.902	113.882	100.830	75.699	28.544	28.544	-3.917	-0.054
5900	13.902	114.124	101.053	77.089	28.209	28.209	-4.647	-0.097
6000	13.902	114.355	101.273	78.479	27.874	27.874	-5.377	-0.140

Mar. 31, 1962; Dec. 31, 1962; Dec. 31, 1964

Point Group [C_{2v}]
 $S^{\circ}_{298.15} = [73.964] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^{\circ}_{f, 0} = [58.5 \pm 15] \text{ kcal. mole}^{-1}$
 $\Delta H^{\circ}_{f, 298.15} = [58.0 \pm 15] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight [2]

Vibrational Levels and Degeneracies

ω , cm.⁻¹
 (550)(1)
 (110)(1)
 (770)(1)

Bond Distance: B-I = [2.06] Å
 Bond Angle: I-B-I = [120°]
 Product of the Moments of Inertia: $I_A I_B I_C = 3.33503 \times 10^{-113} \text{ g. cm.}^2$
 $\sigma = 2$

Heat of Formation

The heat of formation was estimated by analogy with BF₃, specifically the ratio

$$\Delta H_f(BX_3) \rightarrow BX_2 + X / \Delta H_f(BX_3) \rightarrow B + 3X$$

was taken as 0.347.

Heat Capacity and Entropy

The vibrational frequencies were obtained from force constants transferred from the trihalide given by O. Herzberg "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., (1945). The bond length was taken between those of the mono end trihalide and the angle was estimated to be the same as that in the trihalides. The ground state quantum weight was taken as two on account of the one unpaired electron.

The individual moments of inertia were $I_B = 1.8278 \times 10^{-39} \text{ g. cm.}^2$, $I_A = 134.1670 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 135.9946 \times 10^{-39} \text{ g. cm.}^2$

Boron Triiodide (BI₃)
(Ideal Gas) Mol. Wt. = 391.55

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(H°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	∞.000	INFINITE	4.025	17.998	17.998	INFINITE
100	12.788	76.151	3.007	17.917	13.397	-29.277
200	15.334	76.880	84.824	17.488	9.038	-9.876
300	16.919	83.322	83.322	17.000	4.990	-3.658
400	18.510	88.447	84.000	16.581	3.481	-
500	19.486	92.572	85.309	16.216	2.433	-
600	19.878	95.924	86.802	5.474	1.413	-5.15
700	19.854	98.319	88.319	5.129	1.057	-7.83
800	19.783	100.657	91.220	5.093	0.862	-1.137
900	19.680	102.952	93.738	5.091	0.770	-1.261
1000	19.486	105.745	95.572	5.103	0.854	-1.362
1100	19.451	107.606	97.079	5.128	0.934	-1.446
1200	19.400	109.680	98.083	5.213	1.013	-1.521
1300	19.336	111.921	100.352	5.275	1.084	-1.584
1400	19.261	114.336	102.810	5.348	1.150	-1.635
1500	19.177	116.924	105.468	5.434	1.213	-1.684
1600	19.083	119.680	108.328	5.537	1.273	-1.732
1700	18.979	122.592	111.392	5.668	1.330	-1.777
1800	18.866	125.656	114.664	5.824	1.385	-1.819
1900	18.745	128.872	118.148	6.008	1.438	-1.858
2000	18.608	132.240	121.840	6.224	1.488	-1.894
2100	18.458	135.760	125.760	6.476	1.535	-1.926
2200	18.298	139.440	129.920	6.764	1.579	-1.955
2300	18.131	143.280	134.320	7.092	1.620	-1.980
2400	17.951	147.280	138.960	7.460	1.658	-2.001
2500	17.761	151.440	143.840	7.872	1.693	-2.018
2600	17.561	155.760	148.960	8.328	1.725	-2.031
2700	17.351	160.240	154.320	8.832	1.754	-2.040
2800	17.131	164.880	159.920	9.384	1.780	-2.046
2900	16.901	169.680	165.760	9.984	1.803	-2.049
3000	16.661	174.640	171.840	10.632	1.823	-2.050
3100	16.411	179.760	178.160	11.332	1.840	-2.050
3200	16.151	185.040	184.720	12.084	1.854	-2.049
3300	15.881	190.480	191.520	12.892	1.866	-2.046
3400	15.601	196.080	198.560	13.756	1.875	-2.041
3500	15.311	201.840	205.840	14.680	1.882	-2.035
3600	15.011	207.760	213.360	15.664	1.887	-2.027
3700	14.701	213.840	221.120	16.708	1.890	-2.017
3800	14.381	220.080	229.120	17.812	1.891	-2.005
3900	14.051	226.480	237.360	18.976	1.890	-1.991
4000	13.711	233.040	245.840	20.200	1.887	-1.975
4100	13.361	239.760	254.560	21.484	1.882	-1.957
4200	13.001	246.640	263.520	22.828	1.875	-1.937
4300	12.631	253.680	272.720	24.232	1.866	-1.914
4400	12.251	260.880	282.160	25.696	1.854	-1.888
4500	11.861	268.240	291.840	27.220	1.840	-1.859
4600	11.461	275.760	301.760	28.804	1.823	-1.827
4700	11.051	283.440	311.920	30.448	1.803	-1.792
4800	10.631	291.280	322.320	32.152	1.780	-1.754
4900	10.201	299.280	332.960	33.916	1.754	-1.712
5000	9.761	307.440	343.840	35.740	1.725	-1.666
5100	9.311	315.760	354.960	37.624	1.693	-1.616
5200	8.851	324.240	366.320	39.568	1.658	-1.562
5300	8.381	332.880	377.920	41.572	1.620	-1.505
5400	7.901	341.680	389.760	43.636	1.579	-1.445
5500	7.411	350.640	401.840	45.760	1.535	-1.382
5600	6.911	359.760	414.160	47.944	1.488	-1.316
5700	6.401	369.040	426.720	50.188	1.438	-1.247
5800	5.881	378.480	439.520	52.492	1.385	-1.175
5900	5.351	388.080	452.560	54.856	1.329	-1.099
6000	4.811	397.840	465.840	57.280	1.270	-1.020

MOL. WT. = 391.55

(IDEAL GAS)

BORON TRIIODIDE (BI₃)

Point Group D_{3h}
S_{298.15} = 83.322 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight [1]
ΔH_f⁰ = 18.0 ± 12 kcal. mole⁻¹
ΔH_f⁰ 298.15 = 17.0 ± 12 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

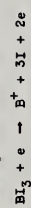
ω, cm. ⁻¹	Deg.
190(1)	339(1)
710(2)	100(2)
100(2)	100(2)

Bond Distances: B-I = [2.03 ± 0.03] Å
Bond Angle: I-B-I = [120°]

Product of the Moments of Inertia = [4.418202] X 10⁻¹¹¹ g.³ cm.⁶
σ = 6

Heat of Formation.

W. S. Koski, J. J. Kaufman and C. F. Pachuki, J. Am. Chem. Soc. 81, 1326 (1959) measured the appearance potential of the B⁺ ion from BI₃. Assuming the reaction



one can calculate the heat of atomization of BI₃ as 8.31 ± 0.5 e.v. The analogous reaction for BI₃ can be checked independently and shows the process to be valid. This value leads to a ΔH_f⁰ 298 = 17.0 ± 12 kcal. mole⁻¹, if the process is assumed to occur at 298°K.

Heat Capacity and Entropy.

Vibrational frequencies were taken from T. Wentink and V. H. Tienau, J. Chem. Phys. 28, 828 (1958) modified according to the natural abundance of boron. The B-I distance was estimated by Koski et al., loc. cit., and the angle was estimated by analogy with the other boron trihalides. The three principal moments of inertia are: I_A = I_B = 1.30238 X 10⁻³⁷ and I_C = 2.60476 X 10⁻³⁷ g. cm.²

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	-0.000	INFINITE	-2.142	-241.960	-241.960	INFINITE
100	4.501	22.434	-2.204	-242.633	-238.940	521.304
200	10.511	7.459	-1.977	-243.633	-235.667	255.067
298	14.291	12.351	-1.223	-243.076	-229.870	168.491
300	14.334	12.351	-1.223	-243.076	-229.870	167.932
400	16.092	10.960	-1.604	-243.360	-228.271	123.077
500	18.854	10.060	-3.400	-244.135	-220.668	96.449
600	20.411	9.538	-5.365	-244.113	-215.074	78.665
700	21.823	9.172	-7.727	-243.780	-206.637	64.448
800	23.157	8.915	-10.272	-243.470	-202.011	53.053
900	24.448	8.714	-12.106	-243.064	-197.423	43.145
1000	25.711	8.557	-14.616	-242.562	-192.884	35.321
1100	26.953	8.434	-17.210	-242.000	-188.397	29.177
1200	28.177	8.336	-20.000	-241.400	-183.957	24.048
1300	29.410	8.254	-22.886	-240.757	-179.578	20.032
1400	30.627	8.181	-25.866	-240.061	-175.262	16.961
1500	31.840	8.116	-28.845	-239.320	-171.007	14.471
1600	33.049	8.056	-31.826	-238.540	-166.804	12.278
1700	34.254	8.000	-34.821	-237.720	-162.641	10.243
1800	35.458	7.948	-37.826	-236.860	-158.516	8.289
1900	36.661	7.900	-40.841	-235.960	-154.429	6.423
2000	37.862	7.856	-43.863	-235.020	-150.376	4.641
2100	39.062	7.815	-46.895	-234.040	-146.356	3.045
2200	40.261	7.777	-49.937	-233.020	-142.369	1.641
2300	41.459	7.742	-52.989	-231.960	-138.417	0.423
2400	42.656	7.710	-56.051	-230.860	-134.496	-0.594
2500	43.852	7.680	-59.123	-229.720	-130.606	-1.706

June 30, 1961; Dec. 31, 1964

$S_{298.15}^0 = 12.351 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1117 \pm 1^\circ \text{K.}$

Heat of Formation.

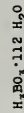
O. C. Sinke, Thermal Research Laboratory, The Dow Chemical Co., private communication, July 1980 has measured ΔH_f^0 298.15 for the following reaction:



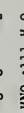
$$\Delta H_f^0 298.15 = -10.93 \pm 0.05 \text{ kcal. mole}^{-1}$$

From this heat of reaction the ΔH_f^0 298.15 for $\text{LiBO}_2(c)$ is calculated to be $-243.29 \text{ kcal. mole}^{-1}$ with the following auxiliary heats of formation:

$$\Delta H_f^0 298.15 (\text{kcal. mole}^{-1})$$



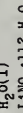
$$-258.23$$



$$-49.44$$



$$-68.315$$



$$-115.747$$

Source

Dilution data from J. Sinaka and L. S. Mason, J. of Am. Chem. Soc. 72, 3879 (1950)

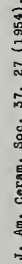
NBS. Rept. 8504, 1 July 1964 - Appendix III by W. H. Evans

W. H. Evans, loc. cit.

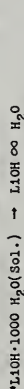
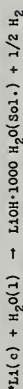
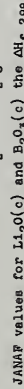
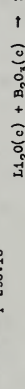
*S. R. Gunn and L. O. Green, J. Am. Chem. Soc. 80, 4782 (1958);
 J. R. Gunn and L. O. Green, J. Am. Chem. Soc. 80, 4782 (1958);
 July, 1958; R. Gunn Lawrence Radiation Lab. UCL-1782, 5,
 July, 1958.

**Dilution and other auxiliary data from W. H. Evans, loc. cit.

L. Shartsa and W. Cappa, J. Am. Ceram. Soc. 37, 27 (1954), measured the heats of solution in nitric acid of various $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses and crystalline mixtures containing 0 to 46 mole % Li_2O . These results were extrapolated to 50 mole % and yielded ΔH_f^0 298.15 = $-45.20 \text{ kcal. mole}^{-1}$ for the following reaction:



With JANAF values for $\text{Li}_2\text{O}(c)$ and $\text{B}_2\text{O}_3(c)$ the ΔH_f^0 298.15 for $\text{LiBO}_2(c)$ was calculated to be $-245.97 \pm .80 \text{ kcal. mole}^{-1}$. This value is in fair agreement with the value adopted for the table.



$$\Delta H_f^0 298.15 = -53.115 \pm 0.019 \text{ kcal. mole}^{-1}$$

$$\Delta H_{\text{dilution}}^0 298.15 = +102 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 298.15 = 0.00$$

$$\Delta H_f^0 298.15 = 0.00$$

$$\Delta H_f^0 \text{ dilution} = .171 \text{ kcal. mole}^{-1}$$

Heat Capacity and Entropy.

P. L. Oetting and W. E. Hutton, The Dow Chemical Company, private communication, April, 1961, have measured C_p from 13° to 328°K. R. A. McDonald, Thermal Research Laboratory The Dow Chemical Company, private communication, April, 1961 has measured H_f^0 - $H_{298.15}^0$ from 289° to 1116°K. The above data were adopted for the table. The C_p values above T_m were obtained by graphical extrapolation.

The entropy was based on $S^\circ = .013 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ at 15°K. calculated from the low temperature C_p values of P. L. Oetting and W. E. Hutton loc. cit.

Melting Data.

The T_m and ΔH_m adopted for this table were obtained from R. A. McDonald loc. cit. The following cryoscopic data have been published: C. Petit and M. Jaeger, Compt. rend. 244, 1734 (1957), $T_m = 1109^\circ \text{K.}$, $\Delta H_m = 7.4 \text{ kcal. mole}^{-1}$; O. Zarsky, colloques Intern, centre, nat'l. recherche sci. (Paris) 39, Electrolyse 634-637 (1952), $\Delta H_m = 8.3 \pm 0.8 \text{ kcal. mole}^{-1}$; C. Sutra, Compt. rend. 234, 1283 (1952), $T_m = 1113^\circ \text{K.}$ and $\Delta H_m = 8.3 \text{ kcal. mole}^{-1}$.



Lithium Metaborate (LiBO_2)
(Liquid) Mol. Wt. = 49.76

LITHIUM METABORATE (LiBO_2) (LIQUID) MOL. WT. = 49.76

T, °K.	C _p	S°	(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100	14.291	15.591	15.591	.000	-238.819	-226.365	165.922
200	14.334	15.680	15.591	.026	-238.822	-226.289	164.643
300	16.092	20.200	16.100	1.604	-238.898	-222.096	121.342
400	18.894	24.200	17.400	3.400	-239.664	-217.817	95.203
500	20.411	27.778	18.896	5.365	-239.642	-213.447	77.744
600	21.823	31.032	20.349	7.478	-239.523	-209.090	65.278
700	23.163	34.072	21.604	10.374	-238.662	-204.781	55.941
800	24.458	36.942	23.576	13.830	-237.277	-200.629	48.717
900	25.718	39.583	25.287	17.286	-235.823	-196.628	42.971
1000	26.958	42.023	27.021	20.741	-234.590	-192.764	38.297
1100	28.188	44.364	28.770	24.195	-233.500	-189.010	34.423
1200	29.408	46.604	30.539	27.653	-232.619	-185.381	31.164
1300	30.618	48.754	32.320	31.109	-231.750	-181.840	28.385
1400	31.818	50.814	34.109	34.565	-230.900	-178.391	25.990
1500	33.008	52.784	35.909	38.020	-230.060	-175.020	23.905
1600	34.188	54.664	37.720	41.476	-229.230	-171.740	22.105
1700	35.358	56.464	39.540	44.932	-228.400	-168.540	20.595
1800	36.518	58.184	41.370	48.388	-227.570	-165.410	19.335
1900	37.668	59.824	43.210	51.844	-226.740	-162.340	18.205
2000	38.808	61.384	45.060	55.299	-225.910	-159.330	17.195
2100	39.938	62.864	46.810	58.755	-225.080	-156.380	16.295
2200	41.058	64.264	48.570	62.211	-224.250	-153.490	15.405
2300	42.168	65.584	50.340	65.667	-223.420	-150.660	14.515
2400	43.268	66.824	52.120	69.123	-222.590	-147.890	13.625
2500	44.358	67.984	53.910	72.578	-221.760	-145.180	12.735
2600	45.438	69.064	55.710	76.034	-220.930	-142.530	11.845
2700	46.508	70.064	57.520	79.490	-220.100	-139.940	10.955
2800	47.568	71.004	59.340	82.946	-219.270	-137.410	10.065
2900	48.618	71.884	61.170	86.402	-218.440	-134.940	9.175
3000	49.658	72.704	63.010	89.857	-217.610	-132.530	8.285
3100	50.688	73.464	64.860	93.313	-216.780	-130.180	7.395
3200	51.708	74.164	66.720	96.769	-215.950	-127.890	6.505
3300	52.718	74.804	68.590	100.225	-215.120	-125.660	5.615
3400	53.718	75.384	70.470	103.681	-214.290	-123.490	4.725
3500	54.708	75.914	72.360	107.136	-213.460	-121.380	3.835
3600	55.688	76.394	74.260	110.592	-212.630	-119.330	2.945
3700	56.658	76.824	76.170	114.048	-211.800	-117.340	2.055
3800	57.618	77.204	78.010	117.504	-210.970	-115.410	1.165
3900	58.568	77.534	79.860	120.960	-210.140	-113.540	0.275
4000	59.508	77.814	81.720		-209.310	-111.720	

$S_{298.15}^o = [15.591] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1117 \pm 1^\circ\text{K.}$
 $T_b = [2284]^\circ\text{K.}$
 $\Delta H_f^o = [50.79] \text{ kcal. mole}^{-1}$

$\Delta F_f^o = [-238.819] \text{ kcal. mole}^{-1}$
 $\Delta H_m^o = 8.09 \pm .10 \text{ kcal. mole}^{-1}$
 $\Delta F_m^o = [50.79] \text{ kcal. mole}^{-1}$

$S_{298.15}^o = [-238.819] \text{ kcal. mole}^{-1}$
 $T_m = 1117 \pm 1^\circ\text{K.}$
 $T_b = [2284]^\circ\text{K.}$

$\Delta H_f^o = [50.79] \text{ kcal. mole}^{-1}$
 $\Delta F_f^o = [-238.819] \text{ kcal. mole}^{-1}$
 $\Delta H_m^o = 8.09 \pm .10 \text{ kcal. mole}^{-1}$
 $\Delta F_m^o = [50.79] \text{ kcal. mole}^{-1}$

Heat of Formation.

$\Delta H_f^o(l)$ was obtained from $\Delta H_f^o(c)$ by addition of ΔH_m^o end difference between ($H_{1117}^o - H_{298.15}^o$) for the crystal and liquid.

Heat Capacity and Entropy.

R. A. McDonald, Thermal Research Laboratory, The Dow Chemical Company, private communication, April 1961, has measured $H_m^o - H_{298.15}^o$ from 1118° to 1707°K. The constant value of C_p measured between 1118° and 1707°K. has been extrapolated above and below this range. Lithium metaborate is assumed to have a glass transformation temperature at 745°K. below which C_p of the glass is assumed equal to that of the crystal.

The entropy of the liquid was calculated from the entropy of the crystal in a manner analogous to the heat of formation.

Melting Data.

The ΔH_m^o and T_m values were obtained from R. A. McDonald loc. cit.

Vaporization Data.

The boiling point was found from graphing the ΔF_f^o of the liquid and gas. The heat of vaporization was found from the difference in ΔH_f^o of the liquid and gas at T_b .



Point Group C_s

$$\Delta H_f^\circ = -159.54 \pm 1.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -160.38 \pm 1.1 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = [61.742] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\text{Ground State Quantum Weight} = [1]$$

Vibrational Frequencies and Degeneracies

ν , cm ⁻¹	ν , cm ⁻¹
[2040](1)	[1100](1)
[1340](1)	[500](1)
	[600](1)

$$\text{Bond Distances: Li-O} = 1.82 \text{ \AA}, \text{ O-B} = 1.36 \text{ \AA}, \text{ B-O} = 1.20 \text{ \AA}$$

$$\text{Bond Angles: LiOB} = 100^\circ, \text{ O-B-O} = 180^\circ$$

$$\text{Product of the Moments of Inertia: } I_A I_B I_C = 4.01933 \times 10^{-115} \text{ g. cm.}^6$$

Heat of Formation.

The adopted heat of formation at 298.15 was evaluated by the third-law method using vapor pressure data reported by D. L. Hildenbrand, M. P. Hall and N. D. Potter, J. Chem. Phys. **39**, No. 2, 296 (1963). The heat of reaction at 298.15 was found to be 82.908 kcal. mole⁻¹ thus giving the value $\Delta H_f^\circ = -160.382$ kcal. mole⁻¹. A second-law method was also used on the data of D. L. Hildenbrand et. al., loc. cit. and yielded a $\Delta H_f^\circ = 91.375$ kcal. mole⁻¹ thus giving $\Delta H_f^\circ = -161.915$ kcal. mole⁻¹. A. Buehler and J. B. Berkowitz-Mattuck, J. Chem. Phys. **39**, No. 2, 286 (1963), have measured the vaporization of lithium metaborate mass spectrometrically in an effusion cell. The second law value reported by A. Buehler and J. B. Berkowitz-Mattuck, loc. cit. for ΔH_f° was 79 ± 3 kcal. mole⁻¹ which yields $\Delta H_f^\circ = 84.078$ kcal. mole⁻¹ thus giving $\Delta H_f^\circ = -159.212$ kcal. mole⁻¹ with JANAF auxiliary values.

Heat Capacity and Entropy.

A. Buehler and E. P. Merram, J. Chem Phys. **39**, No. 2, 292, (1963), observed and assigned two vibrational frequencies to lithium metaborate which were adopted for this table. The other vibrational frequencies were estimated by comparison with similar molecules. D. White, Ohio State University, in a private communication quoted in D. L. Hildenbrand et. al. loc. cit. assigned vibrational frequencies from matrix-isolation experiments. When these frequencies were used in a third and second law analysis of Hildenbrand's data, the drift in the third law was much larger and the agreement between the second and third law was also much poorer than that using the frequencies employed in this table. The molecular constants were obtained from P. A. Akishin and V. P. Spiridonov, Zhur. Strukt. Khim. **2**, 63 (1961). The individual moments of inertia are: $I_A = 1.22164 \times 10^{-38} \text{ g. cm.}^2$, $I_B = 2.2710 \times 10^{-39} \text{ g. cm.}^2$, and $I_C = 1.44875 \times 10^{-38} \text{ g. cm.}^2$.

June 30, 1962; Dec. 31, 1964; Mar. 31, 1965

(Crystal) GFW = 24.8177

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-	628	- 59,270	INFINITE
100	1.183	0.667	6,497	- 583	- 59,578	- 57,728	126.164
200	2.967	2.025	3,910	-	- 59,600	- 55,788	60.862
298	4.713	3.556	3,556	0.000	- 59,970	- 53,783	39.424
300	4.744	3.565	3,536	0.009	- 59,973	- 53,745	39.153
400	6.280	5.148	3,741	5.63	- 60,089	- 51,649	28.220
500	7.500	6.686	4,178	1,254	- 60,162	- 49,530	21.650
600	8.420	8.138	4,718	2,052	- 60,195	- 47,400	17.265
700	9.170	9.479	5,307	3,868	- 60,199	- 45,257	14.133
800	9.746	10.657	6,027	5,604	- 60,188	- 43,108	11.958
900	10.180	11.611	6,810	7,351	- 60,128	- 41,008	9.958
1000	10.600	13.006	7,105	9,901	- 60,061	- 38,866	8.499
1100	10.950	14.033	7,689	12,691	- 59,980	- 36,773	7.306
1200	11.250	14.802	8,012	15,630	- 59,881	- 34,729	6.346
1300	11.500	15.362	8,218	18,608	- 59,771	- 32,736	5.574
1400	11.700	15.752	8,349	21,625	- 59,649	- 30,793	4.958
1500	11.840	16.006	8,409	24,680	- 59,511	- 28,893	4.437
1600	11.950	16.150	8,450	27,772	- 59,366	- 27,026	4.000
1700	12.040	16.210	8,480	30,899	- 59,216	- 25,193	3.646
1800	12.110	16.280	8,500	34,061	- 59,061	- 23,393	3.359
1900	12.170	16.330	8,510	37,257	- 58,902	- 21,625	3.126
2000	12.220	16.370	8,520	40,487	- 58,739	- 19,893	2.931
2100	12.260	16.400	8,530	43,750	- 58,572	- 18,193	2.766
2200	12.290	16.420	8,540	47,045	- 58,402	- 16,526	2.626
2300	12.310	16.430	8,550	50,371	- 58,229	- 14,893	2.506
2400	12.320	16.440	8,560	53,727	- 58,054	- 13,293	2.400
2500	12.330	16.450	8,570	57,113	- 57,877	- 11,726	2.306
2600	12.340	16.460	8,580	60,529	- 57,698	- 10,193	2.226
2700	12.350	16.470	8,590	63,975	- 57,517	- 8,693	2.156
2800	12.360	16.480	8,600	67,451	- 57,334	- 7,226	2.096
2900	12.370	16.490	8,610	70,957	- 57,149	- 5,793	2.046
3000	12.380	16.500	8,620	74,493	- 56,963	- 4,393	2.006
3100	12.390	16.510	8,630	78,059	- 56,776	- 3,026	1.976
3200	12.400	16.520	8,640	81,655	- 56,588	- 1,693	1.946
3300	12.410	16.530	8,650	85,281	- 56,399	- 3,293	1.916
3400	12.420	16.540	8,660	88,937	- 56,209	- 1,926	1.886
3500	12.430	16.550	8,670	92,623	- 56,018	- 5,493	1.856

BORON NITRIDE (BN)

(CRYSTAL)

OFW = 24.8177

$$\Delta H_f^\circ = -59.27 \pm 0.37 \text{ kcal/mol}$$

$$\Delta H_f^{298} = -59.97 \pm 0.37 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 3.556 \text{ gibbs/mol}$$

$$T_D = 2600 \pm 100^\circ\text{K}$$

Heat of Formation.

The adopted heat of formation was determined by Wise et al. using combustion in fluorine. Other recent calorimetric values are in good agreement as summarized below. Torsion-effusion studies of the decomposition $\text{BN(c)} \rightarrow \text{B(am)} + 0.5 \text{ N}_2(\text{g})$ by D. L. Hildenbrand and W. F. Hall, *J. Phys. Chem.* **67**, 888 (1963), yield essentially the same ΔH_f° and indicate that the condensation coefficient, α , is $< 6 \times 10^{-3}$ for $\text{N}_2(\text{g})$ on the surface of the sample. Use of $\alpha = 6 \times 10^{-3}$ brings the following decomposition studies into reasonable agreement: Langmuir studies by L. H. Dreyer, V. V. Dadape and J. L. Margrave, *J. Phys. Chem.* **66**, 1556 (1962); mass spectrometric studies by P. O. Schissel and W. S. Williams, *Bull. Am. Phys. Soc.*, **II**, 4, 139 (1959); and Knudsen effusion studies by M. Hoch and D. White, Technical Research Report MCC-1023-TM-214, Ohio State University Research Foundation, Columbus, Ohio, October, 1956.

Source	Reaction	ΔH_f^{298} kcal/mol	ΔH_f^{298} kcal/mol
1. Dworkin et al. (1954)	$\text{BN(c)} + 3/4 \text{ O}_2(\text{g}) \rightarrow 0.5 \text{ B}_2\text{O}_3(\text{am}) + 0.5 \text{ N}_2$	-90.1 ± 0.5	-59.1 ± 0.7
2. Gal'chenko et al. (1959)	$\text{B(am)} + 0.5 \text{ N}_2(\text{g}) \rightarrow \text{BN(c)}$	-60.8 ± 0.3	-59.6 ± 0.8
3. Oras (1961)	$\text{BN(c)} + 1.5 \text{ F}_2(\text{g}) \rightarrow \text{BF}_3(\text{g}) + 0.5 \text{ N}_2$	-211.2 ± 0.1	-
	$\text{B(c)} + 1.5 \text{ F}_2(\text{g}) \rightarrow \text{BF}_3(\text{g})$	-271.4	-60.2
4. Thompson et al. (1961)	$\text{BN(c)} + \text{NF}_3(\text{g}) \rightarrow \text{BF}_3(\text{g}) + \text{N}_2$	-177.63 ± 0.3	-60.1 ± 2
	$\text{B(c)} + \text{NF}_3(\text{g}) \rightarrow \text{BF}_3(\text{g}) + 0.5 \text{ N}_2$	-237.77 ± 0.5	-59.9 ± 1.5
5. Keavney (1962)	Combustion in O_2 - H_2O	-	-59.97 ± 0.37
6. Wise et al. (1966)	$\text{BN(c)} + 1.5 \text{ F}_2(\text{g}) \rightarrow \text{BF}_3(\text{g}) + 0.5 \text{ N}_2$	-211.68 ± 0.3	-

References

1. A. S. Dworkin, D. J. Samor and E. R. Van Arsdale, *J. Chem. Phys.* **22**, 837 (1954).
2. O. L. Gal'chenko, A. N. Kornilov, and S. M. Skuratov, *Russ. J. Inorg. Chem.* **5**, 1282 (1960).
3. P. Oras, Fulmer Research Institute, Report R. 163/6/15 December 1961, Stoke Poges, England.
4. C. J. Thompson and O. C. Sinks, Dow Chemical Co., Report ARPA 1-164, Jan. 1961.
5. J. J. Keavney, Stamford Research Laboratories, American Cyanamid Co., Stamford, Conn., private communication to Wise et al., loc. cit.
6. S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, *J. Phys. Chem.* **70**, 7 (1966).

Heat Capacity and Entropy.

The low temperature heat capacity was taken from E. F. Westrum, Jr., private communication, May 19, 1960. The intermediate heat capacity (300-1650°K) was obtained from R. A. McDonald and D. R. Stull, *J. Phys. Chem.* **65**, 1918 (1961). The high temperature Cp was taken from H. Prophet and D. R. Stull, *J. Chem. Eng. Data* **8**, No. 1, 78, January 1963. The heat capacities in the three temperature ranges were plotted and then graphically smoothed. A. S. Dworkin, D. J. Samor, and A. R. Van Arsdale, loc. cit., also reported heat capacity (50-300°K) not employed in this table.

The entropy was obtained by integration of the heat capacity data from E. F. Westrum, Jr., loc. cit., based upon $S_{10}^\circ = 0.0028 \text{ eu}$.

Temperature of Decomposition.

Observations by The Dow Chemical Company under Contract No. AF 33(616)-6149 show decomposition to elements at 1 atm total pressure at $2600 \pm 100^\circ\text{K}$. The decomposition temperature calculated from these tables is 2832°K ; presumably this discrepancy is associated with uncertainties in the high temperature enthalpies of BN(c) , B(c) and E(1) and the enthalpy of melting of B(c) .

OPW = 24.8177 (IDEAL GAS)

T, °K	Cp°	g/bm ³ /mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	∞	∞	∞	2.076	113.252	113.252	INFINITE
100	6.957	43.114	56.935	1.382	113.593	-243.024	
200	6.963	47.937	51.368	.686	113.861	-118.772	
298	7.039	50.728	50.728	0	114.000	106.117	-77.786
300	7.041	50.771	50.728	.013	114.002	106.068	-77.270
400	7.237	52.822	51.006	.726	114.044	103.445	-56.503
500	7.489	54.463	51.539	1.462	114.016	100.759	-44.042
600	7.735	55.851	52.145	2.224	113.946	98.114	-35.738
700	7.959	57.059	52.762	3.008	113.851	95.483	-28.411
800	8.162	58.128	53.382	3.816	113.736	92.846	-22.019
1000	8.390	59.976	54.511	4.666	113.474	87.679	-19.162
1100	8.488	60.781	55.045	5.045	113.320	85.105	-16.809
1200	8.570	61.553	55.554	5.453	113.184	82.604	-14.508
1300	8.635	62.298	56.036	5.889	113.062	80.176	-12.256
1400	8.701	62.854	56.504	6.340	112.954	77.816	-10.045
1500	8.755	63.457	56.948	6.763	112.862	74.959	-7.921
1600	8.805	64.023	57.373	7.164	112.786	72.460	-6.000
1700	8.851	64.558	57.770	7.543	112.724	70.262	-4.319
1800	8.893	65.066	58.136	7.900	112.674	68.246	-2.849
1900	8.937	65.548	58.468	8.236	112.634	66.388	-1.558
2000	8.978	66.007	58.768	8.553	112.602	64.669	-0.421
2100	9.018	66.444	59.256	8.851	112.576	63.062	0.484
2200	9.055	66.859	59.518	9.128	112.556	61.556	1.458
2300	9.089	67.250	59.758	9.387	112.540	60.131	2.482
2400	9.133	67.659	60.232	9.617	112.528	58.776	3.449
2500	9.169	68.032	60.537	9.814	112.519	57.481	4.348
2600	9.205	68.392	60.872	10.000	112.512	56.236	5.178
2700	9.240	68.736	61.137	10.166	112.506	55.041	5.939
2800	9.274	69.077	61.337	10.316	112.502	53.896	6.624
2900	9.307	69.403	61.467	10.453	112.500	52.801	7.236
3000	9.339	69.719	61.630	10.576	112.499	51.756	7.774
3100	9.370	70.035	62.187	10.687	112.497	50.761	8.241
3200	9.400	70.346	62.593	10.787	112.496	49.816	8.636
3300	9.429	70.611	62.860	10.876	112.495	48.921	8.961
3400	9.457	70.895	63.091	10.954	112.494	48.076	9.216
3500	9.484	71.169	63.319	11.022	112.493	47.281	9.401
3600	9.510	71.437	63.537	11.080	112.492	46.536	9.516
3700	9.535	71.698	63.744	11.128	112.491	45.841	9.561
3800	9.559	71.952	63.941	11.166	112.490	45.196	9.536
3900	9.582	72.201	64.095	11.195	112.489	44.601	9.441
4000	9.604	72.444	64.233	11.216	112.488	44.056	9.276
4100	9.625	72.681	64.356	11.229	112.487	43.561	9.041
4200	9.645	72.901	64.465	11.234	112.486	43.116	8.736
4300	9.666	73.114	64.561	11.230	112.485	42.721	8.371
4400	9.685	73.363	64.632	11.216	112.483	42.376	7.946
4500	9.704	73.581	64.681	11.191	112.481	42.081	7.471
4600	9.712	73.784	64.716	11.156	112.478	41.836	6.946
4700	9.740	74.004	64.735	11.111	112.474	41.641	6.371
4800	9.757	74.209	64.753	11.056	112.469	41.496	5.746
4900	9.774	74.410	64.768	11.001	112.464	41.401	5.071
5000	9.790	74.608	64.776	10.946	112.459	41.356	4.346
5100	9.806	74.802	64.782	10.891	112.454	41.311	3.571
5200	9.822	74.993	64.786	10.836	112.449	41.266	2.746
5300	9.838	75.180	64.787	10.781	112.444	41.221	1.871
5400	9.853	75.364	64.787	10.726	112.439	41.176	0.946
5500	9.864	75.545	64.786	10.671	112.434	41.131	0.021
5600	9.884	75.723	64.781	10.616	112.429	41.086	-0.854
5700	9.898	75.898	64.772	10.561	112.424	41.041	-1.679
5800	9.913	76.070	64.757	10.506	112.419	40.996	-2.454
5900	9.928	76.240	64.736	10.451	112.414	40.951	-3.179
6000	9.942	76.407	64.711	10.396	112.409	40.906	-3.854

Dec. 31, 1960; Sept. 30, 1963; June 30, 1966

Ground State Configuration 3π $\Delta H^\circ_{298.15} = 113$ kcal/mol $\Delta H^\circ_{298.15} = 114 \pm 30$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	6
(8500)	1
(8900)	2
27877	6

$\omega_e = 1514.6$ cm⁻¹ $\omega_e x_e = 12.3$ cm⁻¹ $\sigma = 1$
 $B_e = 1.666$ cm⁻¹ $\alpha_e = 0.025$ cm⁻¹ $r_e = 1.281$ Å

Heat of Formation.

The heat of formation is based on $D_0 = 5.7$ eV which was calculated from ω_e and $\omega_e x_e$ observed by A. E. Douglas and G. Herzberg, Can. J. Research 18A, 179 (1940). An uncertainty of ± 1.3 eV was assigned from consideration of other information which places the dissociation energy between 4 and 7 eV. The value $D_0 = 4.0 \pm 0.5$ eV was selected by A. G. Gaydon, "Dissociation Energies," second edition, Chapman and Hall Ltd, London, 1953, from his own extrapolation of the spectroscopic data. An upper limit of $D_0 \leq 7.0$ eV results from the upper limit for the pressure of BN(c) $\rightarrow$ BN(g) obtained from the B^+ ion intensity at 1600°C observed by P.A. Akhahin and Yu. S. Klodeev, Zh. Neorgan. Khim. 7, 941 (1962). It is likely that the BN(g) pressure is even smaller since it is known that BN(c) $\rightarrow$ B(s) + 0.5 N₂(g) and Akhahin's pressure limit are the same magnitude as that of B(s) $\rightarrow$ B(g). V. V. Pesenko, Forshkovaya Met., Akad. Nauk Ukr. S. S. R. 3, No. 4, 80-5 (1961) [cf. Chem. Aba. 56, 10997 (1962)], reports a standard heat of sublimation of 160 kcal/mol for BN(c) $\rightarrow$ BN(g) and also gives pressures for BN(g) at 2500 and 3000°K which are stated to be two orders less than the equilibrium pressure of nitrogen. Pesenko's original article is not yet available to us and it is not clear from the abstract whether the values are based on new data or are mere calculations. The reported pressures yield $D_0 = 6.2$ eV, but here again the BN(g) pressures are of the same magnitude as the JANAP values for B(s) $\rightarrow$ B(g).

Some estimated values for D_0 (ranging from 5.4 to 6.4 eV) are summarized below along with the experimental evidence.

Source	D_0 (eV)	ΔH°_{298} (kcal/mol)	ΔH°_{298} (kcal/mol)
Gaydon's extrapolation of spectroscopic data	4.0 $\pm$ 0.5	213	153
Linear Birge-Sponer extrapolation	5.7	174	114
Pesenko's "BN(g) pressures"	6.2	161	101
Akhahin's upper limit for BN(g) pressure	7.0	145	85
Estimate from geometric mean of D_0 for B ₂ and N ₂	5.4	180	120
Estimate from D_0 for series N ₂ , CN, BN, Ben	5.6	177	117
Estimate M ₂ + N ₂ = 2 MN for M-B from M-C	6.0	166	106
Estimate from arithmetic mean of D_0 for B ₂ and N ₂	6.4	158	98

Heat Capacity and Entropy.

The molecular constants are based on emission spectra of the $3\pi - 3\pi$ transition obtained by Douglas and Herzberg, loc. cit. Observation of the same triplet in absorption by B. A. Thrush, Nature 160, 1044 (1960), strongly suggests that the ground state of BN is 3π in contrast to 1Σ as observed for the isoelectronic molecules BeO and C₂. Electronic levels for the 3π states are taken from Douglas and Herzberg while values for $1\Sigma^+$ and 1π have been estimated from the SCF calculations of J. L. Mease and M. Barlocher, Helv. Chim. Acta 47, 314 (1964).

Sodium Metaborate (NaBO₂)

(Crystal) Mol. Wt. = 65.811

SODIUM METABORATE (NaBO₂)

(CRYSTAL)

MOL. WT. = 65.811

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	— kcal. mole ⁻¹ —	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	7.751	4.780	28.394	232.874	-232.874	-232.874	INFINITE
200	12.740	11.890	18.924	233.592	-233.592	-233.592	501.201
298	15.760	17.573	17.573	234.000	-234.000	-234.000	245.806
300	15.780	17.670	17.573	234.001	-234.001	-234.001	161.655
400	17.370	22.634	18.212	234.718	-234.718	-234.718	160.497
500	18.700	26.458	19.469	234.797	-234.797	-234.797	117.949
600	19.880	29.972	20.933	234.819	-234.819	-234.819	92.296
700	20.950	32.417	22.570	234.843	-234.843	-234.843	75.191
800	21.900	34.718	24.370	234.867	-234.867	-234.867	62.974
900	22.750	36.878	26.300	234.891	-234.891	-234.891	53.761
1000	23.500	38.900	28.331	234.915	-234.915	-234.915	46.695
1100	24.150	40.795	30.441	234.939	-234.939	-234.939	41.006
1200	24.750	42.560	32.690	234.963	-234.963	-234.963	36.359
1300	25.300	44.200	35.140	234.987	-234.987	-234.987	32.511
1400	25.800	45.720	37.760	235.011	-235.011	-235.011	29.463
1500	26.250	47.120	40.520	235.035	-235.035	-235.035	26.961
1600	26.650	48.400	43.400	235.059	-235.059	-235.059	24.761
1700	27.000	49.570	46.390	235.083	-235.083	-235.083	22.813
1800	27.300	50.630	49.480	235.107	-235.107	-235.107	20.813
1900	27.550	51.580	52.660	235.131	-235.131	-235.131	18.789
2000	27.750	52.420	55.920	235.155	-235.155	-235.155	16.789
2100	27.900	53.150	59.260	235.179	-235.179	-235.179	14.809
2200	28.000	53.780	62.670	235.203	-235.203	-235.203	12.859
2300	28.050	54.310	66.140	235.227	-235.227	-235.227	10.949
2400	28.050	54.740	69.660	235.251	-235.251	-235.251	9.089
2500	28.000	55.070	73.230	235.275	-235.275	-235.275	7.289
2600	27.900	55.300	76.840	235.300	-235.300	-235.300	5.549
2700	27.750	55.430	80.490	235.324	-235.324	-235.324	3.869
2800	27.550	55.460	84.180	235.348	-235.348	-235.348	2.249
2900	27.300	55.390	87.900	235.372	-235.372	-235.372	0.689
3000	27.000	55.220	91.640	235.396	-235.396	-235.396	-0.811
3100	26.650	54.950	95.400	235.420	-235.420	-235.420	-2.261
3200	26.250	54.580	99.170	235.444	-235.444	-235.444	-3.661
3300	25.800	54.110	102.940	235.468	-235.468	-235.468	-5.011
3400	25.300	53.540	106.710	235.492	-235.492	-235.492	-6.311
3500	24.750	52.870	110.480	235.516	-235.516	-235.516	-7.561
3600	24.150	52.100	114.240	235.540	-235.540	-235.540	-8.761
3700	23.500	51.230	117.990	235.564	-235.564	-235.564	-9.911
3800	22.750	50.260	121.720	235.588	-235.588	-235.588	-11.011
3900	21.900	49.190	125.440	235.612	-235.612	-235.612	-12.061
4000	20.950	48.020	129.140	235.636	-235.636	-235.636	-13.061
4100	20.000	46.750	132.820	235.660	-235.660	-235.660	-14.011
4200	19.050	45.380	136.480	235.684	-235.684	-235.684	-14.911
4300	18.100	43.910	140.120	235.708	-235.708	-235.708	-15.761
4400	17.150	42.340	143.740	235.732	-235.732	-235.732	-16.561
4500	16.200	40.670	147.340	235.756	-235.756	-235.756	-17.311
4600	15.250	38.900	150.920	235.780	-235.780	-235.780	-18.011
4700	14.300	37.030	154.480	235.804	-235.804	-235.804	-18.661
4800	13.350	35.060	158.020	235.828	-235.828	-235.828	-19.261
4900	12.400	33.090	161.540	235.852	-235.852	-235.852	-19.811
5000	11.450	31.120	165.040	235.876	-235.876	-235.876	-20.411
5100	10.500	29.150	168.520	235.900	-235.900	-235.900	-20.961
5200	9.550	27.180	171.980	235.924	-235.924	-235.924	-21.511
5300	8.600	25.210	175.420	235.948	-235.948	-235.948	-22.061
5400	7.650	23.240	178.840	235.972	-235.972	-235.972	-22.611
5500	6.700	21.270	182.240	235.996	-235.996	-235.996	-23.161
5600	5.750	19.300	185.620	236.020	-236.020	-236.020	-23.711
5700	4.800	17.330	188.980	236.044	-236.044	-236.044	-24.261
5800	3.850	15.360	192.320	236.068	-236.068	-236.068	-24.811
5900	2.900	13.390	195.640	236.092	-236.092	-236.092	-25.361
6000	1.950	11.420	198.940	236.116	-236.116	-236.116	-25.911
6100	1.000	9.450	202.220	236.140	-236.140	-236.140	-26.461
6200	0.050	7.480	205.480	236.164	-236.164	-236.164	-27.011
6300	-0.900	5.510	208.720	236.188	-236.188	-236.188	-27.561
6400	-1.850	3.540	211.940	236.212	-236.212	-236.212	-28.111
6500	-2.800	1.570	215.140	236.236	-236.236	-236.236	-28.661
6600	-3.750	-0.400	218.320	236.260	-236.260	-236.260	-29.211
6700	-4.700	-2.370	221.480	236.284	-236.284	-236.284	-29.761
6800	-5.650	-4.340	224.620	236.308	-236.308	-236.308	-30.311
6900	-6.600	-6.310	227.740	236.332	-236.332	-236.332	-30.861
7000	-7.550	-8.280	230.840	236.356	-236.356	-236.356	-31.411
7100	-8.500	-10.250	233.920	236.380	-236.380	-236.380	-31.961
7200	-9.450	-12.220	236.980	236.404	-236.404	-236.404	-32.511
7300	-10.400	-14.190	240.020	236.428	-236.428	-236.428	-33.061
7400	-11.350	-16.160	243.040	236.452	-236.452	-236.452	-33.611
7500	-12.300	-18.130	246.040	236.476	-236.476	-236.476	-34.161
7600	-13.250	-20.100	249.020	236.500	-236.500	-236.500	-34.711
7700	-14.200	-22.070	251.980	236.524	-236.524	-236.524	-35.261
7800	-15.150	-24.040	254.920	236.548	-236.548	-236.548	-35.811
7900	-16.100	-26.010	257.840	236.572	-236.572	-236.572	-36.361
8000	-17.050	-27.980	260.740	236.596	-236.596	-236.596	-36.911
8100	-18.000	-29.950	263.620	236.620	-236.620	-236.620	-37.461
8200	-18.950	-31.920	266.480	236.644	-236.644	-236.644	-38.011
8300	-19.900	-33.890	269.320	236.668	-236.668	-236.668	-38.561
8400	-20.850	-35.860	272.140	236.692	-236.692	-236.692	-39.111
8500	-21.800	-37.830	274.940	236.716	-236.716	-236.716	-39.661
8600	-22.750	-39.800	277.720	236.740	-236.740	-236.740	-40.211
8700	-23.700	-41.770	280.480	236.764	-236.764	-236.764	-40.761
8800	-24.650	-43.740	283.220	236.788	-236.788	-236.788	-41.311
8900	-25.600	-45.710	285.940	236.812	-236.812	-236.812	-41.861
9000	-26.550	-47.680	288.640	236.836	-236.836	-236.836	-42.411
9100	-27.500	-49.650	291.320	236.860	-236.860	-236.860	-42.961
9200	-28.450	-51.620	293.980	236.884	-236.884	-236.884	-43.511
9300	-29.400	-53.590	296.620	236.908	-236.908	-236.908	-44.061
9400	-30.350	-55.560	299.240	236.932	-236.932	-236.932	-44.611
9500	-31.300	-57.530	301.840	236.956	-236.956	-236.956	-45.161
9600	-32.250	-59.500	304.420	236.980	-236.980	-236.980	-45.711
9700	-33.200	-61.470	306.980	237.004	-237.004	-237.004	-46.261
9800	-34.150	-63.440	309.520	237.028	-237.028	-237.028	-46.811
9900	-35.100	-65.410	312.040	237.052	-237.052	-237.052	-47.361
10000	-36.050	-67.380	314.540	237.076	-237.076	-237.076	-47.911

$$\Delta H_f^0 = -232.9 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 298.15 = -234 \pm 2 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 8.86 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^0 298.15 = 77.00 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 17.573 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1239^\circ \text{K.}$$

Heat of Formation.

W. H. Evans, D. D. Magman and E. J. Prosen in NBS Report No. 4943, "Thermodynamic Properties of Some Boron Compounds", August, 1956, extrapolated from the graph of L. Shartais and W. Cappa, J. Am. Ceram. Soc. **37**, 27 (1954) the heat of solution to be -25.4 kcal. mole⁻¹ for the first reaction in 2N nitric acid. G. Grenier and D. White, J. Chem. Phys. **51**, 1661 (1957) measured the heat of solution at 273.15°K. in 2N nitric acid for the first reaction and found a value of -20.43 kcal. mole⁻¹. The heats of solution for the second and third reactions were obtained from L. Shartais and W. Cappa, loc. cit.

1. Na₂O·B₂O₃(c) + Solvent I = end Solution I
2. B₂O₃(c) + Solvent II = end Solution I
3. Na₂O(c) + Solvent I = Solvent II

The combination of the above reactions yields:

$$\text{Na}_2\text{O}(c) + \text{B}_2\text{O}_3(c) = \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3(c)$$

$$1/2 \text{ Na}_2\text{O}(c) + 1/2 \text{ B}_2\text{O}_3(c) = \text{NaBO}_2(c)$$

The ΔH_f⁰ 298.15's for Na₂O and B₂O₃ are JANAF values. The ΔH_f⁰ 298.15 value of -234.000 kcal. mole⁻¹ employed in this table was obtained by taking the average of the values given above for reaction 1. Since there were uncertainties in the extrapolation and in assuming no correction for the measurements at 273.15°K., an average value was considered preferable.

Heat Capacity and Entropy.

The low temperature heat capacities (5-298.15°K.) and S_{298.15}⁰ were obtained from G. Grenier and E. P. Westrum, J. Am. Chem. Soc. **78**, 6226 (1956). The heat capacities at the higher temperatures were altered slightly from the estimate of K. K. Kelley, U. S. Bureau of Mines Bulletin 393 (1936).

Melting Data.

The T_m was obtained from H. S. Van Klooster, Z. Anorg. Chem. **53**, 122 (1911). The adopted ΔH_m⁰ was calculated by K. K. Kelley loc. cit. from H. S. Van Klooster's work. K. K. Kelley also calculated a ΔH_m⁰ of 9.3 kcal. mole⁻¹ from M. H. LaChâtelier, Compt. rend. **118**, 800 (1894).

Sublimation Data.

The ΔH_g⁰ was obtained from the mass spectrometric investigations of A. Büchler and J. B. Berkowitz-Mattuck, J. Chem. Phys. **39**, 286 (1963).

Sodium Metaborate (NaBO₂)

(Liquid) Mol. Wt. = 65.811

SODIUM METABORATE (NaBO₂)

(LIQUID)

MOL. WT. = 65.811

$\Delta H_f^{298.15} = 20.560 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1239^\circ\text{K.}$
 $\Delta H_f^{298.15} = [-229.339] \text{ kcal. mole}^{-1}$
 $\Delta H_m^0 = 8.66 \text{ kcal. mole}^{-1}$

$\Delta H_f^{298.15(1)}$ was obtained from $\Delta H_f^0(c)$ by addition of ΔH_m^0 end difference between ($H_{1239}^0-H_{298.15}^0$) for the crystal end liquid.

Heat Capacity and Entropy.

Sodium metaborate is assumed to have a glass transformation at 826°K. below which C_p of the glass is assumed equal to that of the crystal. Above 826°K. the heat capacity was estimated as a constant value by assuming 8.75 calories contribution from each atom. The $S_{298.15}$ was obtained in a manner analogous with $\Delta H_f^{298.15}$.

Melting Data.

See crystal table.

T, °K.	C_p	$\text{cal. mole}^{-1}\text{deg.}^{-1}$	S°	$-(F^\circ-H_{298}^\circ)/T$	$H^\circ-H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _f
0								
100								
200								
298	15.760	20.560	20.560	0.000	-229.339	-216.773	158.692	
300	15.780	20.658	20.560	0.020	-229.340	-216.695	157.855	
400	17.370	25.421	21.999	1.029	-220.840	-216.095	156.015	
500	18.700	29.443	22.456	3.494	-230.137	-207.909	90.912	
600	19.880	32.957	23.919	5.423	-230.159	-203.568	74.146	
700	21.050	36.108	25.439	7.469	-230.113	-199.139	62.171	
800	22.200	38.981	26.995	9.585	-229.885	-194.723	53.193	
900	23.330	42.721	28.688	12.813	-229.879	-190.323	46.192	
1000	24.450	46.411	30.100	16.311	-227.481	-186.161	40.683	
1100	25.560	49.747	31.737	19.811	-226.120	-182.098	36.178	
1200	26.660	52.772	33.360	23.311	-224.810	-177.699	32.361	
1300	27.750	55.592	34.977	26.811	-223.547	-173.095	29.045	
1400	28.830	58.187	36.537	30.311	-222.323	-168.413	25.946	
1500	29.900	60.602	38.061	33.811	-221.143	-164.213	23.404	
1600	30.960	62.861	39.542	37.311	-220.009	-155.155	21.192	
1700	32.000	64.983	40.976	40.811	-218.922	-149.765	19.253	
1800	33.030	66.978	42.366	44.311	-217.883	-148.000	17.539	
1900	34.050	68.873	43.712	47.811	-216.891	-138.232	16.536	
2000	35.000	70.671	45.015	51.311	-215.945	-134.070	14.631	
2100	35.000	72.379	46.278	54.811	-215.062	-128.995	13.424	
2200	35.000	73.907	47.502	58.311	-214.239	-123.076	12.315	
2300	35.000	75.357	48.691	61.811	-213.471	-116.491	11.299	
2400	35.000	76.732	49.839	65.311	-212.752	-109.391	10.391	
2500	35.000	78.041	50.957	68.811	-212.082	-101.172	9.543	
2600	35.000	79.284	52.042	72.311	-211.463	-92.463	8.755	
2700	35.000	80.475	53.096	75.811	-210.893	-83.600	8.030	
2800	35.000	81.620	54.120	79.311	-210.372	-74.192	7.360	
2900	35.000	82.726	55.120	82.811	-209.899	-64.835	6.740	
3000	35.000	83.796	56.092	86.311	-209.474	-55.021	6.164	

Dec. 31, 1960; Mar. 31, 1965

Sodium Metaborate (NaBO₂)

(Ideal Gas) Mol. Wt. = 65.811

SODIUM METABORATE (NaBO₂)

MOL. WT. = 65.811

(IDEAL GAS)

Point Group C_s
 $S_{298.15}^\circ = [64.937] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = [1]

$\Delta H_f^\circ = [-156 \pm 3] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [-157 \pm 3] \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

ν , cm. ⁻¹	λ , μ , cm. ⁻¹
[800] (1)	[400] (1)
1355 (1)	600 (1)
[2040] (1)	[1000] (1)

Bond Distances: Na-O = 2.14 Å, O-B = 1.36 Å, B-O = 1.20 Å

Bond Angle: NaOB = 100°, O-B-O = 180°

Product of the Moments of Inertia: $I_A I_B I_C = 2.566657 \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$

 $\sigma = 1$

Heat of Formation.

The heat of formation was calculated from the heat of sublimation of $73 \pm 3 \text{ kcal. mole}^{-1}$ measured mass spectrometrically at 1070°K. by A. Eichler and J. B. Berkowitz - Mattuck, *J. of Chem. Phys.* 39, 286 (1963) by addition of the difference between ($1070^\circ\text{H}_{298.15}^\circ$) for the crystal and gas.

Heat Capacity and Entropy.

A. Eichler and E. P. Murrell, *J. Chem. Phys.* 32, No. 2, 292, (1963), observed and assigned two vibrational metaborate frequencies, which were adopted for this table. The other vibrational frequencies were estimated by comparison with lithium metaborate. The molecular constants were obtained from P. A. Akishin and V. P. Spiridonov, *Zhur. Strukt. Khim.* 2, 63 (1961). The individual moments of inertia are: $I_A = 4.2923 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 26.6933 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C _p	S°	$-(F^\circ - H_{298}^\circ)/T$	H° - H ₂₉₈ °	ΔH_f°	ΔF_f°	Log K _p
0	∞	INFINITE	-	2.738	-155.830	-155.830	INFINITE
100	8.186	54.584	73.971	-1.939	-156.070	-156.070	342.667
200	9.784	60.701	65.936	-1.047	-156.525	-157.356	171.942
296	11.504	64.937	64.937	∞	-157.000	-157.000	115.566
300	11.534	65.008	64.937	∞	-157.009	-157.009	114.856
400	12.939	68.527	65.408	1.248	-158.159	-157.764	86.194
500	14.062	71.539	66.340	2.600	-158.692	-157.602	66.884
600	14.984	74.187	67.431	4.053	-159.190	-157.307	57.307
700	15.745	76.556	68.429	5.493	-159.659	-156.822	48.728
800	16.371	78.701	69.703	7.198	-160.083	-156.582	42.774
900	16.884	80.660	70.813	8.862	-160.489	-156.120	37.909
1000	17.305	82.461	71.889	10.572	-160.881	-155.611	34.007
1100	17.651	84.127	72.927	12.320	-161.272	-155.048	30.806
1200	17.937	85.676	73.926	14.100	-161.659	-154.429	28.006
1300	18.174	87.121	74.886	15.906	-162.044	-153.759	25.440
1400	18.373	88.475	75.808	17.734	-162.428	-153.036	23.236
1500	18.541	89.749	76.696	19.579	-162.811	-152.260	21.308
1600	18.683	90.950	77.550	21.441	-163.193	-151.436	19.618
1700	18.804	92.086	78.372	23.315	-163.574	-150.560	18.158
1800	18.909	93.164	79.164	25.201	-163.954	-149.636	16.798
1900	18.999	94.188	79.928	27.097	-164.333	-148.668	15.537
2000	19.077	95.166	80.665	29.001	-164.711	-147.654	14.363
2100	19.146	96.098	81.378	30.912	-165.088	-146.596	13.285
2200	19.206	96.990	82.048	32.830	-165.464	-145.494	12.307
2300	19.260	97.845	82.715	34.753	-165.839	-144.348	11.429
2400	19.307	98.666	83.382	36.681	-166.213	-143.156	10.651
2500	19.349	99.455	84.009	38.614	-166.588	-141.916	10.043
2600	19.387	100.215	84.618	40.551	-166.962	-140.630	9.794
2700	19.420	100.947	85.204	42.492	-167.336	-139.298	9.634
2800	19.451	101.654	85.784	44.435	-167.711	-137.920	9.574
2900	19.478	102.337	86.343	46.381	-168.086	-136.500	9.514
3000	19.503	102.997	86.887	48.330	-168.461	-135.036	9.454
3100	19.526	103.637	87.417	50.282	-168.836	-133.530	9.394
3200	19.546	104.258	87.934	52.235	-169.211	-131.986	9.334
3300	19.565	104.859	88.438	54.191	-169.586	-130.400	9.274
3400	19.583	105.444	88.929	56.148	-169.961	-128.774	9.214
3500	19.598	106.012	89.409	58.108	-170.336	-127.108	9.154
3600	19.613	106.564	90.878	60.068	-170.711	-125.400	9.094
3700	19.627	107.101	92.337	62.027	-171.086	-123.654	9.034
3800	19.639	107.625	93.785	63.983	-171.461	-121.874	8.974
3900	19.651	108.135	95.223	65.938	-171.836	-120.054	8.914
4000	19.661	108.633	96.642	67.894	-172.211	-118.194	8.854
4100	19.671	109.119	97.927	69.850	-172.586	-116.294	8.794
4200	19.681	109.593	99.197	71.807	-172.961	-114.354	8.734
4300	19.689	110.056	99.887	73.766	-173.336	-112.374	8.674
4400	19.697	110.509	99.887	75.726	-173.711	-110.354	8.614
4500	19.705	110.951	99.670	77.686	-174.086	-108.294	8.554
4600	19.712	111.385	99.451	79.647	-174.461	-106.194	8.494
4700	19.719	111.809	99.226	81.607	-174.836	-104.054	8.434
4800	19.725	112.224	98.997	83.567	-175.211	-101.874	8.374
4900	19.731	112.631	98.762	85.527	-175.586	-99.654	8.314
5000	19.736	113.029	98.526	87.487	-175.961	-97.394	8.254
5100	19.742	113.420	98.281	89.447	-176.336	-95.094	8.194
5200	19.747	113.800	98.031	91.407	-176.711	-92.754	8.134
5300	19.751	114.180	97.771	93.367	-177.086	-90.374	8.074
5400	19.756	114.549	97.501	95.327	-177.461	-87.954	8.014
5500	19.760	114.911	97.226	97.287	-177.836	-85.494	7.954
5600	19.764	115.268	96.941	99.247	-178.211	-83.014	7.894
5700	19.767	115.617	96.651	101.207	-178.586	-80.514	7.834
5800	19.771	115.961	96.351	103.167	-178.961	-77.994	7.774
5900	19.774	116.299	96.041	105.127	-179.336	-75.454	7.714
6000	19.778	116.632	95.726	107.087	-179.711	-72.894	7.654

T, °K	C _p ^a	$\frac{\text{gibbs/mol}}{S^b}$	$-(G^c - H_{298})/T$	$H^c - H_{298}$	$\frac{\text{kcal/mol}}{\Delta H^c}$	ΔG^c	Log K _p
0	6.994	0.00	INFINITE	- 2.073	- .744	- .744	INFINITE
100	6.996	41.001	54.776	- 1.373	- .744	- 2.425	5.300
200	6.988	45.824	49.241	- .684	- 1.135	- 4.560	4.961
298	6.978	48.604	48.604	0.000	- 1.000	- 6.768	
300	6.978	48.667	48.668	.013	.001	- 6.841	
400	6.968	52.259	46.808	1.713	.021	- 9.087	4.965
500	7.230	52.259	46.401	1.429	- .4038	- 11.359	4.965
600	7.627	53.594	49.991	2.162	- 1.58	- 13.612	4.958
700	8.084	54.784	50.590	2.914	- 3.111	- 15.842	4.946
800	8.610	55.753	51.176	4.676	- 4.666	- 18.104	4.914
900	9.208	56.541	51.768	6.466	- .861	- 20.236	4.861
1000	9.876	57.561	52.221	8.280	- .861	- 22.399	4.795
1100	10.625	58.340	52.777	10.314	- 1.067	- 24.544	4.779
1200	11.461	59.060	53.289	12.544	- 1.283	- 26.668	4.757
1300	12.380	59.726	53.759	14.971	- 1.509	- 28.762	4.736
1400	13.386	60.352	54.208	17.595	- 1.688	- 30.822	4.709
1500	14.476	60.950	54.639	20.410	- 1.822	- 32.850	4.676
1600	15.655	61.527	55.049	23.414	- 2.243	- 34.998	4.779
1700	16.927	62.088	55.444	26.602	- 2.507	- 37.028	4.760
1800	18.297	62.633	55.823	30.077	- 2.780	- 39.051	4.741
1900	19.767	63.166	56.188	33.836	- 3.061	- 41.064	4.704
2000	21.340	63.691	56.539	37.881	- 3.348	- 43.051	4.666
2100	22.999	64.209	56.877	42.214	- 3.638	- 45.028	4.686
2200	24.740	64.728	57.204	46.840	- 3.935	- 46.992	4.668
2300	26.560	65.240	57.520	51.760	- 4.236	- 48.949	4.651
2400	28.466	65.747	57.825	56.975	- 4.540	- 50.898	4.634
2500	30.455	66.250	58.121	62.486	- 4.846	- 52.836	4.607
2600	32.534	66.740	58.407	68.291	- 5.154	- 54.767	4.580
2700	34.700	67.218	58.685	74.390	- 5.464	- 56.697	4.553
2800	36.960	67.686	58.955	80.793	- 5.775	- 58.627	4.527
2900	39.312	68.144	59.216	87.500	- 6.087	- 60.557	4.500
3000	41.754	68.593	59.473	94.513	- 6.399	- 62.487	4.473
3100	44.285	69.031	59.721	101.841	- 6.711	- 64.417	4.446
3200	46.904	69.459	59.963	109.484	- 7.023	- 66.347	4.419
3300	49.610	69.878	60.198	117.441	- 7.335	- 68.277	4.392
3400	52.401	70.288	60.426	125.713	- 7.647	- 70.207	4.365
3500	55.276	70.691	60.652	134.306	- 7.959	- 72.136	4.338
3600	58.244	71.088	60.871	143.229	- 8.271	- 74.066	4.311
3700	61.306	71.480	61.085	152.483	- 8.583	- 76.000	4.284
3800	64.463	71.868	61.284	162.069	- 8.895	- 77.929	4.257
3900	67.716	72.253	61.479	171.996	- 9.207	- 79.858	4.230
4000	71.066	72.635	61.664	182.265	- 9.519	- 81.787	4.203
4100	74.513	72.999	61.839	192.876	- 9.831	- 83.716	4.176
4200	78.059	73.359	62.006	203.831	- 10.143	- 85.645	4.149
4300	81.704	73.718	62.168	215.130	- 10.455	- 87.574	4.122
4400	85.448	74.076	62.325	226.865	- 10.767	- 89.503	4.095
4500	89.291	74.434	62.478	239.036	- 11.079	- 91.432	4.068
4600	93.235	74.791	62.616	251.643	- 11.389	- 93.361	4.041
4700	97.279	75.148	62.750	264.686	- 11.699	- 95.290	4.014
4800	101.423	75.505	62.880	278.164	- 12.009	- 97.219	3.987
4900	105.667	75.861	62.999	292.076	- 12.319	- 99.148	3.960
5000	110.011	76.218	63.110	306.421	- 12.629	- 101.077	3.933
5100	114.455	76.575	63.213	321.200	- 12.939	- 103.006	3.906
5200	119.000	76.932	63.301	336.413	- 13.249	- 104.935	3.879
5300	123.645	77.289	63.385	352.060	- 13.559	- 106.864	3.852
5400	128.390	77.646	63.465	368.141	- 13.869	- 108.793	3.825
5500	133.235	77.999	63.541	384.656	- 14.179	- 110.722	3.798
5600	138.180	78.356	63.613	401.605	- 14.489	- 112.651	3.771
5700	143.225	78.713	63.681	419.088	- 14.799	- 114.580	3.744
5800	148.370	79.070	63.745	437.005	- 15.109	- 116.509	3.717
5900	153.615	79.427	63.806	455.356	- 15.419	- 118.438	3.690
6000	158.960	79.784	63.864	474.141	- 15.729	- 120.367	3.663

Dec. 31, 1960; June 30, 1962; Mar. 31, 1963; June 30, 1968

Dec. 31, 1960; June 30, 1962; Mar. 31, 1965; June 30, 1968

Heat Capacity and Entropy

The molecular and vibrational constants for the ground etate are from G. Herzberg "Spectra of Diatomic Molecules,"

D. Van Nostrand Co., Inc., New York, 1950. The electronic levels are also given by Herzberg with the exception of the level at 3395957, a $\frac{1}{2}$ level designated B' by A. Mal'tsev and D. I. Kataev, *Vestn. Mosk. Univ. Ser. II* 22, 2 (1967). The molecular constants were all adjusted to reflect normal isotopic abundances.

BORON DIOXIDE UNINEGATIVE ION (BO₂⁻) (IDEAL GAS) GFN = 42.81035

$$\Delta H_f^\circ = -166 \pm 6 \text{ kcal/mol}$$

$$\Delta H_f^{298.15} = -166 \pm 6 \text{ kcal/mol}$$

Point Group {D_{oh}}

$$S_{298.15}^\circ = [51.6 \pm 2] \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

State	$\epsilon_i, \text{cm}^{-1}$	g_i
1 ₂ ⁺	0	1
1 _{B₂}	[35000]	1

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
[1150] (1)
[580] (2)
[2200] (1)

Bond Distances: B-O = [1.25] Å

Bond Angle: O-B-O = [180]°

Rotational Constant: B₀ = [0.3172] cm⁻¹

Heat of Formation

D. E. Jensen, AeroChem TP-187A, Dec. 1968, AeroChem Research Laboratories, Inc., Princeton, N. J., has obtained equilibrium constants for the reaction $\text{HBO}_2 + e^- \rightarrow \text{H} + \text{BO}_2^-$. This involves several assumptions the most basic of which is that boron added to H_2/O_2 flames is converted completely to HBO_2 . The free electrons are produced by addition of potassium to the flames, and their concentration is measured directly by a microwave cavity resonance method. The hydrogen atom concentration is taken from previous studies on such flames. The BO_2^- concentration is obtained from the difference between the K' concentration and the free electron measurement. The K' concentration is measured by an electrostatic probe.

By 2nd and 3rd law analysis of the data, 11 points read back from a plot, we obtain $\Delta H_f^{298}(\text{II}) = 27.5 \pm 4 \text{ kcal/mol}$ and $\Delta H_f^{298}(\text{III}) = 20 \pm 2 \text{ kcal/mol}$ with a drift of $-3.7 \pm 1.5 \text{ eu}$. The third law value yields $\Delta H_f^{298}(\text{BO}_2^-) = -166 \pm 6 \text{ kcal/mol}$ where the uncertainty includes possible errors in the functions. This corresponds to an electron affinity of BO_2^- equal to $98 \pm 6 \text{ kcal/mol}$ (4.25 eV).

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh (1) prediction for 16 valence electron XV_2 molecules.

The electronic states are taken from those for $\text{CO}_2(\text{g})$ (2), which is isoelectronic with $\text{BO}_2^-(\text{g})$. The electronic level 35000 cm⁻¹ and vibrational frequencies are estimated by comparison with the corresponding values for CO_2 , CO_2^+ , and BO_2 , and, the data of Vasco and Spb (3) on the BO_2^- ion in alkali halide lattices. The B-O bond distance in $\text{BO}_2^-(\text{g})$ is assumed to be smaller than the B-O bond in $\text{BO}_2(\text{g})$, because the $\text{BO}_2^-(\text{g})$ molecule has one more bonding electron than the $\text{BO}_2(\text{g})$ molecule. The moment of inertia is $8.302 \times 10^{-39} \text{ g cm}^2$. The enthalpy at 0°K is -2.30 kcal/mol .

References

1. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
2. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
3. A. Vasco and I. Spb, Czech. J. Phys. 17, 1110 (1967).

Boron Dioxide Uninegative Ion (BO₂⁻) (Ideal Gas) GFN = 42.81035

T, °K	C _p ^o	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
100							
200							
298	9.349	51.579	51.579	.000	-166.000	-164.862	120.687
300	9.371	51.580		.017	-166.010	-164.855	120.097
400	11.111	51.581	51.581	1.006	-166.106	-163.764	71.596
500	11.121	56.873	52.709	2.092	-167.116	-163.764	71.590
600	11.725	56.956	53.580	3.225	-167.700	-163.063	59.396
700	12.214	60.801	54.482	4.423	-168.292	-162.242	50.654
800	12.614	62.459	55.377	5.665	-168.890	-161.339	44.076
900	13.000	63.845	56.270	6.948	-169.494	-160.356	38.616
1000	13.212	65.132	57.091	8.252	-170.089	-159.312	34.616
1100	13.435	66.612	57.899	9.584	-170.697	-158.206	31.433
1200	13.620	67.790	58.675	10.938	-171.307	-157.044	28.602
1300	13.775	68.866	59.419	12.307	-171.925	-155.829	26.197
1400	13.912	69.842	60.122	13.694	-172.549	-154.566	24.137
1500	14.015	70.875	60.816	15.098	-173.181	-153.263	22.330
1600	14.108	71.783	61.474	16.494	-173.822	-151.912	20.750
1700	14.188	72.640	62.106	17.909	-174.471	-150.524	19.351
1800	14.257	73.453	62.718	19.331	-175.129	-149.096	18.103
1900	14.317	74.224	63.308	20.766	-175.796	-147.633	17.000
2000	14.369	74.962	63.884	22.195	-176.466	-146.133	15.969
2100	14.415	75.664	64.440	23.634	-177.144	-144.598	15.048
2200	14.455	76.335	64.936	25.077	-177.830	-143.033	14.209
2300	14.491	76.979	65.446	26.525	-178.519	-141.436	13.437
2400	14.522	77.596	65.970	27.978	-179.211	-139.806	12.727
2500	14.551	78.190	66.418	29.429	-180.000	-138.144	12.068
2600	14.576	78.761	66.882	30.885	-180.813	-136.450	11.443
2700	14.598	79.311	67.332	32.344	-181.671	-134.720	10.863
2800	14.617	79.843	67.769	33.805	-182.586	-132.950	10.327
2900	14.634	80.358	68.178	35.268	-183.558	-131.156	9.834
3000	14.654	80.852	68.606	36.732	-184.555	-129.325	9.383
3100	14.669	81.333	69.011	38.199	-185.572	-127.424	8.899
3200	14.683	81.799	69.403	39.666	-186.604	-125.452	8.441
3300	14.696	82.251	69.766	41.135	-187.650	-123.404	7.996
3400	14.708	82.689	70.106	42.605	-188.710	-121.376	7.561
3500	14.719	83.116	70.523	44.077	-189.774	-119.377	7.131
3600	14.728	83.531	70.879	45.549	-190.820	-117.402	6.706
3700	14.736	83.935	71.226	47.022	-191.843	-115.457	6.290
3800	14.743	84.326	71.558	48.496	-192.840	-113.546	5.882
3900	14.754	84.711	71.886	49.972	-193.820	-111.666	5.480
4000	14.762	85.095	72.223	51.446	-194.780	-109.819	5.072
4100	14.769	85.449	72.581	52.924	-195.724	-107.991	4.669
4200	14.776	85.805	72.953	54.401	-196.644	-106.186	4.270
4300	14.782	86.154	73.330	55.878	-197.540	-104.404	3.876
4400	14.786	86.493	73.716	57.358	-198.412	-102.644	3.486
4500	14.794	86.825	73.751	58.837	-199.260	-100.916	3.100
4600	14.799	87.151	74.036	60.316	-200.084	-99.220	2.717
4700	14.803	87.471	74.328	61.797	-200.894	-97.556	2.335
4800	14.807	87.781	74.598	63.277	-201.680	-95.924	1.956
4900	14.815	88.086	74.870	64.759	-202.445	-94.325	1.580
5000	14.820	88.386	75.137	66.240	-203.188	-92.756	1.207
5100	14.825	88.679	75.400	67.722	-203.911	-91.215	0.835
5200	14.830	88.965	75.658	69.205	-204.612	-89.700	0.464
5300	14.835	89.245	75.912	70.688	-205.290	-88.210	0.092
5400	14.840	89.527	76.162	72.172	-205.945	-86.744	-0.280
5500	14.845	89.799	76.407	73.654	-206.578	-85.304	-0.646
5600	14.850	90.067	76.649	75.141	-207.190	-83.886	-1.015
5700	14.855	90.330	76.886	76.625	-207.780	-82.490	-1.386
5800	14.860	90.588	77.119	78.108	-208.348	-81.116	-1.752
5900	14.866	90.842	77.351	79.596	-208.894	-79.764	-2.115
6000	14.871	91.092	77.578	81.085	-209.418	-78.436	-2.474

June 30, 1968; Dec. 31, 1968

Boron Monosulfide (BS)

(Ideal Gas) Mol. Wt. = 42.89

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f	ΔF _f	Log K _p
0	0.000	INFINITE	2.085	79.260	79.260	INFINITE
100	6.957	43.998	57.902	79.785	79.785	-165.411
200	6.988	48.825	52.295	80.008	71.485	-78.111
298	7.182	51.645	50.000	80.000	67.296	-49.327
300	7.188	51.690	51.645	79.998	67.216	-48.965
400	7.499	53.799	51.931	79.311	62.997	-34.418
500	7.799	55.506	52.480	78.726	58.985	-25.761
600	8.044	56.950	53.108	78.186	55.089	-20.065
700	8.231	58.170	53.799	77.686	51.300	-15.646
800	8.379	59.314	54.576	77.216	47.737	-11.646
900	8.491	60.308	55.481	76.774	44.398	-8.703
1000	8.579	61.207	55.559	76.358	41.277	-6.152
1100	8.649	62.029	56.111	75.968	38.389	-4.785
1200	8.703	62.782	56.640	75.602	35.734	-3.547
1300	8.753	63.482	57.136	75.257	33.317	-2.407
1400	8.792	64.133	57.613	74.932	31.148	-1.454
1500	8.825	64.740	58.068	74.627	29.217	-0.663
1600	8.854	65.311	58.503	74.342	27.514	-0.001
1700	8.879	65.846	58.919	74.076	26.029	0.342
1800	8.901	66.356	59.317	73.830	24.752	0.673
1900	8.920	66.838	59.702	73.599	23.677	0.984
2000	8.938	67.296	60.070	73.382	22.792	1.275
2100	8.954	67.733	60.425	73.179	22.000	1.548
2200	8.968	68.149	60.764	72.986	21.302	1.802
2300	8.982	68.546	61.096	72.802	20.697	2.037
2400	8.995	68.931	61.415	72.627	20.184	2.254
2500	9.007	69.299	61.723	72.462	19.761	2.454
2600	9.018	69.652	62.021	72.306	19.428	2.638
2700	9.029	69.991	62.300	72.159	19.184	2.807
2800	9.039	70.321	62.569	72.020	18.929	2.962
2900	9.048	70.638	62.822	71.886	18.664	3.104
3000	9.057	70.945	63.127	71.758	18.390	3.234
3100	9.066	71.242	63.384	71.636	18.107	3.354
3200	9.074	71.530	63.637	71.519	17.814	3.464
3300	9.081	71.811	63.886	71.406	17.511	3.564
3400	9.091	72.081	64.115	71.296	17.200	3.654
3500	9.099	72.345	64.346	71.190	16.889	3.734
3600	9.107	72.601	64.572	71.088	16.578	3.804
3700	9.112	72.851	64.792	70.989	16.267	3.864
3800	9.119	73.091	65.007	70.892	15.956	3.914
3900	9.129	73.331	65.218	70.797	15.644	3.954
4000	9.136	73.562	65.424	70.703	15.332	3.984
4100	9.143	73.788	65.625	70.611	15.020	3.994
4200	9.150	74.009	65.822	70.520	14.708	3.994
4300	9.157	74.225	66.015	70.430	14.396	3.984
4400	9.164	74.434	66.204	70.341	14.084	3.964
4500	9.170	74.640	66.389	70.253	13.772	3.934
4600	9.177	74.842	66.571	70.166	13.460	3.894
4700	9.183	75.039	66.749	70.080	13.148	3.844
4800	9.190	75.231	66.922	70.000	12.836	3.784
4900	9.196	75.422	67.095	69.916	12.524	3.714
5000	9.203	75.608	67.263	69.833	12.212	3.634
5100	9.209	75.791	67.429	69.750	11.900	3.544
5200	9.215	75.969	67.591	69.667	11.588	3.444
5300	9.222	76.145	67.751	69.584	11.276	3.334
5400	9.228	76.317	67.908	69.501	10.964	3.214
5500	9.234	76.487	68.062	69.418	10.652	3.084
5600	9.240	76.653	68.214	69.335	10.340	2.944
5700	9.246	76.817	68.364	69.252	10.028	2.794
5800	9.252	76.978	68.511	69.169	9.716	2.634
5900	9.259	77.134	68.656	69.086	9.404	2.464
6000	9.265	77.292	68.799	69.003	9.092	2.284

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1962; Mar. 31, 1965

BORON MONOSULFIDE (BS)

(IDEAL GAS)

MOL. WT. = 42.89

Ground State Configuration 2Σ $\Delta H_f^0 = 79 \pm 18 \text{ kcal. mole}^{-1}$ $S_{298.15}^0 = 51.645 \text{ cal. deg}^{-1} \text{ mole}^{-1}$ $\Delta H_f^0 = 80 \pm 18 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

 $\frac{E_1}{0}$ $\omega_e = 1188.23 \text{ cm}^{-1}$ $\omega_e x_e = 6.396 \text{ cm}^{-1}$ $\sigma = 1$ $B_e = 0.80596 \text{ cm}^{-1}$ $\alpha'_e = 0.00618 \text{ cm}^{-1}$ $r_e = 1.609 \text{ \AA}$

Heat of Formation.

The value of ΔH_f^0 298.15 for BS(g) was calculated based on $D_0^0 = 5.1 \pm 0.8 \text{ e.v.}$ for BS(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy.

The ground state configuration, ω_e , $\omega_e x_e$, B_e , α'_e and r_e were reported by P. B. Zeeman, Can. J. Phys. 29, 336 (1951). The molecular constants used for calculation were corrected to the average isotopic species. The moment of inertia is $3.4762 \times 10^{-39} \text{ g. cm}^2$.

T, °K.	C _p ^a	S ^b	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ^c	ΔF _f ^d	Log K _p
0						
100						
200						
298	7.092	8.300	8.300	.000	- 38.300	27.679
300						
350	7.150	8.344	8.300	.013	- 38.303	27.606
400	7.040	8.014	8.014	.863	- 38.395	20.821
500	10.926	13.071	9.279	1.866	- 38.424	16.624
600	11.608	15.128	10.086	3.025	- 38.463	13.824
700	11.160	16.568	11.793	5.414	- 38.472	11.823
800	12.160	18.193	13.733	8.116	- 38.519	10.321
900	12.306	20.002	17.626	6.638	- 38.586	9.151
1000	12.408	21.304	13.430	7.874	- 38.675	8.213
1100	12.474	22.490	14.201	9.118	- 38.789	7.444
1200	12.506	23.577	14.937	10.260	- 38.822	6.823
1300	12.506	24.568	15.637	11.300	- 38.868	6.232
1400	12.570	25.509	16.313	12.875	- 40.216	5.752
1500	12.602	26.378	16.955	14.134	- 40.418	5.333
1600	12.634	27.192	17.570	15.395	- 40.661	4.963
1700	12.658	27.954	18.164	16.581	- 40.942	4.634
1800	12.698	28.684	18.724	17.699	- 41.139	4.343
1900	12.730	29.371	19.266	19.200	- 41.412	4.079
2000	12.762	30.025	19.788	20.475	- 45.371	3.830
2100	12.794	30.649	20.290	21.752	- 45.609	3.594
2200	12.826	31.242	20.764	23.021	- 45.906	3.377
2300	12.858	31.815	21.242	24.318	- 46.088	3.179
2400	12.890	32.363	21.694	25.605	- 46.331	2.996
2500	12.922	32.890	22.132	26.866	- 51.961	2.817
2600	12.954	33.397	22.555	28.189	- 52.198	2.672
2700	12.986	33.884	22.964	29.464	- 52.424	2.547
2800	13.018	34.360	23.365	30.787	- 52.660	2.437
2900	13.050	34.817	23.752	32.050	- 52.887	2.185
3000	13.082	35.260	24.128	33.397	- 53.110	2.052
3100	13.114	35.690	24.494	34.704	- 53.331	1.927
3200	13.146	36.107	24.850	36.019	- 53.568	1.809
3300	13.178	36.512	25.198	37.336	- 53.791	1.698
3400	13.210	36.905	25.536	38.655	- 53.972	1.593
3500	13.242	37.289	25.867	39.978	- 54.179	1.494
3600	13.274	37.662	26.189	41.303	- 54.404	1.312
3700	13.306	38.024	26.504	42.624	- 54.647	1.154
3800	13.338	38.382	26.812	43.945	- 54.907	1.005
3900	13.370	38.729	27.113	45.300	- 55.178	.878
4000	13.402	39.067	27.408	46.639	- 55.461	.740

Mar. 31, 1963; June 30, 1965

TITANIUM MONOBORIDE (TiB)

(CRYSTAL)

MOL. WT. = 58.711

 $\Delta H_f^\circ O = \text{Unknown}$ $\Delta H_f^\circ 298.15 = -38.3 \pm 9 \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = [8.3 \pm 1.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $T_d = [2500]^\circ K.$

Heat of Formation.

P. O. Schuessel and O. C. Trulsen, *J. Phys. Chem.*, **66**, 1492 (1962) used a mass spectrometer with Knudsen cells to study the vaporization of the titanium-boron system and obtained $\Delta F_{2340}^\circ = -118.54 \text{ kcal. mole}^{-1}$ for the reaction $\text{TiB}(c) = \text{Ti}(g) + \text{B}(g)$. This corresponds to $\Delta F_{2340}^\circ(\text{TiB}(c)) = -33.266 \pm 9 \text{ kcal. mole}^{-1}$, where 4 kcal. mole⁻¹ of the uncertainty is due to the heat of sublimation of boron. When this is reduced to 298°K. one obtains $\Delta H_f^\circ 298(\text{TiB}(c)) = -38.3 \pm 9 \text{ kcal. mole}^{-1}$. This value implies a high stability for TiB. This is also indicated by the phase studies of H. Nowotny, P. Benesovsky, C. Bruckl and O. Schob, *Monatshefte für Chemie* **92**, 403 (1961).

Heat Capacity and Entropy.

The heat capacities from 298 to 1200°K. were estimated from that of TiB₂ by assuming the difference to be the same as that between CrB and CrB₂ as determined by R. Mezaki, E. W. Tillieux, D. W. Barnes and J. L. Margrave (Paper presented at the International Symposium on Nuclear Materials, Vienna, May 1962). A linear extrapolation was assumed above 1200°K.

The heat capacities above 298°K. were also estimated from the relationship $C_p(\text{Ti}) + C_p(2\text{B}) - C_p(\text{TiB}_2) = 2/3 [C_p(\text{Ti}) + C_p(\text{B}) - C_p(\text{TiB})]$. This estimation agreed with the above to 4% over the temperature range 400 to 1000°K.

$S_{298}^\circ(\text{TiB}, c) = 8.3 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ was calculated by the method of W. M. Latimer, *J. Am. Chem. Soc.*, **73**, 1480 (1951). Using JANAP $S_{298}^\circ(\text{TiB}_2, c) = 6.8 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ and Latimer's value of 9.8 e.u. for the entropy contribution of Ti, an entropy contribution of -1.5 e.u. per Boron atom was calculated.

Decomposition Data.

The phase diagram given in, "The Metallurgy of the Rarer Metals - No. 4 Titanium", by A. D. McQuillan and M. K. McQuillan, Academic Press, New York (1956) was used to estimate the decomposition temperature. This diagram shows the decomposition products are TiB₂ and Ti₃B. However, Nowotny et al. (loc. cit.) have shown Ti₃B to be nonexistent and so the decomposition products are not defined, probably a eutectic of TiB and TiB₂ is involved.

Boron, Diatomic (B₂)

(Ideal Gas) Mol. Wt. = 21.64

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	kcal. mole ⁻¹	ΔH° _f	ΔF°	Log K _p
0	-0.000	INFINITE	-2.094	193.490	193.490	193.490	INFINITE	INFINITE
100	6.958	40.545	54.536	1.399	104.135	104.135	415.510	415.510
200	7.023	45.378	48.885	.702	104.710	104.710	203.100	203.100
298	7.301	48.228	48.228	.000	195.000	195.000	181.457	181.457
300	7.307	48.273	48.273	.014	195.004	195.004	181.473	181.473
400	7.667	50.423	48.519	.762	195.108	195.108	182.124	182.124
500	7.976	52.170	49.080	1.545	195.065	195.065	172.237	172.237
600	8.212	53.646	49.721	2.355	194.925	194.925	167.684	167.684
800	8.521	54.926	50.375	3.186	194.724	194.724	163.159	163.159
900	8.623	57.065	51.030	3.847	194.566	194.566	158.743	158.743
1000	8.703	57.978	52.223	5.755	193.901	193.901	149.777	149.777
1100	8.767	58.811	52.784	6.629	193.567	193.567	145.379	145.379
1200	8.808	59.576	53.319	7.308	193.208	193.208	141.016	141.016
1300	8.836	60.282	53.813	7.823	192.815	192.815	136.690	136.690
1400	8.852	60.942	54.275	8.281	192.415	192.415	132.415	132.415
1500	8.859	61.557	54.775	10.173	191.989	191.989	128.102	128.102
1600	8.864	62.135	55.217	11.068	191.538	191.538	123.860	123.860
1800	8.891	62.678	55.641	11.966	191.066	191.066	119.644	119.644
2000	8.904	63.184	56.024	12.864	190.575	190.575	115.425	115.425
2100	8.907	63.682	56.495	13.769	189.975	189.975	111.205	111.205
2200	8.909	64.146	56.809	14.673	189.359	189.359	107.163	107.163
2300	8.912	64.588	57.109	15.580	188.636	188.636	103.057	103.057
2400	8.915	65.011	57.516	16.488	187.904	187.904	98.975	98.975
2500	8.917	65.416	57.911	17.310	187.164	187.164	94.885	94.885
2600	8.919	65.803	58.294	18.130	186.416	186.416	90.785	90.785
2700	8.921	66.176	58.647	18.923	185.687	185.687	86.673	86.673
2800	8.923	66.535	58.989	19.789	184.941	184.941	82.541	82.541
2900	8.925	66.881	59.321	20.138	184.188	184.188	78.391	78.391
3000	8.926	67.204	59.643	20.574	183.428	183.428	74.222	74.222
3100	8.927	67.517	59.957	21.054	182.654	182.654	69.946	69.946
3200	8.928	67.821	60.263	21.571	181.867	181.867	65.566	65.566
3300	8.929	68.116	60.561	22.027	181.067	181.067	61.081	61.081
3400	8.930	68.402	60.851	22.511	180.254	180.254	56.491	56.491
3500	8.931	68.679	61.132	22.991	179.428	179.428	51.796	51.796
3600	8.932	68.948	61.405	23.467	178.589	178.589	46.996	46.996
3700	8.933	69.210	61.670	23.939	177.736	177.736	42.091	42.091
3800	8.934	69.466	61.927	24.407	176.869	176.869	37.081	37.081
3900	8.935	69.717	62.177	24.872	175.988	175.988	31.966	31.966
4000	8.936	69.963	62.421	25.334	175.093	175.093	26.746	26.746
4100	8.937	70.204	62.659	25.792	174.184	174.184	21.521	21.521
4200	8.938	70.441	62.891	26.246	173.261	173.261	16.291	16.291
4300	8.939	70.674	63.117	26.696	172.325	172.325	11.056	11.056
4400	8.940	70.902	63.338	27.142	171.376	171.376	5.816	5.816
4500	8.941	71.126	63.554	27.584	170.414	170.414	0.571	0.571
4600	8.942	71.346	63.765	28.022	169.439	169.439	-4.679	-4.679
4700	8.943	71.562	63.971	28.456	168.451	168.451	-9.924	-9.924
4800	8.944	71.774	64.172	28.886	167.449	167.449	-15.164	-15.164
4900	8.945	71.982	64.368	29.312	166.434	166.434	-20.399	-20.399
5000	8.946	72.186	64.559	29.734	165.406	165.406	-25.629	-25.629
5100	8.947	72.386	64.745	30.152	164.364	164.364	-30.854	-30.854
5200	8.948	72.582	64.926	30.566	163.308	163.308	-36.074	-36.074
5300	8.949	72.774	65.102	30.976	162.238	162.238	-41.289	-41.289
5400	8.950	72.962	65.273	31.382	161.154	161.154	-46.499	-46.499
5500	8.951	73.146	65.439	31.784	160.056	160.056	-51.704	-51.704
5600	8.952	73.326	65.600	32.182	158.944	158.944	-56.904	-56.904
5700	8.953	73.502	65.756	32.576	157.818	157.818	-62.099	-62.099
5800	8.954	73.674	65.907	32.966	156.678	156.678	-67.289	-67.289
5900	8.955	73.842	66.053	33.352	155.524	155.524	-72.474	-72.474
6000	8.956	74.006	66.194	33.734	154.356	154.356	-77.654	-77.654

Dec. 31, 1960; Dec. 31, 1964

BORON, DIATOMIC (B₂)

MOL. WT. = 21.64

(IDEAL GAS)

Ground State Configuration Σ_g^-
 $\Delta H_f^0 = 193.5 \pm 6.4$ kcal. mole⁻¹
 $S_{298.15}^0 = 48.228$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^0 298.15 = 195.0 \pm 6.4$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

ϵ	ϵ , cm. ⁻¹	g_i
0	0	3
$\omega_e x_e = 9.59$ cm. ⁻¹		
$\omega_e = 1081.0$ cm. ⁻¹		
$B_e = 1.235$ cm. ⁻¹		
$\alpha_e = 0.0144$ cm. ⁻¹		
$r_e = 1.589$ Å		
$\sigma = 2$		

Heat of Formation.

The equilibrium vapor pressure of the reaction $B_2(g) \rightarrow B(g) + B(g)$ was determined by O. Verhaegen and J. Drowart, J. Chem. Phys. 37, 1367 (1962). Using the value, $P_{B_2}(g)/P_{B(g)} = 9 \times 10^{-5}$ at 2330°K. where P is partial pressure, the heat of reaction ($\Delta H_f^0 298.15$) was evaluated to be -62.2 ± 5.0 kcal. mole⁻¹. This leads to $\Delta H_f^0 298.15 = 195.0 \pm 6.4$ kcal. mole⁻¹ for B₂(g) or B₀ = 3.0 e.v. which is in excellent agreement with the value, B₀ = 3.0 ± 0.5 e.v. reported by A. O. Oeydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The value, B₀ = 3.6 e.v., estimated by O. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950, yields $\Delta H_f^0 298.15 = 181.6$ kcal. mole⁻¹ for B₂(g) which is not used.

Heat Capacity and Entropy.

Molecular and spectroscopic constants were obtained from O. Herzberg, loc. cit. and corrected to the average isotopic species. The principal moment of inertia (I) is 2.26779×10^{-39} g. cm.²

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	.000	INFINITE	-	4.455	-322.253	INFINITE	-322.253	INFINITE
100	12.01	59.799	94.638	-3.94	-320.376	700.148	-320.376	700.148
200	17.99	78.079	119.786	-1.98	-318.400	170.993	-318.400	170.993
298	21.932	78.079	121.466	.000	-315.562	231.287	-315.562	231.287
300	22.001	78.215	121.580	.001	-315.496	229.628	-315.496	229.628
400	25.297	85.016	128.985	2.412	-312.974	170.993	-312.974	170.993
500	27.839	90.946	130.797	5.075	-310.417	130.677	-310.417	130.677
600	29.782	96.202	132.935	7.960	-307.836	112.124	-307.836	112.124
700	31.266	100.909	134.672	11.016	-305.236	95.295	-305.236	95.295
800	32.407	105.162	136.101	14.202	-302.626	82.670	-302.626	82.670
900	33.294	109.032	137.489	17.489	-300.000	72.846	-300.000	72.846
1000	33.989	112.577	138.770	20.854	-297.362	64.985	-297.362	64.985
1100	34.543	115.844	139.969	24.282	-294.718	58.552	-294.718	58.552
1200	34.988	118.869	141.085	27.759	-292.058	53.168	-292.058	53.168
1300	35.350	121.685	142.125	31.277	-289.387	48.648	-289.387	48.648
1400	35.647	124.315	143.089	34.857	-286.699	44.754	-286.699	44.754
1500	35.895	126.784	143.980	38.405	-284.000	41.377	-284.000	41.377
1600	36.102	129.107	144.854	42.005	-281.198	38.408	-281.198	38.408
1700	36.278	131.301	145.663	45.624	-278.285	35.774	-278.285	35.774
1800	36.427	133.379	146.413	49.259	-275.361	33.432	-275.361	33.432
1900	36.555	135.352	147.105	52.909	-272.421	31.334	-272.421	31.334
2000	36.666	137.230	147.745	56.570	-269.470	29.445	-269.470	29.445
2100	36.763	139.021	148.335	60.242	-266.500	27.734	-266.500	27.734
2200	36.847	140.734	148.878	63.922	-263.522	26.177	-263.522	26.177
2300	36.922	142.373	149.377	67.611	-260.527	24.755	-260.527	24.755
2400	36.987	143.946	149.835	71.306	-257.514	23.446	-257.514	23.446
2500	37.046	145.457	150.255	75.008	-254.479	22.228	-254.479	22.228
2600	37.098	146.911	150.636	78.715	-251.400	21.081	-251.400	21.081
2700	37.144	148.312	150.973	82.427	-248.306	20.017	-248.306	20.017
2800	37.186	149.664	151.268	86.144	-245.193	18.942	-245.193	18.942
2900	37.224	150.969	151.521	89.864	-242.068	17.830	-242.068	17.830
3000	37.258	152.232	151.738	93.588	-238.938	16.742	-238.938	16.742
3100	37.289	153.454	151.915	97.316	-235.802	15.620	-235.802	15.620
3200	37.317	154.638	152.061	101.046	-232.652	14.509	-232.652	14.509
3300	37.343	155.787	152.183	104.779	-229.496	13.409	-229.496	13.409
3400	37.366	156.902	152.281	108.515	-226.327	12.324	-226.327	12.324
3500	37.388	157.986	152.351	112.252	-223.146	11.266	-223.146	11.266
3600	37.408	159.039	152.401	116.019	-219.952	10.231	-219.952	10.231
3700	37.426	160.064	152.434	119.734	-216.744	9.214	-216.744	9.214
3800	37.443	161.063	152.452	123.477	-213.522	8.214	-213.522	8.214
3900	37.459	162.035	152.458	127.223	-210.287	7.246	-210.287	7.246
4000	37.474	162.984	152.452	130.969	-207.037	6.306	-207.037	6.306
4100	37.487	163.909	152.434	134.717	-203.772	5.394	-203.772	5.394
4200	37.500	164.813	152.401	138.467	-200.492	4.509	-200.492	4.509
4300	37.511	165.695	152.352	142.217	-197.196	3.648	-197.196	3.648
4400	37.522	166.558	152.291	145.969	-193.884	2.814	-193.884	2.814
4500	37.533	167.401	152.210	149.722	-190.558	2.006	-190.558	2.006
4600	37.542	168.226	152.111	153.475	-187.218	1.234	-187.218	1.234
4700	37.551	169.034	152.000	157.230	-183.864	0.509	-183.864	0.509
4800	37.560	169.825	151.878	160.986	-180.496	0.830	-180.496	0.830
4900	37.568	170.599	151.748	164.742	-177.114	0.114	-177.114	0.114
5000	37.575	171.358	151.608	168.499	-173.718	0.014	-173.718	0.014
5100	37.582	172.102	151.458	172.257	-170.308	0.014	-170.308	0.014
5200	37.589	172.832	151.298	176.015	-166.884	0.014	-166.884	0.014
5300	37.595	173.548	151.128	179.775	-163.446	0.014	-163.446	0.014
5400	37.601	174.251	150.948	183.534	-159.994	0.014	-159.994	0.014
5500	37.607	174.941	150.758	187.295	-156.528	0.014	-156.528	0.014
5600	37.612	175.619	150.558	191.056	-153.048	0.014	-153.048	0.014
5700	37.617	176.284	150.351	194.817	-149.554	0.014	-149.554	0.014
5800	37.622	176.939	150.131	198.579	-146.046	0.014	-146.046	0.014
5900	37.626	177.584	149.898	202.341	-142.524	0.014	-142.524	0.014
6000	37.631	178.214	149.653	206.104	-138.988	0.014	-138.988	0.014

Dec. 31, 1962; June 30, 1965

Point Group [C_{2h}]
S_{298.15} = [78.079] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight (1)

Vibrational Frequencies and Degeneracies		
$\bar{\nu}$, cm. ⁻¹	$\bar{\nu}$, cm. ⁻¹	ν , cm. ⁻¹
[2000] (1)	[1050] (1)	[400] (1)
[1600] (1)	[650] (1)	[350] (1)
[1200] (1)	[600] (1)	[200] (1)
[1200] (1)	[600] (1)	[150] (1)
[1050] (1)	[500] (1)	[120] (1)

Bond Distance: Be-O = [1.63] Å O-B = [1.34] Å B-O = [1.20] Å
Bond Angle: O-B-O = [180°] O-Be-O = [180°] B-O-Be = [95°]
Product of Moments of Inertia: I_AI_BI_C = 5.3801 X 10⁻¹¹³ g.³ cm.⁶

Heat of Formation.
The heat of formation was obtained from mass spectrometric studies; the following reactions at 1500°K. were reported by P. E. Blackburn and A. Eichler, Interim Technical Report No. 1, March 1965:

1. B₂O₃(l) → B₂O₃(g) ΔH₁ = 92.226 kcal/mole
2. 1/3 Be₃P₂O₆(c) + 2/3 B₂O₃(l) → Be(BO₂)₂(g) ΔH₂ = 118 ± 2 kcal/mole
3. Be₃P₂O₆(c) → 3BeO(c) + B₂O₃(g) ΔH₃ = 112 ± 1 kcal/mole
4. Be₃P₂O₆(c) → 2BeO(c) + Be(BO₂)₂(g) ΔH₄ = 137 ± 3 kcal/mole
5. 3BeO(c) + B₂O₃(l) → Be₃P₂O₆(c) ΔH₅ = -23 kcal/mole
6. BeO(c) + B₂O₃(g) → Be(BO₂)₂(g) ΔH₆ = 22 kcal/mole

The value of ΔH₁ was obtained from JANAP values for B₂O₃(l) and B₂O₃(g). The values for ΔH₂, ΔH₃ and ΔH₄ were obtained from P. E. Blackburn and A. Eichler loc. cit. The value for ΔH₅ was obtained by taking the average of ΔH₂-ΔH₁ + 1/3 ΔH₃ = -19.774 kcal/mole, and ΔH₅ = 3/2 (ΔH₂-ΔH₄) = -28.5 kcal/mole. The ΔH₆ value was obtained by taking the average of ΔH₆ = ΔH₄-ΔH₃ = 25 kcal/mole and ΔH₆ = ΔH₂-ΔH₁ + 1/3 ΔH₃ = 18.107 kcal/mole. The ΔH_f 298.15 of BeB₂O₄ was calculated from reaction 6 with auxiliary JANAP values.

Heat Capacity and Entropy.

The vibrational frequencies estimated by comparison with B₂O₃, were adjusted to obtain an S₂₉₈ = 127 obtained in a manner analogous with ΔH_f from the report of P. E. Blackburn and A. Eichler loc. cit. The frequencies listed are not in point group order. All other molecular constants were estimated by comparison with related boron oxide molecules. The individual moments of inertia are I_A = 8.5561 X 10⁻³⁹ g.² cm.², I_B = 75.1345 X 10⁻³⁹ g.² cm.² and I_C = 83.6903 X 10⁻³⁹ g.² cm.²

(1)
 (2)
 (3)
 (4)
 (5)
 (6)

(continued)

2025 (2025)

.....

[illegible][illegible][illegible][illegible][illegible]

Boron Dichloride, Dimeric (B₂Cl₄)
(Ideal Gas) Mol. Wt. = 163.468

BORON DICHLORIDE, DIMERIC (B₂Cl₄) (IDEAL GAS)

MOL. WT. = 163.468

Point Group D_{2d}
S_{298.15} = 85.767 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 1
ΔF_f⁰ = Unknown
ΔF_f⁰ 298.15 = -116.9 ± 1.2 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
113(1)	Rotation	917(2)
401(1)	730(1)	617(2)
225(1)	291(1)	180(2)

Bond Distances: B-Cl = 1.73 ± 0.02 Å B-B = 1.75 ± 0.01 Å

Bond Angle: Cl-B-Cl = 120 ± 2°

Dihedral angle between two BCl₂ planes = 90°Product of the Moments of Inertia: I_AI_BI_C = 5.33449 X 10⁻¹¹² g.³ cm.⁶

Heat of Formation

S. R. Gunn, L. G. Green and A. I. Von Egidy, J. Phys. Chem. 63, 1787 (1959) determined the enthalpy change (ΔH_f⁰) of the reaction B₂Cl₄(l) + Cl₂(g) = 2BCl₃(g). From the value, ΔH_f⁰ 298.15 = -87.3 ± 0.6 kcal. mole⁻¹, the heat of formation for B₂Cl₄(l) was calculated as -125.32 ± 1.20 kcal. mole⁻¹. Based on ΔH_f⁰ 318.7 = 8.029 kcal. mole⁻¹ reported by G. Urry, T. Sarti, R. E. Moore and H. I. Schlesinger, J. Am. Chem. Soc. 76, 5293 (1954), the heat of formation for B₂Cl₄(g) was derived to be -116.9 ± 1.2 kcal. mole⁻¹.

Heat Capacity and Entropy

The vibrational frequencies, molecular structure and constants were taken from D. E. Mann and L. Pano, J. Chem. Phys. 25, 1665 (1957). The barrier restricting internal rotation about the B-B single bond is fixed at 1.53 ± 0.60 kcal. mole⁻¹ obtained from E. A. Mason and M. Kreevy, J. Am. Chem. Soc. 77, 5608 (1955). The three principal moments of inertia are: I_A = 1.00465 X 10⁻³⁷, I_B = 5.28520 X 10⁻³⁸ and I_C = 1.00465 X 10⁻³⁷ g. cm.². The reduced moment of inertia for BCl₂ top is I_r = 1.3213 X 10⁻³⁸ g. cm.².

Dec. 31, 1963; Dec. 31, 1964

T. °K.	C _p	S ⁰	-(F ⁰ -H ₂₉₈ °)/T	H ⁰ -H ₂₉₈ °	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	14.151	65.880	103.472	-3.758	-117.100	-114.635	250.523
100	19.277	77.397	87.739	-2.069	-117.013	-112.194	122.594
200	22.667	85.767	85.767	0.000	-116.900	-109.859	80.525
300	22.710	85.907	85.767	0.042	-116.898	-109.815	76.997
400	25.048	92.780	86.482	2.437	-116.807	-107.469	58.715
500	26.603	98.544	88.469	5.024	-116.752	-105.140	45.955
600	27.659	103.494	90.586	7.740	-116.725	-102.820	37.451
700	28.270	107.628	92.478	10.000	-116.713	-100.513	31.823
800	28.670	111.628	94.478	12.000	-116.711	-98.214	27.823
900	29.217	115.049	96.432	14.305	-116.721	-95.874	23.280
1000	29.511	118.144	98.491	16.242	-116.742	-93.557	20.446
1100	29.684	120.964	100.781	22.202	-116.784	-91.238	18.126
1200	29.778	123.484	103.281	28.149	-116.827	-88.962	16.156
1300	29.878	125.944	105.781	34.173	-116.870	-86.683	14.423
1400	30.009	128.174	108.068	31.173	-117.025	-84.243	13.112
1500	30.203	130.254	110.042	34.168	-117.144	-81.900	11.932
1600	30.263	132.204	108.986	37.212	-117.282	-79.543	10.865
1700	30.259	134.056	107.796	40.275	-117.416	-77.177	9.902
1800	30.370	135.774	111.734	43.275	-117.610	-74.806	9.042
1900	30.417	137.418	113.642	46.315	-117.800	-72.418	8.330
2000	30.460	138.976	114.500	49.359	-118.013	-70.023	7.651
2100	30.485	140.464	115.411	52.406	-118.226	-67.620	7.027
2200	30.508	141.884	116.272	55.456	-118.456	-65.266	6.456
2300	30.530	143.242	117.084	58.507	-118.689	-62.960	5.965
2400	30.551	144.542	117.844	61.561	-118.937	-60.743	5.495
2500	30.571	145.790	119.493	64.618	-120.070	-57.680	5.042
2600	30.589	146.980	120.945	67.676	-120.222	-54.783	4.604
2700	30.604	148.114	122.095	70.735	-120.372	-51.876	4.189
2800	30.622	149.232	123.001	73.797	-120.739	-48.960	3.821
2900	30.637	150.332	123.848	76.860	-131.002	-46.032	3.469
3000	30.650	151.371	124.730	79.924	-131.270	-43.103	3.140
3100	30.658	152.374	125.655	82.986	-131.543	-40.161	2.831
3200	30.666	153.340	126.607	86.056	-131.820	-37.201	2.541
3300	30.673	154.293	127.284	89.123	-132.103	-34.242	2.268
3400	30.680	155.209	128.084	92.190	-132.390	-31.270	2.010
3500	30.687	156.098	128.882	95.259	-132.681	-28.299	1.767
3600	30.693	156.964	129.649	98.328	-132.980	-25.308	1.536
3700	30.699	157.804	130.389	101.397	-133.283	-22.312	1.312
3800	30.705	158.624	131.111	104.467	-133.589	-19.311	1.111
3900	30.710	159.421	131.847	107.538	-133.900	-16.303	0.914
4000	30.715	160.190	132.556	110.609	-134.215	-13.295	0.735
4100	30.710	160.957	133.236	113.681	-134.531	-10.281	0.566
4200	30.722	161.697	133.890	116.753	-134.853	-7.262	0.400
4300	30.726	162.420	134.524	119.823	-135.183	-4.248	0.246
4400	30.729	163.124	135.195	122.898	-135.524	-1.238	0.100
4500	30.733	163.817	135.823	125.971	-135.877	1.783	0.000
4600	30.736	164.493	136.449	129.045	-136.244	4.783	0.100
4700	30.739	165.154	137.064	132.118	-136.624	7.783	0.200
4800	30.742	165.801	137.674	135.192	-137.014	10.783	0.300
4900	30.744	166.435	138.271	138.267	-137.415	13.783	0.400
5000	30.747	167.056	138.868	141.341	-137.831	16.783	0.500
5100	30.749	167.665	139.448	144.414	-138.260	19.783	0.600
5200	30.752	168.262	140.024	147.481	-138.701	22.783	0.700
5300	30.754	168.848	140.599	150.557	-139.153	25.783	0.800
5400	30.756	169.423	141.171	153.642	-139.618	28.783	0.900
5500	30.758	169.987	141.738	156.728	-140.097	31.783	1.000
5600	30.760	170.541	142.300	159.814	-140.587	34.783	1.100
5700	30.762	171.085	142.857	162.904	-141.087	37.783	1.200
5800	30.763	171.620	143.409	166.004	-141.597	40.783	1.300
5900	30.765	172.144	143.958	169.118	-142.118	43.783	1.400
6000	30.766	172.663	144.500	172.239	-142.643	46.783	1.500

Boron Difluoride, Dimeric (B₂F₄)
(Ideal Gas) Mol. Wt. = 97.64

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg ⁻¹	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0							
100	10.384	60.935	89.691	-2.866	-341.694	-339.632	742.229
200	14.856	99.483	77.666	-1.637	-341.995	-337.438	568.718
298	16.376	76.093	76.093	-1.000	-342.200	-335.668	
300	16.436	76.207	76.093	-0.934	-342.204	-335.119	244.122
400	21.204	81.907	76.852	2.022	-342.400	-332.726	181.784
500	23.313	86.876	78.370	4.253	-342.609	-330.285	144.361
600	24.896	91.274	80.142	6.463	-342.809	-327.800	119.395
700	26.077	95.205	82.035	8.519	-342.991	-325.280	104.104
800	26.964	98.747	83.906	11.673	-343.159	-322.744	88.105
900	27.638	101.964	85.737	14.605	-343.311	-320.183	77.747
1000	28.137	104.904	87.508	17.395	-343.461	-317.605	69.409
1100	28.593	107.607	89.214	20.222	-343.616	-315.012	62.584
1200	28.886	110.107	90.863	23.102	-343.771	-312.407	56.077
1300	29.115	112.430	92.424	26.007	-343.947	-309.783	50.077
1400	29.337	114.598	93.931	28.933	-344.129	-307.147	44.594
1500	29.531	116.659	95.378	31.877	-344.329	-304.499	44.363
1600	29.676	118.540	96.766	34.838	-344.544	-301.837	41.227
1700	29.798	120.343	98.100	37.812	-344.776	-299.160	38.458
1800	29.902	122.049	99.384	40.797	-345.025	-296.474	35.995
1900	29.990	123.668	100.620	43.792	-345.284	-293.768	33.789
2000	30.066	125.208	101.811	46.795	-345.553	-291.045	31.802
2100	30.132	126.677	102.961	49.805	-345.833	-288.317	30.004
2200	30.190	128.080	104.071	52.821	-346.123	-285.570	28.407
2300	30.241	129.423	105.144	55.842	-346.422	-282.811	26.872
2400	30.285	130.711	106.182	58.869	-346.731	-280.038	25.500
2500	30.325	131.948	107.189	61.899	-347.045	-277.255	24.217
2600	30.362	133.138	108.164	64.924	-347.364	-274.458	23.014
2700	30.392	134.285	109.109	67.937	-347.688	-271.646	21.892
2800	30.418	135.391	110.029	71.012	-348.017	-268.820	20.852
2900	30.445	136.458	110.922	74.055	-348.350	-265.979	19.895
3000	30.468	137.491	111.791	77.101	-348.687	-263.132	18.993
3100	30.489	138.490	112.636	80.149	-349.029	-260.279	18.148
3200	30.508	139.450	113.456	83.199	-349.376	-257.418	17.360
3300	30.526	140.398	114.251	86.240	-349.727	-254.549	16.610
3400	30.541	141.309	115.043	89.304	-350.080	-251.672	15.908
3500	30.556	142.195	115.807	92.359	-350.435	-248.788	15.245
3600	30.569	143.056	116.552	95.415	-350.793	-245.896	14.618
3700	30.582	143.893	117.276	98.471	-351.155	-242.998	14.025
3800	30.593	144.709	117.991	101.531	-351.522	-240.098	13.462
3900	30.603	145.504	118.686	104.591	-351.892	-237.192	12.929
4000	30.613	146.279	119.366	107.652	-352.265	-234.282	12.416
4100	30.622	147.035	120.032	110.714	-352.641	-231.366	11.930
4200	30.631	147.773	120.682	113.777	-353.019	-228.444	11.480
4300	30.638	148.494	121.322	116.840	-353.400	-225.516	11.060
4400	30.646	149.198	121.947	119.904	-353.783	-222.582	10.670
4500	30.653	149.887	122.561	122.969	-354.168	-219.642	10.300
4600	30.659	150.561	123.162	126.034	-354.555	-216.696	9.950
4700	30.665	151.220	123.752	129.100	-354.944	-213.746	9.620
4800	30.671	151.866	124.331	132.167	-355.335	-210.792	9.300
4900	30.676	152.498	124.899	135.235	-355.728	-207.834	8.990
5000	30.681	153.118	125.458	138.303	-356.122	-204.872	8.690
5100	30.686	153.724	126.006	141.371	-356.517	-201.906	8.400
5200	30.690	154.322	126.545	144.440	-356.913	-198.936	8.120
5300	30.694	154.906	127.074	147.509	-357.310	-195.962	7.850
5400	30.698	155.480	127.595	150.578	-357.708	-192.984	7.590
5500	30.702	156.043	128.107	153.648	-358.107	-189.999	7.340
5600	30.705	156.597	128.611	156.710	-358.507	-186.999	7.090
5700	30.709	157.140	129.107	159.769	-358.908	-183.994	6.850
5800	30.712	157.674	129.595	162.861	-359.310	-180.984	6.620
5900	30.715	158.199	130.075	165.942	-359.713	-177.969	6.400
6000	30.718	158.716	130.548	169.004	-360.117	-174.949	6.190

Point Group V_d
ΔH_f° 0 = Unknown
ΔH_f° 298.15 = -342.2 ± 1.0 kcal. mole⁻¹
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies		
ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
1380 (1)	1155 (1)	325 (1)
[630] (1)	542 (1)	1378 (1)
[304] (1)	1386 (1)	662 (1)
Rotation	857 (1)	325 (1)

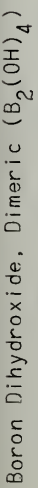
Bond Distance: B-B = 1.67 Å B-P = 1.32 Å
Bond Angle: P-B-P = 120° P-B-B = 120°
Product of the Moments of Inertia: I_AI_BI_C = 2.50147 × 10⁻¹¹³ g.³ cm.⁶

Heat of Formation

The heat of formation was calculated based on the value, ΔH_f° = -82.0 ± 1.0 kcal. mole⁻¹ for the reaction B₂F₄(g) + Cl₂(g) = 0.92 BP₃(g) + 0.46 BP₂Cl(g) + 0.32 BP₂Cl₂(g) + 0.30 BP₂Cl₃(g) reported by S. R. Gunn and L. G. Green, J. Phys. Chem. 65, 178 (1961).

Heat Capacity and Entropy

The molecular and spectroscopic constants were obtained from J. N. Gayles and J. Self, J. Chem. Phys. 40, 3530 (1964). The vibrational frequencies were corrected to the average isotopic species. The molecular configuration was reported to be staggered, analogous to that observed for BCl₃(g). The angle between two B-P₂ planes is approximately 90°. The thermodynamic functions were evaluated based on an assumption that there is free rotation at B-B bond between the two BP₂ rotating tops. The internal moment of inertia is 4.12218 × 10⁻³⁹ g. cm.². The three principal moments of inertia are: I_A = 3.89497 × 10⁻³⁸ g. cm.², I_B = 1.64887 × 10⁻³⁸ g. cm.², and I_C = 3.89497 × 10⁻³⁸ g. cm.². The reduced moment of inertia for BP₂ top is I_r = 4.12218 × 10⁻³⁹ g. cm.².



Mol. Wt. = 89.65148

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0							
100	27.770	30.000	30.000	0.000	- 337.100	- 297.377	217.983
200							
298							
300	27.910	30.172	30.001	-0.052	- 337.110	- 297.132	216.460
400	34.210	39.097	31.175	3.169	- 337.447	- 283.744	155.031
500	39.140	47.272	33.589	6.842	- 337.460	- 270.311	118.153
600	43.430	54.787	36.505	10.276	- 337.186	- 256.902	93.577
700	47.090	61.773	39.622	15.505	- 336.679	- 243.519	65.014
800	50.270	68.278	42.742	22.542	- 335.894	- 231.175	52.737
900	52.930	74.354	45.974	29.542	- 334.894	- 217.175	44.618
1000	55.290	80.056	49.100	36.056	- 333.740	- 204.154	
1100	57.360	85.425	52.160	36.591	- 332.443	- 191.259	38.000
1200	59.140	90.284	55.150	42.418	- 331.018	- 178.495	27.890
1300	60.780	94.729	58.121	48.461	- 329.461	- 165.861	23.932
1400	61.900	98.832	60.874	54.241	- 327.895	- 153.304	
1500	62.860	104.137	63.616	60.781	- 326.251	- 140.892	20.528

BORON DIHYDROXIDE, DIMERIC (B₂(OH)₄)
(CRYSTAL)

MOL. WT. = 89.65148

$\Delta H_f^\circ 0$ = Unknown
 $\Delta H_f^\circ 298.15 = -337.1 \pm 2.0$ kcal. mole⁻¹
 $S_{298.15}^\circ = [30 \pm 1]$ cal. deg.⁻¹ mole⁻¹
 T_m = Unknown
 ΔH_m° = Unknown
 $\Delta H_g^\circ 298.15 = [30.1]$ kcal. mole⁻¹

Heat of Formation.

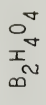
The enthalpy change, $\Delta H_f^\circ 298.15 = -91.3 \pm 1.0$ kcal. mole⁻¹, for the reaction $B_2(OH)_4(c) + (m + 2) \cdot AgNO_3(aq.) + (n + 2) \cdot H_2O(l) = 2Ag(c) + \{2m_3BO_3 + 2HNO_3 + mAgNO_3\} \cdot nH_2O(aq.)$ was determined calorimetrically by A. Finch, P. J. Gardner and I. J. Hyams, Trans. Faraday Soc. 61, 649 (1965). The heat of formation of $B_2(OH)_4(c)$ was reported to be -335.1 kcal. mole⁻¹. This value was corrected to be -337.1 $\pm$ 2 kcal. mole⁻¹ by use of more recent data on the $\Delta H_f^\circ 298.15$ values used for calculation.

Heat Capacity and Entropy.

The heat capacity for $B_2(OH)_4(c)$ was estimated by comparison with those for $B(OH)_3(c)$. The value of $S_{298.15}^\circ$ was calculated based on 3 cal. deg.⁻¹ mole⁻¹ per atom for $B_2(OH)_4(c)$, which was obtained from the corresponding values for $HBO_2(c)$ and $B(OH)_3(c)$.

Heat of Sublimation.

The value, $\Delta H_g^\circ 298.15$, was calculated as the difference between $\Delta H_f^\circ 298.15$ for $B_2(OH)_4(g)$ and $B_2(OH)_4(c)$.





Boron Dihydroxide, Dimeric ($\text{B}_2(\text{OH})_4$)
(Ideal Gas) Mol. Wt. = 89.65148

T, °K.	C_p°	S°	$\text{cal. mole}^{-1}\text{deg.}^{-1}$	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0								
100	12.326	64.168	101.205	-	3.704	- 304.878	- 288.086	651.489
200	18.820	74.732	85.444	- 2.142	- 306.042	- 280.852	- 260.852	317.829
298	24.721	83.369	83.369	+0.000	- 307.000	- 280.852	- 207.963	207.963
300	24.824	83.222	83.369	+0.046	- 307.016	- 283.043	- 206.106	206.106
400	29.857	91.360	84.407	- 2.789	- 307.727	- 274.937	- 150.218	150.218
500	33.765	98.482	86.523	- 5.972	- 308.223	- 266.679	- 116.565	116.565
600	36.761	104.015	89.061	- 9.512	- 308.550	- 258.337	- 94.099	94.099
700	39.115	108.765	91.360	- 13.217	- 308.632	- 241.546	- 69.987	69.987
800	41.023	112.117	94.467	- 17.320	- 308.632	- 223.134	- 56.613	56.613
900	42.614	121.043	97.149	- 21.504	- 308.632	- 224.724	- 46.113	46.113
1000	43.863	125.605	99.770	- 25.835	- 308.761	- 216.327	- 42.890	42.890
1100	44.120	129.850	102.314	- 30.291	- 308.643	- 207.950	- 33.551	33.551
1200	44.119	133.820	104.821	- 34.864	- 308.296	- 194.570	- 28.645	28.645
1300	43.986	137.547	107.154	- 39.510	- 308.089	- 181.213	- 23.942	23.942
1400	43.741	141.057	109.452	- 44.247	- 307.877	- 167.873	- 19.170	19.170
1500	43.400	144.374	111.671	- 49.055	- 307.664	- 154.547	- 14.365	14.365
1600	42.977	147.516	113.814	- 53.924	- 307.239	- 141.216	- 9.657	9.657
1700	42.481	150.500	115.884	- 58.844	- 306.636	- 127.873	- 4.916	4.916
1800	41.931	153.342	117.887	- 63.819	- 305.871	- 114.504	- 0.151	0.151
1900	41.336	156.053	119.825	- 68.832	- 304.966	- 101.070	4.380	4.380
2000	40.706	158.643	121.702	- 73.883	- 303.930	- 87.600	8.732	8.732
2100	40.088	161.123	123.520	- 78.946	- 302.766	- 74.094	13.051	13.051
2200	39.467	163.500	125.280	- 84.029	- 301.482	- 60.566	17.370	17.370
2300	38.841	165.786	126.996	- 89.210	- 300.091	- 47.004	21.684	21.684
2400	38.210	167.984	128.658	- 94.382	- 298.596	- 33.416	25.990	25.990
2500	37.574	170.100	130.274	- 99.566	- 297.000	- 19.830	30.296	30.296
2600	36.931	172.141	131.845	- 104.760	- 295.307	- 6.244	34.600	34.600
2700	36.289	174.111	133.375	- 109.960	- 293.516	7.353	38.904	38.904
2800	35.649	176.016	134.863	- 115.227	- 291.627	13.606	43.208	43.208
2900	35.007	177.858	136.314	- 120.477	- 289.643	19.860	47.512	47.512
3000	34.364	179.643	137.729	- 125.741	- 287.566	26.114	51.816	51.816
3100	33.719	181.373	139.109	- 131.037	- 285.396	32.368	56.120	56.120
3200	33.074	183.051	140.504	- 136.304	- 283.130	38.622	60.424	60.424
3300	32.429	184.681	141.772	- 141.560	- 280.770	44.876	64.728	64.728
3400	31.784	186.265	143.057	- 146.806	- 278.316	51.130	69.032	69.032
3500	31.139	187.805	144.314	- 152.021	- 275.766	57.384	73.336	73.336
3600	30.494	189.305	145.543	- 157.243	- 273.120	63.638	77.640	77.640
3700	29.849	190.765	146.743	- 162.467	- 270.379	69.892	81.944	81.944
3800	29.204	192.188	147.923	- 167.692	- 267.543	76.146	86.248	86.248
3900	28.559	193.576	149.075	- 172.917	- 264.612	82.400	90.552	90.552
4000	27.914	194.930	150.205	- 178.142	- 261.586	88.654	94.856	94.856
4100	27.269	196.252	151.312	- 183.367	- 258.466	94.908	99.160	99.160
4200	26.624	197.543	152.397	- 188.592	- 255.252	101.162	103.464	103.464
4300	25.979	198.805	153.462	- 193.817	- 251.944	107.416	107.768	107.768
4400	25.334	200.039	154.507	- 199.042	- 248.542	113.670	112.072	112.072
4500	24.689	201.246	155.532	- 204.267	- 245.046	119.924	116.376	116.376
4600	24.044	202.428	156.530	- 209.492	- 241.456	126.178	120.680	120.680
4700	23.399	203.585	157.527	- 214.717	- 237.770	132.432	124.984	124.984
4800	22.754	204.718	158.499	- 219.942	- 234.000	138.686	129.288	129.288
4900	22.109	205.829	159.453	- 225.167	- 230.120	144.940	133.592	133.592
5000	21.464	206.917	160.392	- 230.392	- 226.156	151.194	137.896	137.896
5100	20.819	207.985	161.314	- 235.617	- 222.100	157.448	142.200	142.200
5200	20.174	209.033	162.222	- 240.842	- 217.770	163.702	146.504	146.504
5300	19.529	210.061	163.115	- 246.067	- 213.340	169.956	150.808	150.808
5400	18.884	211.070	163.994	- 251.292	- 208.810	176.208	155.112	155.112
5500	18.239	212.061	164.859	- 256.517	- 204.120	182.460	159.416	159.416
5600	17.594	213.035	165.710	- 261.742	- 199.370	188.712	163.720	163.720
5700	16.949	213.992	166.549	- 266.967	- 194.570	194.964	168.024	168.024
5800	16.304	214.933	167.375	- 272.192	- 189.720	201.216	172.328	172.328
5900	15.659	215.857	168.189	- 277.417	- 184.830	207.468	176.632	176.632
6000	15.014	216.767	168.991	- 282.642	- 179.900	213.720	180.936	180.936

Ref. 31, 1966

BORON DIHYDROXIDE, DIMERIC ($\text{B}_2(\text{OH})_4$) (IDEAL GAS) MOL. WT. = 89.65148

Point Group $[C_2]$
 $\Delta H_f^\circ = 0$ = Unknown
 $\Delta H_f^\circ = 298.15$ = $[-307 \pm 5]$ kcal. mole $^{-1}$
 $S^\circ_{298.15} = [83.37]$ cal. deg. $^{-1}$ mole $^{-1}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. $^{-1}$	ω , cm. $^{-1}$	ω , cm. $^{-1}$	Deg.
[1380](1)	[1386](1)	[824](2)	1
[650](1)	[657](1)	[209](2)	1
[304](1)	[325](1)	[3200](4)	1
[1378](1)	[1378](1)	[1200](2)	1
[862](1)	[862](1)	[880](2)	1

Rotation (1) B-H = $[1.36]$ Å B-H = $[1.06]$ Å

Bond Distances: B-B = $[1.67]$ Å O-B-O = $[120]^\circ$ O-B-B = $[120]^\circ$ O = 2

Bond Angles: H-O-B = $[114]^\circ$ O-B-O = $[120]^\circ$ O-B-B = $[120]^\circ$

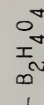
Product of the Moments of Inertia: $I_A I_B I_C = [2.2995 \times 10^{-41}] \text{g.}^3 \text{cm.}^6$

Heat of Formation.

The heat of formation (ΔH_f° 298.15) for $\text{B}_2(\text{OH})_4(\text{g})$ was calculated, using bond energies, $D(\text{B-OH}) = 132$ and $D(\text{B-B}) = 79$ kcal. mole $^{-1}$. The bond energy $D(\text{B-OH})$ was taken from that in $\text{B}(\text{OH})_3(\text{g})$ and $D(\text{B-B})$ was estimated by comparison with that in $\text{B}_2\text{P}_4(\text{g})$.

Heat Capacity and Entropy.

The molecular structure was assumed to be the same as that for $\text{B}_2\text{P}_4(\text{g})$, i.e. the two $\text{B}(\text{OH})_2$ units have staggered configuration, and free rotation about B-B bond. The B-B bond distance was taken as that in B_2P_4 molecule. Those for B-O and B-H bond and bond angles were adopted from H_2BO_3 molecule. Eleven vibrational frequencies were assumed to be the same as those for $\text{B}_2\text{P}_4(\text{g})$. In addition to these were added four OH torsion frequencies, 824(2) and 209(2), four OH stretching, 3200(4), and four B-O-H bending frequencies, 1200(2) and 880(2). The thermodynamic functions were evaluated based on a molecular model having free internal rotation of two $\text{B}(\text{OH})_2$ groups about B-B bond. The reduced moment of inertia for the rotation is calculated as $4.10146 \times 10^{-39} \text{g.}^2 \text{cm.}^2$. The three principal moments of inertia are: $I_A = 1.64037 \times 10^{-38}$ and $I_B = I_C = 3.7441 \times 10^{-38} \text{g.}^2 \text{cm.}^2$.





(IDEAL GAS)

DIBORANE (B₂H₆)

MOL. WT. = 27.668

Diborane (B₂H₆)
(Ideal Gas) Mol. Wt. = 27.668

Point Group D_{2h}
S_{298.15} = 55.709 cal. deg. mole⁻¹
Ground State Quantum Weight = (1)
ΔH_f⁰ = 13.6 ± 4.0 kcal. mole⁻¹
ΔH_f^{298.15} = 9.8 ± 4.0 kcal. mole⁻¹

T, °K.	C _p	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.268	44.554	6.485	2.904	13.552	11.522
200	10.397	50.934	5.686	2.103	12.053	10.438
298	13.886	55.709	5.000	1.185	9.800	8.958
300	13.957	55.795	5.000	1.026	9.777	8.938
400	17.075	60.673	3.613	0.563	8.636	7.454
500	21.196	65.673	2.356	0.303	7.405	6.000
600	24.219	68.811	1.508	0.181	6.890	5.498
700	26.835	72.746	0.904	0.102	6.308	4.936
800	29.077	76.480	0.624	0.062	5.898	4.523
900	31.000	80.000	0.400	0.036	5.636	4.273
1000	32.600	83.368	0.250	0.022	5.493	4.058
1100	33.966	86.541	0.161	0.013	5.437	3.900
1200	35.123	89.547	0.100	0.008	5.453	3.780
1300	36.100	92.399	0.069	0.005	5.516	3.685
1400	36.956	95.046	0.046	0.003	5.614	3.607
1500	37.656	97.679	0.030	0.002	5.742	3.541
1600	38.271	100.130	0.019	0.001	5.881	3.484
1700	38.802	102.466	0.011	0.001	6.026	3.434
1800	39.262	104.697	0.007	0.000	6.176	3.389
1900	39.656	106.871	0.004	0.000	6.329	3.348
2000	40.016	108.973	0.003	0.000	6.484	3.310
2100	40.325	110.935	0.002	0.000	6.640	3.274
2200	40.599	112.717	0.001	0.000	6.796	3.240
2300	40.836	114.377	0.001	0.000	6.952	3.207
2400	41.039	115.950	0.000	0.000	7.108	3.175
2500	41.225	117.472	0.000	0.000	7.264	3.144
2600	41.391	118.950	0.000	0.000	7.420	3.113
2700	41.541	120.380	0.000	0.000	7.576	3.082
2800	41.676	121.763	0.000	0.000	7.732	3.051
2900	41.800	123.100	0.000	0.000	7.888	3.020
3000	41.916	124.400	0.000	0.000	8.044	2.989
3100	42.072	126.618	0.000	0.000	8.200	2.958
3200	42.169	128.755	0.000	0.000	8.356	2.927
3300	42.258	130.817	0.000	0.000	8.512	2.896
3400	42.338	132.804	0.000	0.000	8.668	2.865
3500	42.413	134.729	0.000	0.000	8.824	2.834
3600	42.482	136.594	0.000	0.000	8.980	2.803
3700	42.546	138.406	0.000	0.000	9.136	2.772
3800	42.606	140.163	0.000	0.000	9.292	2.741
3900	42.660	141.868	0.000	0.000	9.448	2.710
4000	42.710	143.521	0.000	0.000	9.604	2.679
4100	42.758	145.124	0.000	0.000	9.760	2.648
4200	42.802	146.680	0.000	0.000	9.916	2.617
4300	42.842	148.190	0.000	0.000	10.072	2.586
4400	42.881	149.654	0.000	0.000	10.228	2.555
4500	42.917	151.072	0.000	0.000	10.384	2.524
4600	42.951	152.446	0.000	0.000	10.540	2.493
4700	42.982	153.774	0.000	0.000	10.696	2.462
4800	43.012	155.057	0.000	0.000	10.852	2.431
4900	43.040	156.295	0.000	0.000	11.008	2.400
5000	43.067	157.490	0.000	0.000	11.164	2.369
5100	43.092	158.645	0.000	0.000	11.320	2.338
5200	43.117	159.759	0.000	0.000	11.476	2.307
5300	43.141	160.832	0.000	0.000	11.632	2.276
5400	43.158	161.866	0.000	0.000	11.788	2.245
5500	43.178	162.857	0.000	0.000	11.944	2.214
5600	43.197	163.804	0.000	0.000	12.100	2.183
5700	43.213	164.717	0.000	0.000	12.256	2.152
5800	43.232	165.597	0.000	0.000	12.412	2.121
5900	43.248	166.444	0.000	0.000	12.568	2.090
6000	43.264	167.257	0.000	0.000	12.724	2.059

Dec. 31, 1960; Dec. 31, 1964.

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
2532(1)	2600(1)	1025(1)	2615(1)
2103(1)	919(1)	584(1)	1601(1)
1184(1)	1755(1)	1305(1)	1174(1)
786(1)	942(1)	973(1)	
2612(1)	950(1)	366(1)	

Bond Distance: B-B = 1.775 ± 0.004 Å B-H₂ = 1.196 ± 0.016 Å B-H₂ = 1.339 ± 0.013 Å
Bond Angles: H₂-B-H₂ = 120.2 ± 1.6° H₂-B-H₂ = 118.6 ± 0.4°
Product of the Moments of Inertia: I_AI_BI_C = 2.46822 × 10⁻¹¹⁶ g.³ cm.⁶
Heat of Formation:
ΔH_f^{298.15} is a weighted average of the following data. The older data of W. A. Roth et al. (8) deviates from the rest of the investigations and is not included.

Investigator

Gunn and Green (1) B₂H₆(g) → 2B(am) + 3H₂(g) ΔH_f^{298.15} (kcal. mole⁻¹) = -5.0 7.4
E. J. Prosen et al. (2) B₂H₆(g) → 2B(am) + 3H₂(g) ΔH_f^{298.15} (kcal. mole⁻¹) = -6.73 9.13
J. R. Lacher et al. (3) B₂H₆(g) + 6Cl₂ → 2BCl₃(g) + 6HCl(g) ΔH_f^{298.15} (kcal. mole⁻¹) = -342.3 17.3
E. J. Prosen et al. (4) B₂H₆(g) + 6H₂O(l) + [2000H₂O(l)] → 2H₂BO₃ + 1000H₂O(soln.) + 6H₂(g) ΔH_f^{298.15} (kcal. mole⁻¹) = -111.46 ± 0.54 9.32
Gunn and Green (7) (a) B₂H₆(g) + 2000H₂O → 2(H₂BO₃ + 1000H₂O) + 6H₂(g) ΔH_f^{298.15} (kcal. mole⁻¹) = -112.22 ± 0.10 10.08
Gunn and Green (7) (b) BCl₃(l) + 130.3H₂O → (H₃BO₃ + 1000H₂O) ΔH_f^{298.15} (kcal. mole⁻¹) = -68.14
(c) B₂H₆(g) + 6(HCl-100H₂O) → 2BCl₃(l) + 6H₂(g) ΔH_f^{298.15} (kcal. mole⁻¹) = +24.06 10.06
(CH₃)₃N(g) + 1/2 B₂H₆(g) → (CH₃)₃NBH₃(c) ΔH_f^{298.15} (kcal. mole⁻¹) = -32.33 ± 0.06 8.3
McCoey and Bauer (13) (CH₃)₃N(g) + 1/2 B₂H₆(g) → (CH₃)₃NBH₃(c) ΔH_f^{298.15} (kcal. mole⁻¹) = -31.40 6.5

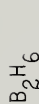
Sources of Auxiliary data: From the JANAF tables, ΔH_f^{298.15} = 1.2, -96.31, -22.063 kcal. mole⁻¹ of B(am), BCl₃(g) and HCl(g) respectively. From P. D. Rossini et al. (11) The ΔH_f^{298.15} = 5.6 kcal. mole⁻¹ of BCl₃. From D. D. Wagman (12) the ΔH_f^{298.15} of HCl + 100H₂O = -39.657 kcal. mole⁻¹. From Good et al. (5) the ΔH_f^{298.15} of H₃BO₃(c) = -261.47 ± 0.20 kcal. mole⁻¹ and the H₃BO₃ solution data of Rasolno (6). ΔH_f^{298.15} of (CH₃)₃N(g) = -5.9 ± 0.4 kcal. mole⁻¹ from I Jaffe (10).

(1) S. R. Gunn and L. O. Green, J. Phys. Chem. **65**, 779-83(1961); J. Chem. Phys. **36**, 1118 (1962). Explosive decomposition while mixed with acetylene.
(2) E. J. Prosen, W. H. Johnson and F. Y. Fergiel, J. Res. N.B.S. **61**, 247-250 (1958). Decomposition by heating in a flow-type calorimeter.
(3) J. R. Lacher, R. E. Scruby, and J. D. Park, J. Am. Chem. Soc. **74**, 5292-4 (1952). A vapor phase chlorination in a flow-type calorimeter.
(4) E. J. Prosen, W. H. Johnson, and F. Y. Fergiel, J. Res. N.B.S. **62**, 43-47 (1959). Heat of reaction of diborane with water in a flow-type calorimeter.
(5) W. D. Good, W. Mansson, and J. P. McCullough, "Thermochemistry of Boron and Some of its Compounds. The heats of Formation of Trimethylamineborane and Orthoboric Acid" a pre-print from the proceedings of the symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July 1963.
(6) L. G. Rasolno, "Heats of Formation of B₂O₃(c) and B₂O₃(amp)" Special Report NOKR-360, National Research Corporation, Cambridge, Mass. June 2, 1964.
(7) S. R. Gunn and L. O. Green, J. Phys. Chem. **64**, 61-63(1960). Heats of hydrolysis of diborane and boron trichloride in a sealed rocking bomb type calorimeter.
(8) W. A. Roth, W. Berger, and A. Bertram, Ber. **70B**, 49 (1937) Ber. **70B**, 971 (1937) and W. A. Roth, Z. Naturforsch., **1**, 574 (1946). Heat of hydrolysis in a bomb type calorimeter.
(9) S. R. Gunn, abstract (No. 42) of a paper presented at the 19th annual Calorimetry Conference, Washington, D. C., and Bethesda, Maryland, Oct. 13-16, 1964.
(10) I. Jaffe, Thesis University of Maryland, 1959.
(11) D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected Values of Chemical Thermodynamic Properties, N.B.S. Circ. 500.
(12) W. H. Evans, Appendix III, National Bureau of Standards Report 8504, July 1, 1964.
(13) R. E. McCoey and S. H. Bauer, J. Am. Chem. Soc. **78**, 2061 (1956).

Heat Capacity and Entropy.

The molecular constants reported by B. L. Gornoll, "Electron Diffraction Investigation of Diborane and Boron-alkyls", Thesis, Iowa State University of Science and Technology, 1963, were selected. They agree well with those reported by K. Hedberg, and V. Schomaker, J. Chem. Phys. **22**, 985 (1954). The principal moments are I_A = 1.0578 × 10⁻³⁹, I_B = 4.6416 × 10⁻³⁹, and I_C = 5.0229 × 10⁻³⁹ g. cm.²

The vibrational frequencies for B₂H₆ were those listed by E. C. Wu, Thesis, University of Minn. 1962, "Assignments and Force Constants of Diborane and Isotopic Derivatives" except for ν₈, ν₁₀ and ν₁₄ which were taken from the calculated frequency column of table VIII-1 page 55 of the Thesis.





Magnesium Diboride (MgB_2)
(Crystal) Mol. Wt. = 45.96

MOL. WT. = 45.96

(CRYSTAL)

MAGNESIUM DIBORIDE (MgB_2)

T. °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	0.000	0.000	INFINITE	1.435	21.825	21.825	INFINITE
100	2.670	8.962	16.485	1.542	21.913	21.913	1.718
200	8.220	4.590	8.990	1.000	22.088	21.664	23.277
298	11.430	8.600	0.000	0.000	21.980	21.378	15.670
300	11.440	8.671	0.021	0.021	21.980	21.374	15.571
400	13.000	12.110	9.089	1.248	22.011	21.170	11.566
500	13.980	15.198	10.002	2.598	22.129	20.947	9.156
600	14.670	17.808	11.090	4.030	22.316	20.696	7.538
700	15.300	20.117	12.218	5.529	22.542	20.407	6.371
800	15.900	22.199	13.337	7.089	22.797	20.086	5.487
900	16.480	24.068	14.429	8.711	23.068	19.751	4.781
1000	17.140	25.681	15.487	10.394	23.474	19.162	4.168
1100	17.705	27.041	16.508	12.137	23.741	18.520	3.679
1200	18.270	28.106	17.493	13.935	24.008	17.851	3.251
1300	18.830	28.997	18.444	15.780	24.274	17.162	2.885
1400	19.390	29.827	19.363	17.672	24.540	16.454	2.569
1500	19.991	30.600	20.251	19.612	24.806	15.734	2.302
1600	20.630	31.324	21.112	21.699	25.072	15.006	2.086
1700	21.310	32.000	21.947	23.780	25.338	14.271	1.932
1800	22.030	32.630	22.758	25.913	25.604	13.531	1.733
1900	22.790	33.220	23.547	28.094	25.870	12.786	1.586
2000	23.590	33.770	24.315	30.321	26.136	12.041	1.497

$$\Delta H^\circ_f 0 = -21.8 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$\Delta H^\circ_f 298.15 = -22.0 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$S^\circ_{298.15} = 8.60 \pm 0.04 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_d = [1320]^\circ\text{K}$$

Heat of Formation.

The equilibrium constants (933 - 1108°K.) for the reaction $2\text{MgB}_2(c) = \text{Mg}(g) + \text{MgB}_4(c)$ were determined by M. Wright and P. N. Walsh, "The Vaporization of $\text{MgB}_4(c)$ ", Technical Research Report OMCO-HEP-55, Jan. 9, 1958, Ohio State University Research Foundation. The corresponding second and third law values of $\Delta H^\circ_f 298.15$ for this reaction were derived as 53.1 ± 4.7 and $54.1 \text{ kcal. mole}^{-1}$, respectively. Using the third law value obtained, i.e. $\Delta H^\circ_f 298.15 = 54.1 \text{ kcal. mole}^{-1}$, for the reaction, the $\Delta H^\circ_f 298.15$ for $\text{MgB}_2(c)$ was evaluated as $-22.0 \pm 2.0 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The low temperature (21.12 - 304.22°K.) heat capacities were measured by R. M. Swift and D. White, J. Am. Chem. Soc. **79**, 3641 (1957). Above 298.15°K. the values of C_p were estimated by comparison with those of other related borides. $S^\circ_{298.15}$ was reported by R. M. Swift and D. White, loc. cit., using S°_{20} (extrap.) = 0.005 cal. deg.⁻¹ mole⁻¹.

Temperature of Decomposition.

T_d was taken from L. Y. Markovskiy, Y. D. Kondrashev, and G. V. Kaputovskaya, Zhur. Obshchei Khim., **25**, 409 (1955). On heating to high temperatures $\text{MgB}_2(c)$ decomposes into boride phases A, B, and C with the separation of Mg. The composition of phase A is close to MgB_6 and that of C is close to MgB_{12} .



(Ideal Gas) GFW = 37.6214

DIBORON MONOXIDE (B₂O)

(IDEAL GAS)

OFW = 37.6214

Point Group [C_{2v}]
 $S^{\circ}_{298.15} = [54.4]$ gibbs/mol
 $\Delta H^{\circ}_{298.15} = 23 \pm 25$ kcal/mol
 $\Delta H^{\circ}_0 = 22 \pm 25$ kcal/mol

Vibrational Frequencies and Degeneracies

ω , cm⁻¹
 (1250)(1)
 (600)(1)
 (1800)(1)

Bond Distance: B-O = [1.26] Å
 Bond Angle: B-O-B = [150]°

Product of the Moments of Inertia: $I_A I_B I_C = [4.7324] \times 10^{-117}$ g³ cm⁶

$\sigma = [2]$

Heat of Formation.

The heat of formation was calculated from the estimated heat of reaction $\Delta H^{\circ}_0 = 300 \pm 25$ kcal/mol for B₂O(g) → 2B(g) + O(g), using the JANAF auxiliary data for B(g) and O(g). The value of ΔH°_0 was assumed to be the sum of the heats of dissociation, 120 kcal/mol for B₂O(g) → B₂(g) + B(g) and 180 kcal/mol for B₂(g) → B(g) + O(g). The former was estimated and the latter was derived from the JANAF values.

The possible existence of B₂O(g) in the burning of boron under reducing conditions was discussed by Gilbert S. Bohn in a paper presented at the Combustion Institute, at University of Denver, Apr. 25-27, 1966. He estimated the heat of formation to lie between -27 and +23 kcal/mol, but favored the value of +23 kcal/mol in the theoretical calculations of boron burning in air.

Heat Capacity and Entropy.

The bent molecular structure and the molecular constants were estimated by comparison with those in BO(g), AlO(g) and Al₂O(g).² The three principal moments of inertia are $I_A = 0.1624 \times 10^{-39}$, $I_B = 5.319 \times 10^{-39}$ and $I_C = 5.4804 \times 10^{-39}$ g cm².

June 30, 1966

B₂O

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	Log Kp
0	∞	∞	∞	∞	∞	∞
100	7.975	45.239	62.095	2.480	22.142	INFINITE
200	8.477	50.890	55.222	1.685	22.578	20.140
298	9.183	54.405	54.405	∞	22.888	- 19.196
300	9.193	54.462	54.462	∞	23.000	- 10.937
400	9.493	57.295	54.775	4.977	23.000	- 10.833
500	10.556	59.486	55.495	1.996	22.788	- 6.146
600	11.211	61.462	56.328	3.080	22.544	- 2.493
700	11.568	62.713	57.169	4.277	22.261	- 1.327
800	11.783	63.283	57.891	5.593	21.950	- 0.817
900	12.269	66.213	58.872	6.607	21.623	- 0.198
1000	12.514	67.519	59.672	7.847	21.279	- 0.719
1100	12.712	68.721	60.441	9.108	20.913	- 1.138
1200	12.875	70.830	61.178	11.285	20.521	- 1.487
1300	13.015	72.746	62.551	13.498	20.109	- 1.780
1400	13.115	74.483	63.625	15.746	19.679	- 2.006
1500	13.206	76.059	64.421	18.026	19.227	- 2.161
1600	13.284	77.421	65.007	20.349	18.756	- 2.282
1700	13.345	78.599	65.407	22.716	18.266	- 2.382
1800	13.405	79.613	65.652	25.126	17.761	- 2.461
1900	13.445	80.484	65.776	27.576	17.241	- 2.521
2000	13.475	81.224	65.806	30.066	16.700	- 2.571
2100	13.501	81.844	65.750	32.596	16.140	- 2.611
2200	13.521	82.364	65.612	35.166	15.560	- 2.641
2300	13.536	82.794	65.400	37.776	14.970	- 2.661
2400	13.546	83.144	65.126	40.426	14.370	- 2.671
2500	13.551	83.414	64.800	43.116	13.760	- 2.671
2600	13.551	83.604	64.426	45.846	13.140	- 2.661
2700	13.546	83.724	63.996	48.616	12.510	- 2.641
2800	13.536	83.774	63.526	51.426	11.870	- 2.611
2900	13.521	83.754	63.016	54.276	11.220	- 2.571
3000	13.501	83.674	62.466	57.166	10.570	- 2.521
3100	13.475	83.534	61.886	60.096	9.920	- 2.461
3200	13.445	83.344	61.266	63.066	9.270	- 2.382
3300	13.415	83.104	60.616	66.076	8.620	- 2.282
3400	13.376	82.814	59.846	69.126	7.970	- 2.161
3500	13.326	82.474	58.956	72.216	7.320	- 2.006
3600	13.266	82.084	57.946	75.346	6.670	- 1.826
3700	13.196	81.644	56.816	78.516	6.020	- 1.626
3800	13.116	81.154	55.566	81.726	5.370	- 1.406
3900	13.026	80.614	54.206	85.076	4.720	- 1.166
4000	12.926	80.024	52.736	88.566	4.070	- 0.906
4100	12.816	79.384	51.156	92.196	3.420	- 0.626
4200	12.696	78.694	49.486	95.966	2.770	- 0.326
4300	12.566	77.954	47.726	100.000	2.120	- 0.006
4400	12.426	77.164	45.886	104.290	1.470	0.314
4500	12.276	76.324	43.976	108.830	0.820	0.644
4600	12.116	75.434	42.006	113.620	0.170	0.984
4700	11.946	74.494	39.986	118.660	- 0.480	1.324
4800	11.766	73.504	37.916	123.950	- 1.130	1.654
4900	11.576	72.464	35.796	129.490	- 1.780	1.974
5000	11.376	71.374	33.626	135.280	- 2.420	2.284
5100	11.166	70.234	31.406	141.320	- 3.060	2.584
5200	10.946	69.044	29.136	147.610	- 3.690	2.874
5300	10.716	67.804	26.816	154.150	- 4.320	3.154
5400	10.476	66.514	24.446	160.940	- 4.950	3.424
5500	10.226	65.174	22.026	167.980	- 5.580	3.684
5600	9.966	63.784	19.556	175.270	- 6.210	3.934
5700	9.696	62.344	17.036	182.810	- 6.840	4.174
5800	9.416	60.854	14.466	190.600	- 7.470	4.404
5900	9.126	59.314	11.846	198.640	- 8.100	4.624
6000	8.826	57.724	9.176	206.930	- 8.730	4.834

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0	4.000	INFINITE	2.218	-302.162	-302.162	INFINITE
100	4.987	22.984	2.218	-302.162	-302.162	22.984
200	5.974	45.968	4.436	-303.598	-303.598	45.968
298	15.056	12.870	0.000	-303.640	-303.640	208.699
300	15.140	12.963	0.028	-303.642	-303.642	207.327
400	18.350	17.787	1.712	-303.668	-303.668	152.025
500	20.800	22.148	3.671	-303.631	-303.631	118.845
600	23.250	26.153	5.872	-303.513	-303.513	96.729
700	26.200	29.951	8.239	-302.245	-259.265	80.942
800	29.650	33.873	11.131	-302.740	-253.015	69.117
900	32.050	37.316	14.226	-301.998	-246.443	59.939
1000	33.450	40.789	17.304	-301.130	-240.157	52.613
1100	34.300	44.000	20.895	-300.206	-234.766	46.642
1200	34.700	47.003	24.347	-299.264	-228.857	41.679
1300	34.900	49.789	27.827	-298.337	-223.029	37.493
1400	35.000	52.379	31.823	-297.432	-217.268	33.915
1500	35.000	54.794	36.323	-296.560	-211.576	30.825
1600	35.000	57.053	38.101	-295.722	-205.936	28.128
1700	35.000	59.175	34.573	-294.915	-200.350	25.755
1800	35.000	61.175	35.996	-294.138	-194.810	23.652
1900	35.000	63.068	37.372	-293.387	-189.313	21.775
2000	35.000	64.863	38.702	-292.655	-183.855	20.090

Dec. 31, 1960; Dec. 31, 1964

Heat of Formation.

The heat of formation (ΔH_f° 298.15°) for B₂O₃(c) has been reported by many investigators. However, the values obtained were not in good agreement. The value of ΔH_f° 298.15° for B₂O₃(c) adopted was taken from L. G. Fasolino, "Heats of Formation of B₂O₃(c) and B₂O₃(am.)", NMR-3608 (OO), National Research Corporation, Massachusetts, June 2, 1964. The other derived values of ΔH_f° 298.15° for B₂O₃(c) are listed in the following table.

Investigator	Reaction	ΔH_f° 298.15° kcal. mole ⁻¹	ΔH_f° 298.15° kcal. mole ⁻¹
Roth ¹	B ₂ O ₃ (gl) + 3 H ₂ O(l) = 2 H ₃ BO ₃ (c)	-18.15	-304.2 ± 0.4
Eggersgluessa et al. ²	2B(am.) + 3/2 O ₂ (g) = B ₂ O ₃ (gl.)	-281.1 ± 3.1	-283.1 ± 3.1
Artadalen and Anderson ³	1/2 B ₂ O ₃ (am.) + 3/2 H ₂ O(l) = H ₃ BO ₃ (c)	-9.13 ± 0.04	-304.1 ± 0.4
Ekstein and Artadalen ⁴	2B(c) + 3/2 O ₂ (g) = B ₂ O ₃ (gl.)	-304.6 ± 4.2	-309.0 ± 4.2
Gal'chenko et al. ⁵	2B(am.) + 3/2 O ₂ (g) = B ₂ O ₃ (gl.)	-298.7 ± 1.8	-300.7 ± 2.0
Fasolino	B ₂ O ₃ (c) + 348 H ₂ O(l) = 2 H ₃ BO ₃ ·348 H ₂ O(Sol.)	-3.45 ± 0.03	-303.64 ± 0.40

¹W. A. Roth, Z. Naturforsch., **1**, 574 (1946).²V. Eggersgluessa, A. G. Monroe and W. G. Parker, Trans. Faraday Soc., **45**, 661 (1949).³E. R. Vsn Artadalen and K. P. Anderson, J. Am. Chem. Soc., **73**, 579 (1951).⁴B. H. Eckstein and E. R. Van Artadalen, J. Am. Chem. Soc., **80**, 1352 (1958).⁵S. L. Gal'chenko, A. N. Kornilov and S. M. Skuratov, Russ. J. Inorg. Chem., **5**, 1039 (1960).

In order to evaluate the values of ΔH_f° 298.15° for B₂O₃(c) from the corresponding ΔH_f° 298.15° values, the following auxiliary data (298.15°K) were used: ΔH_f° (B₂am.) = 1.2 ± 0.4 kcal. mole⁻¹, ΔH_f° = 4.36 kcal. mole⁻¹ for the reaction B₂O₃(c) = B₂O₃(gl.), ΔH_f° (H₃BO₃, c) = -261.47 ± 0.20 kcal. mole⁻¹, ΔH_f° (2 H₃BO₃·348 H₂O, Sol.) = -512.04 ± 0.40 kcal. mole⁻¹ and ΔH_f° (H₂O, l) = -68.317 kcal. mole⁻¹.

Heat Capacity and Entropy.

The low temperature (18.08 - 296.60°K.) heat capacities used were reported by E. C. Kerr, H. N. Hersh and H. L. Johnston, J. Am. Chem. Soc., **72**, 4738 (1950). The high temperature (350.6 - 718.4°K.) heat capacities were derived from the heat content measurements determined by J. C. Southard, J. Am. Chem. Soc., **63**, 3147 (1941). These two sets of C_p data were plotted and joined smoothly at 298°K. The C_p values above 718.4°K. were estimated by graphical extrapolation. ΔH_f° 298.15° was obtained from E. C. Kerr, H. N. Hersh and H. L. Johnston, loc. cit., based on S₂₉₈^o = 0.027 cal. deg.⁻¹ mole⁻¹. The specific heats of B₂O₃(c) in the temperature range 51 to 298°K. were also determined by K. K. Kelley, J. Am. Chem. Soc., **63**, 1137 (1941). The C_p values reported are in good agreement with the values adopted.

Melting Data.

Melting temperature (T_m) was taken from P. C. Kracek, O. W. Morey and H. E. Merwin, Am. J. Sci. [S] **35A**, 143 (1938). The heat of melting (ΔH_m°) was converted from ΔH_m° 298.15° = 4.36 ± 0.02 kcal. mole⁻¹ reported by J. C. Southard, loc. cit.

Heat of Sublimation.

The value of heat of sublimation (ΔH_s° 298.15°) was calculated as the difference in the heats of formation (ΔH_f° 298.15°) for B₂O₃(g) and B₂O₃(c).



Boron Oxide (B₂O₃)

(Liquid) Mol. Wt. = 69.64

BORON OXIDE (B₂O₃)

(LIQUID)

MOL. WT. = 69.64

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _f
0						
100	15.050	18.739	18.739	-0.000	-282.115	206.786
200	15.140	18.832	18.739	-0.028	-282.009	205.433
300	18.350	23.656	19.475	1.712	-296.308	150.926
400	20.800	28.017	20.675	3.671	-299.271	118.222
500	28.400	32.354	22.248	6.064	-298.961	96.426
600	31.700	36.703	24.184	8.910	-298.739	80.426
700	34.950	41.073	26.582	12.313	-298.585	68.571
800	38.150	45.468	29.454	16.263	-298.491	60.266
900	41.300	49.891	32.817	20.671	-298.358	53.078
1000	44.500	54.367	36.678	25.544	-298.196	47.212
1100	47.750	58.910	41.046	30.893	-297.910	42.333
1200	51.050	63.520	45.910	36.724	-297.500	38.466
1300	54.400	68.203	51.263	43.046	-296.973	34.635
1400	57.750	72.957	57.197	49.859	-296.334	30.969
1500	61.100	77.782	63.712	57.165	-295.598	28.469
1600	64.450	82.587	70.807	65.000	-294.778	26.134
1700	67.800	87.372	78.482	73.393	-293.885	23.969
1800	71.150	92.137	86.737	82.351	-292.930	21.978
1900	74.500	96.882	95.582	91.885	-291.924	20.154
2000	77.850	101.607	104.917	101.999	-290.878	18.478
2100	81.200	106.312	114.742	112.707	-289.803	16.944
2200	84.550	111.007	125.057	123.997	-288.707	15.544
2300	87.900	115.692	135.862	135.862	-287.600	14.260
2400	91.250	120.367	147.157	148.313	-286.483	13.096
2500	94.600	125.042	158.952	161.367	-285.356	12.042
2600	97.950	129.717	171.247	175.000	-284.219	11.093
2700	101.300	134.392	184.042	189.213	-283.072	10.242
2800	104.650	139.067	197.337	203.999	-281.915	9.487
2900	108.000	143.742	211.132	219.362	-280.748	8.816
3000	111.350	148.417	225.427	235.307	-279.571	8.226
3100	114.700	153.092	240.222	251.830	-278.384	7.713
3200	118.050	157.767	255.517	268.933	-277.187	7.263
3300	121.400	162.442	271.312	286.616	-275.980	6.876
3400	124.750	167.117	287.607	304.879	-274.763	6.555
3500	128.100	171.792	304.402	323.722	-273.536	6.298
3600	131.450	176.467	321.697	343.145	-272.309	6.064
3700	134.800	181.142	339.492	363.145	-271.072	5.846
3800	138.150	185.817	357.787	383.722	-269.825	5.640
3900	141.500	190.492	376.582	404.875	-268.568	5.446
4000	144.850	195.167	395.877	426.600	-267.301	5.263

$\Delta H_f^\circ 298.15 = -299.28 \pm 0.40 \text{ kcal. mole}^{-1}$
 $\Delta H_g^\circ = 5.26 \pm 0.02 \text{ kcal. mole}^{-1}$
 $\Delta H_v^\circ = 87.55 \text{ kcal. mole}^{-1}$

$S_{298.15}^\circ = 18.739 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 723 \pm 2^\circ \text{K.}$
 $T_b = 2316^\circ \text{K.}$

Heat of Formation

$\Delta H_f^\circ 298.15$ for B₂O₃(l) was obtained from $\Delta H_f^\circ 298.15$ for B₂O₃(c) by adding ΔH_v° and the difference between $H_{298.15}^\circ$ for crystal and liquid.

Heat Capacity and Entropy

The heat content ($H^\circ - H_{298.15}^\circ$) measurements on B₂O₃(glass) and B₂O₃(l) were determined, from 381.7 to 1778.8°K., by J. C. Southard, J. Am. Chem. Soc. **63**, 3147 (1941) and, from 1015 to 2154°K., by R. M. Krasovitskaya, P. B. Kantor, L. S. Kan, V. V. Kandyba, L. M. Fomichev, Russ. J. Phys. Chem. **35**, 737 (1961). Based on these data the corresponding heat capacities (C_p) were derived. The C_p values thus obtained were plotted and joined smoothly, assuming a glass transition temperature at 550°K. The heat capacities above 2154°K. were estimated by graphical extrapolation. The entropy was obtained in a manner analogous to that of the heat of formation. The heat capacities of B₂O₃ glass and liquid have also been measured between 35 and 350°C with a radiation calorimeter by S. B. Thomas and G. S. Parks, J. Phys. Chem. **35**, 2091 (1931). The heat capacity curves obtained have been compared and discussed.

Melting Data

See the B₂O₃(c) table.

Vaporization Data

The boiling point (T_b) was calculated as the temperature at which the difference in ΔH_f° values for B₂O₃(g) and B₂O₃(l) becomes zero. The corresponding difference in ΔH_f° values at T_b is the heat of vaporization (ΔH_v°).



T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100	9.590	147.016	3.427	-198.870	-198.870	INFINITE
200	13.224	69.150	1.443	-199.148	-199.148	413.326
298	15.979	67.798	1.000	-199.140	-199.140	215.738
300	16.020	67.799	1.000	-199.140	-199.140	144.106
400	17.651	72.774	1.729	-199.151	-199.151	143.204
500	19.207	76.911	3.566	-199.217	-199.217	106.939
600	20.272	80.510	5.561	-199.324	-199.324	85.175
700	21.158	83.573	7.783	-199.462	-199.462	70.659
800	21.907	86.153	10.269	-199.627	-199.627	58.499
900	22.427	88.191	13.043	-199.726	-199.726	48.439
1000	22.903	91.569	16.266	-199.869	-199.869	41.567
1100	23.295	93.771	18.702	-200.025	-200.025	37.615
1200	23.619	95.912	20.940	-200.189	-200.189	34.302
1300	23.880	97.925	22.955	-200.356	-200.356	31.402
1400	24.116	99.843	24.869	-200.526	-200.526	29.089
1500	24.307	101.163	26.120	-200.761	-200.761	27.002
1600	24.469	102.737	26.888	-200.985	-200.985	25.172
1700	24.607	103.235	27.085	-201.204	-201.204	23.579
1800	24.727	103.655	27.210	-201.415	-201.415	22.186
1900	24.830	104.015	27.269	-201.752	-201.752	20.961
2000	24.920	104.251	27.266	-202.032	-202.032	19.869
2100	24.999	104.468	27.212	-202.323	-202.323	18.896
2200	25.069	104.659	27.110	-202.626	-202.626	18.040
2300	25.129	104.826	26.963	-202.942	-202.942	17.284
2400	25.178	104.970	26.780	-203.271	-203.271	16.629
2500	25.213	105.098	26.566	-203.613	-203.613	16.069
2600	25.235	105.209	26.325	-203.968	-203.968	15.595
2700	25.248	105.303	26.066	-204.336	-204.336	15.220
2800	25.253	105.382	25.793	-204.716	-204.716	14.898
2900	25.250	105.446	25.510	-205.107	-205.107	14.626
3000	25.240	105.496	25.217	-205.509	-205.509	14.400
3100	25.225	105.533	24.915	-205.922	-205.922	14.218
3200	25.206	105.558	24.606	-206.346	-206.346	14.076
3300	25.183	105.572	24.293	-206.781	-206.781	13.970
3400	25.156	105.576	23.978	-207.227	-207.227	13.897
3500	25.125	105.569	23.663	-207.684	-207.684	13.852
3600	25.090	105.551	23.349	-208.151	-208.151	13.834
3700	25.053	105.522	23.036	-208.628	-208.628	13.840
3800	25.015	105.483	22.724	-209.115	-209.115	13.869
3900	24.976	105.435	22.413	-209.612	-209.612	13.920
4000	24.936	105.378	22.104	-210.119	-210.119	13.985
4100	24.895	105.312	21.800	-210.636	-210.636	14.062
4200	24.853	105.237	21.502	-211.163	-211.163	14.150
4300	24.810	105.153	21.210	-211.700	-211.700	14.248
4400	24.766	105.060	20.925	-212.247	-212.247	14.356
4500	24.721	104.958	20.647	-212.804	-212.804	14.473
4600	24.676	104.848	20.375	-213.371	-213.371	14.598
4700	24.631	104.730	20.110	-213.948	-213.948	14.730
4800	24.586	104.603	19.852	-214.535	-214.535	14.868
4900	24.541	104.468	19.600	-215.132	-215.132	15.012
5000	24.496	104.325	19.354	-215.739	-215.739	15.161
5100	24.451	104.175	19.114	-216.356	-216.356	15.314
5200	24.406	104.019	18.880	-216.983	-216.983	15.471
5300	24.361	103.857	18.652	-217.620	-217.620	15.631
5400	24.316	103.689	18.430	-218.267	-218.267	15.794
5500	24.271	103.515	18.214	-218.924	-218.924	15.960
5600	24.226	103.336	18.004	-219.591	-219.591	16.128
5700	24.181	103.151	17.800	-220.268	-220.268	16.298
5800	24.136	102.961	17.602	-220.955	-220.955	16.469
5900	24.091	102.766	17.410	-221.652	-221.652	16.641
6000	24.046	102.566	17.224	-222.359	-222.359	16.814

Mar. 31, 1961; Dec. 31, 1964.

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
2073(1)	172(1)	1240(1)
730(1)	460(1)	457(1)
521(1)	2073(1)	480(1)

Bond Distance: O-B = 1.36 ± 0.02 Å B-O = 1.20 ± 0.03 Å

Bond Angle: O-B-O = 180° B-O-B = 120°

Product of the Moments of Inertia: I_AI_BI_C = 3.15283 X 10⁻¹¹⁴ g.³ cm.⁶

σ = 2

Heat of Formation

The heat of formation (ΔH_f⁰ 298.15) for B₂O₃(g) was calculated from the values of ΔH_f⁰ 298.15 and ΔH_f⁰ 298.15 for B₂O₃(l). The ΔH_f⁰ 298.15 value was obtained from the analyses of the vapor pressure data of B₂O₃(l) by both the second and third law methods. Ten sets vapor pressure data were employed for examination. The results obtained are presented as follows.

Investigator

Investigator	Temperature, °K.	Third Law Value	Second Law Value	ΔH _f ⁰ 298.15, kcal. mole ⁻¹
Cole and Taylor ¹	1473 - 1673	87.77	72.92 ± 2.3	-211.51
Speiser, et al. ²	1331 - 1642	99.25	87.10 ± 1.8	-200.03
Soulen, et al. ³	1567 - 1808	98.49	65.87 ± 7.8	-200.79
Searcy and Myers ⁴	1501 - 1566	98.70	101.3 ± 12.5	-200.58
Scheer ⁵	1414 - 1621	101.89	95.25 ± 0.9	-197.39
Nemesyov and Firsova ⁶	1299 - 1515	98.86	82.36 ± 2.9	-200.42
White, et al. ⁷	1220 - 1641	99.36	90.52 ± 0.6	-199.92
Sommer ⁸	1228 - 1641	99.63	93.08 ± 0.7	-199.65
Blackburn ⁹	1325 - 1547	99.43	92.78 ± 1.4	-199.85
Hildenbrand, et al. ¹⁰	1436 - 1584	100.14	100.75 ± 1.1	-199.14
Büchler, et al. ¹¹	1300	—	100.2 ± 3.0	-199.08

All calculations based on the third law values listed except the last one.

¹S. S. Cole and N. W. Taylor, J. Am. Chem. Soc. **82**, 82 (1955).²R. Speiser, S. Waditch and H. L. Johnston, J. Am. Chem. Soc. **72**, 2578 (1950).³J. R. Soulen, P. Schapitzmonda and J. L. Margrave, J. Phys. Chem. **59**, 132 (1955).⁴A. W. Searcy and C. E. Myers, J. Phys. Chem. **61**, 857 (1957).⁵M. D. Scheer, J. Phys. Chem. **61**, 1184 (1957).⁶A. N. Nemesyov and L. P. Firsova, Russ. J. Phys. Chem. **34**, 490 (1960).⁷D. White, P. N. Walsh, H. W. Ooldstein and D. P. Dever, J. Phys. Chem. **65**, 1404 (1961).⁸A. Sommer, Ph. D. Thesis, The Ohio State University, 1962.⁹P. B. Blackburn, "Research on Thermodynamics of the Al-B-O and Be-B-O Systems," Quarterly Report No. 4, Mar. 1 - May 31, 1963, Arthur D. Little, Inc.¹⁰D. L. Hildenbrand, V. P. Hall and N. D. Potter, J. Chem. Phys. **39**, 296 (1963).¹¹A. Büchler and J. B. Berkowitz-Matuck, J. Chem. Phys. **39**, 286 (1963).

The free energy functions of B₂O₃(g) used for calculation are based on two estimated vibrational frequencies, 172 and 460 cm.⁻¹. Similar evaluations were made using 259 and 460 cm.⁻¹ instead, each corresponding third law values of ΔH_f⁰ obtained was lower by more than 1 kcal. mole⁻¹ than that of the previous ones. The value of ΔH_f⁰ 298.15 for B₂O₃(g) adopted is the third law value based on the vapor pressures reported by D. L. Hildenbrand, M. P. Hall and N. D. Potter, loc. cit.

Heat Capacity and Entropy

The bond distances were reported by P. A. Akshin and V. P. Spiridonov, Doklady Akad. Nauk. S.S.S.R. **131**, 557 (1960). The bond angle was taken from W. Leitner, Jr. and J. R. W. Mann, J. Chem. Phys. **37**, 292 (1962). The vibrational frequencies were obtained from A. Sommer, D. White, M. J. Linevsky and D. E. Mann, J. Chem. Phys. **38**, 87 (1963) and corrected to the average isotopic species. The three principal moments of inertia are: I_A = 3.10959 X 10⁻³⁸, I_B = 2.9758 X 10⁻³⁹ and I_C = 3.40717 X 10⁻³⁸ g. cm.²

Lead Diborate (PbB_2O_4)
(Crystal) Mol. Wt. = 292.85



MOL. WT. = 292.85

LEAD DIBORATE (PbB_2O_4) (CRYSTAL)

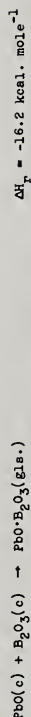
$\Delta H_f^\circ = \text{Unknown}$

$\Delta H_f^\circ 298.15 = -372 \pm 1.5 \text{ kcal. mole}^{-1}$

$S_{298.15}^\circ = [31.2 \pm 3] \text{ cal. deg}^{-1} \text{ mole}^{-1}$

Heat of Formation.

W. H. Evans in NBS Report 7192, July 1, 1961, analysed the heats of formation of the lead borate system. L. Shartsis and E. Newman, J. Am. Ceram. Soc. 31, 213 (1948) measured heats of solution of the lead borate glasses in 2 N HNO_3 . In their phase studies C. Mazzetti and P. De Carli, Gazz. chim. Ital. 56, 19 (1926) established that the compounds formed were $\text{PbO} \cdot \text{B}_2\text{O}_3$, $\text{PbO} \cdot 2\text{B}_2\text{O}_3$, $\text{PbO} \cdot 3\text{B}_2\text{O}_3$ and 2 $\text{PbO} \cdot 5\text{B}_2\text{O}_3$. From the Shartsis and Newman paper loc. cit. Evans obtained the following:



$\Delta H_r^\circ = -16.2 \text{ kcal. mole}^{-1}$

and estimated a $\Delta H_{298.15}^\circ$ of 7.0 kcal. mole⁻¹ for the conversion to the $\text{PbO} \cdot \text{B}_2\text{O}_3(\text{crystal})$. With auxiliary JANAF values the $\Delta H_f^\circ 298.15$ was calculated to be -372 kcal./mole. The results of B. M. Lepinskikh and O. A. Esin, Zhur. Neorg. Khim. 5, 1223 (1961) studying the lead borate system at 1000°K. with cells of the type $\text{Pb(lig.)}/\text{PbO} \cdot \text{B}_2\text{O}_3/\text{Pt}/\text{O}_2(\text{g})$ were in fair agreement with this results of Shartsis and Newman.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities for B_2O_3 and PbO .

The entropy at 298.15 was obtained from a consideration of the entropies of sodium and calcium borates and those of the constituent oxides, as given by K. K. Kailley and E. G. King, Bureau of Mines Bull. 592 (1961). These indicate for the reaction:



that the simple addition of entropies will give values at least 2.7 e.u. too low for the reaction. The reason for this is probably structural, the $\text{B}_2\text{O}_4^{--}$ ion is a flexible chain. Therefore, the $S_{298.15}^\circ$ for PbB_2O_4 was obtained from the summation of JANAF $S_{298.15}^\circ$ for constituent oxides and the addition of 2.7 e.u.

T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0							
100	25.600	31.200	11.200	•000	-372.000	-346.628	254.073
200	31.359	31.200	31.200	•047	-372.001	-346.671	252.392
300	30.980	39.501	32.275	2.890	-371.876	-337.972	184.651
400	35.180	46.875	34.469	6.203	-371.524	-329.533	144.032
500	38.830	53.623	37.107	9.909	-370.968	-321.183	116.985
600	41.140	55.578	42.710	18.246	-370.490	-312.431	89.640
700	44.420	57.807	48.380	27.427	-369.461	-296.239	71.933
800	47.420	60.383	51.084	32.728	-367.103	-280.206	55.669
900	49.280	62.639	56.261	42.118	-363.504	-262.425	44.681
1000	50.830	64.383	58.600	47.170	-363.161	-256.992	40.116
1100	51.420	65.911	61.055	52.283	-361.796	-249.458	36.344
1200	51.930	67.246	63.339	57.451	-360.415	-242.012	33.056
1300	52.400	68.416	65.527	62.654	-359.022	-234.583	29.165
1400	52.800	69.479	67.527	67.826	-357.627	-227.150	25.326
1500	53.200	70.479	69.479	73.226	-356.219	-220.183	21.826
1600	53.580	71.418	71.735	78.565	-354.801	-213.061	18.735



Titanium Diboride (TiB₂)

(Crystal)

Mol. Wt. = 69.522

T, °K.	C _p ^a	S ^b	-(F ^c -H ₂₉₈)/T	H ^c -H ₂₉₈	ΔH _f ^d	ΔF _f ^e	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	1.798	3.602	13.472	1.287	66.399	66.399	INFINITE
200	10.282	10.601	66.651	66.116	66.347	144.995	
298	10.283	6.808	6.808	0.000	66.860	72.245	48.2236
300	10.641	6.874	6.808	0.020	66.801	65.802	47.934
400	13.119	10.310	7.260	1.220	66.865	65.459	35.763
500	14.739	13.422	8.188	2.618	66.942	65.099	28.453
600	15.814	16.208	9.296	4.147	67.036	64.721	23.573
700	16.610	18.708	10.465	5.770	67.139	63.919	20.083
800	17.225	20.866	11.639	7.462	67.247	63.091	17.461
900	17.614	22.791	12.814	9.214	67.352	62.246	15.418
1000	18.377	24.936	13.912	11.074	67.452	61.362	13.782
1100	18.914	26.713	14.995	12.889	67.549	62.420	12.441
1200	19.427	28.380	16.042	14.806	67.646	62.129	11.315
1300	19.914	29.955	17.052	16.773	67.665	61.589	10.354
1400	20.375	31.448	18.028	18.788	67.734	61.041	9.528
1500	20.810	32.868	18.970	20.848	67.796	60.491	8.813
1600	21.219	34.225	19.881	22.949	67.852	59.933	8.186
1700	21.602	35.523	20.764	25.090	67.902	59.376	7.633
1800	21.959	36.768	21.618	27.269	67.944	58.816	7.141
1900	22.290	37.964	22.447	29.481	67.979	58.251	6.700
2000	22.595	39.115	23.252	31.726	67.977	57.591	6.293
2100	22.874	40.224	24.034	34.000	67.933	56.835	5.915
2200	23.127	41.294	24.794	36.300	67.857	55.984	5.571
2300	23.354	42.327	25.534	38.624	67.749	55.036	5.248
2400	23.554	43.316	26.245	40.969	67.614	54.004	4.941
2500	23.735	44.261	26.921	43.335	67.454	52.890	4.650
2600	23.955	45.227	27.642	45.720	67.265	51.695	4.380
2700	24.155	46.135	28.310	48.126	67.049	50.428	4.131
2800	24.355	47.017	28.963	50.551	66.804	49.094	3.902
2900	24.535	47.875	29.600	52.997	66.530	47.691	3.690
3000	24.735	48.711	30.223	55.462	66.235	46.223	3.483
3100	24.955	49.526	30.833	57.948	65.927	44.699	3.290
3200	25.155	50.321	31.429	60.453	65.602	43.110	3.110
3300	25.355	51.098	32.014	62.979	65.266	41.464	2.940
3400	25.535	51.858	32.586	65.524	64.914	39.762	2.782
3500	25.735	52.602	33.148	68.090	64.545	38.000	2.633
3600	25.955	53.330	33.698	70.675	64.162	36.172	2.495
3700	26.155	54.044	34.238	73.281	63.766	34.281	2.365
3800	26.355	54.744	34.769	75.906	63.356	32.321	2.240
3900	26.535	55.411	35.290	78.552	62.932	30.297	2.120
4000	26.735	56.100	35.802	81.217	62.496	28.217	1.995

Sept. 30, 1952; Dec. 31, 1952; June 30, 1955

TITANIUM DIBORIDE (TiB₂)

(CRYSTAL)

B₂Ti

MOL. WT. = 69.522

ΔH_f⁰ = -66.4 ± 4.0 kcal. mole⁻¹ΔH_f^{298.15} = -68.8 ± 4.0 kcal. mole⁻¹ΔH_m⁰ = [24] kcal. mole⁻¹S^{298.15} = 6.808 ± 0.1 cal. deg.⁻¹ mole⁻¹T_m = 3193°K.

Heat of Formation.

G. M. Kibler, T. P. Lyon, M. J. Linevsky, and V. J. DeSantis, General Electric Co., report No. WADD-TR-60-646, Part IV (August 1964) studied the vapor pressure of the reaction TiB₂(c) + 1/2 C(c) = Ti(g) + 1/2 B₂(c) by comparing the absorption intensity of the 3371.4 Å Ti resonance line of the above reaction at temperature T₁ to Ti(g) over pure titanium metal at temperature T₂. Using JANAF auxiliary data ΔH₂₉₇₅ = 81.612 kcal. mole⁻¹ for the above reaction and ΔH₂₉₈⁰(TiB₂(c)) = -66.9 kcal. mole⁻¹ were calculated.

W. S. Williams, J. Phys. Chem. 65, 2213 (1961) found 2150 ± 25°K. to be the temperature at which TiB₂(c) was formed from a mixture of Ti(c) and B(c). If ΔH₂₁₅₀⁰ is assumed for the reaction TiN(c) + 2B(c) = TiB₂(c) + 3/2 N₂(g) then ΔH₂₉₈⁰(TiB₂(c)) = -70.7 kcal. mole⁻¹. If, however, N₂(g) is 1/2 atm. then ΔH₂₁₅₀⁰ = 4.4 kcal. mole⁻¹ and ΔH₂₉₈⁰(TiB₂(c)) = -66.3 kcal. mole⁻¹. He has also shown by stability comparisons that ΔF and ΔH > 0 for the reaction TiB₂ + 3/2 C = TiC + 1/2 B₂. Thus ΔH₂₉₈⁰ TiB₂ < -51 kcal. mole⁻¹.

F. O. Schissel and O. C. Truison, J. Phys. Chem. 65, 1492 (1962) used a mass spectrometer with Knudsen cells to study the vaporization of the titanium-boron system. Only the set of measurements without excess boron or titanium was used. The value ΔH₂₉₈⁰ = 194.9 kcal. mole⁻¹ for the reaction TiB₂(c) = Ti(g) + 2B(g) was obtained. This corresponds to ΔH₂₉₈⁰(TiB₂(c)) = -62.9 kcal. mole⁻¹ using JANAF auxiliary data.

V. A. Epeibaum and M. I. Starostina, Bor Trudy Konf. Khim. Bora 1 Ego Soedinenii 57 (1955-pub.1956) report ΔH₂₉₈⁰(TiB₂(c)) = -66.85 ± 2.7 kcal. mole⁻¹ from combustion calorimetry.

C. E. Lowell and W. S. Williams, Rev. Sci. Instr. 32, 1120 (1961) used high temperature calorimetry to obtain the heat of formation of TiB₂(c). From their data and JANAF auxiliary data ΔH₂₉₈⁰ TiB₂(c) = -48.2 ± 5 kcal. mole⁻¹ was calculated. We question the adiabaticity of the experiment and believe their value is an upper limit.

ΔH₂₉₈⁰(TiB₂(c)) = -66.8 ± 4 kcal. mole⁻¹ was chosen as representative of the first four investigations.

Heat Capacity and Entropy.

The heat capacity of TiB₂(c) has been determined by the following investigators:

Investigator	Method	Temperature Range
Westrum ¹	Adiabatic Calorimetry	5- 850°K.
Walker et al. ²	Drop calorimeter	373- 377°K.
Southern Research Institute ³	Drop type ice calorimeter	586-2689°K.
Mezaki ⁴	Copper-block drop calorimeter	420-1180°K.
Prophet ⁵	Arc-Imaging furnace	1300-2150°K.
Barriault et al. ⁶	Fulac-method	1733-2417°K.

¹L. Kaufman and E. V. Clougherty, Technical Documentary Report No. RDT-TDR-63-4086 Part 1 p. 239 (Dec. 1963).

²G. E. Walker, C. T. Ewing, and R. R. Miller, J. Phys. Chem. 61, 1682 (1957).

³Southern Research Institute, Technical Documentary Report No. ASD-TDR-62-675 p. 253 (Jan. 1963).

⁴R. Mezaki, M. S. Theiss, University of Wisconsin (1961).

⁵H. Prophet, Annual Report for 1962 of the Dow Chemical Co. to ARPA under Contract AF 04(611)7554.

⁶R. J. Barriault et al., Thermodynamics of Certain Refractory Compounds, AVCO Corporation, report ASD-TDR-61-260, Part I, Vol. 1, (May 1962).

The low temperature data of Westrum¹ and the medium range data of Walker et al.² were used to obtain the C_p of this tabulation. Their data were fitted to a Shomate plot and extrapolated to 4000°K.

S^{298.15} = 6.808 cal. deg.⁻¹ mole⁻¹ was determined by Westrum¹.

Melting Data.

The melting point has been reported as 3063°, 3193°, and 3203°K. by P. W. Glaeser, Trans. AIME 194, 391 (1952), E. Post, F. W. Glaeser, and D. Moskowitz, Acta. Met. 2, 20 (1954), and by O. V. Samonov and O. V. Petrushin, Metalloved. Obrabotka Metalov No. 4, 19 (1955) respectively. The heat of melting is derived from an estimated ΔS_m = 2.5 cal. deg.⁻¹ g. atom⁻¹ at 3193°K. It should be pointed out that an error of 0.5 cal. deg.⁻¹ g. atom⁻¹ in the estimation of ΔS_m is 5 kcal. mole⁻¹ in ΔH_m⁰.

B₂Ti

Titanium Diboride (TiB₂)

(Liquid) Mol. Wt. = 69.522

T, °K.	C _p ^a	S ^b	cal. mole ⁻¹ deg. ⁻¹	(H° - H ₂₉₈ °)/T	cal. mole ⁻¹	ΔH _f ^c	Log K _p
0							
100							
200							
298	10.593	13.455	13.455	.000	- 44.993	- 45.983	33.705
300	10.641	13.455	13.455	.020	- 44.994	- 45.989	33.501
400	13.119	16.957	13.907	1.220	- 45.058	- 46.311	25.302
500	14.739	20.069	14.834	2.618	- 45.135	- 46.615	20.375
600	15.814	22.855	15.943	4.147	- 45.220	- 46.902	17.083
700	17.225	27.613	18.286	7.462	- 45.440	- 47.429	12.956
800	17.814	29.676	19.438	9.214	- 45.545	- 47.671	11.576
900	18.377	31.593	20.559	11.024	- 45.645	- 47.902	10.468
1000	18.914	33.360	21.642	12.889	- 45.742	- 48.125	9.561
1100	19.417	35.007	22.688	14.788	- 45.829	- 48.343	8.860
1200	19.894	36.602	23.699	16.778	- 45.909	- 48.549	8.140
1300	20.375	38.095	24.675	18.768	- 46.027	- 48.740	7.577
1400	20.810	39.515	25.617	20.848	- 46.089	- 48.954	7.089
1500	21.219	40.872	26.528	22.949	- 46.145	- 49.162	6.660
1600	21.600	42.178	27.415	25.069	- 46.197	- 49.363	6.282
1700	21.959	43.441	28.255	27.260	- 46.245	- 49.557	5.953
1800	22.298	44.661	29.054	29.481	- 46.272	- 49.748	5.664
1900	22.595	45.762	29.899	31.726	- 46.300	- 49.934	5.403
2000	22.859	46.871	30.681	34.000	- 46.326	- 50.116	5.168
2100	23.090	47.891	31.415	36.200	- 46.350	- 50.293	4.951
2200	23.298	48.837	32.113	38.300	- 46.372	- 50.467	4.744
2300	23.480	49.708	32.788	40.300	- 46.394	- 50.637	4.544
2400	23.640	50.503	33.445	42.300	- 46.415	- 50.803	4.353
2500	23.780	51.225	34.088	44.300	- 46.435	- 50.965	4.171
2600	23.900	51.875	34.715	46.300	- 46.454	- 51.123	3.998
2700	24.000	52.454	35.327	48.300	- 46.472	- 51.277	3.833
2800	24.090	52.963	35.925	50.300	- 46.489	- 51.427	3.676
2900	24.170	53.411	36.508	52.300	- 46.505	- 51.573	3.525
3000	24.240	53.808	37.075	54.300	- 46.520	- 51.715	3.378
3100	24.300	54.154	37.625	56.300	- 46.534	- 51.853	3.234
3200	24.350	54.450	38.163	58.300	- 46.547	- 51.987	3.091
3300	24.400	54.700	38.685	60.300	- 46.559	- 52.117	2.949
3400	24.450	54.910	39.198	62.300	- 46.570	- 52.243	2.808
3500	24.500	55.080	39.695	64.300	- 46.580	- 52.365	2.668
3600	24.550	55.210	40.178	66.300	- 46.589	- 52.483	2.528
3700	24.600	55.310	40.645	68.300	- 46.597	- 52.597	2.388
3800	24.650	55.380	41.098	70.300	- 46.604	- 52.707	2.248
3900	24.700	55.420	41.538	72.300	- 46.610	- 52.813	2.108
4000	24.750	55.440	41.965	74.300	- 46.615	- 52.915	1.968
4100	24.800	55.450	42.378	76.300	- 46.620	- 53.013	1.828
4200	24.850	55.450	42.778	78.300	- 46.625	- 53.107	1.688
4300	24.900	55.450	43.165	80.300	- 46.629	- 53.197	1.548
4400	24.950	55.450	43.540	82.300	- 46.633	- 53.283	1.408
4500	25.000	55.450	43.905	84.300	- 46.637	- 53.365	1.268
4600	25.050	55.450	44.260	86.300	- 46.640	- 53.443	1.128
4700	25.100	55.450	44.605	88.300	- 46.643	- 53.517	0.988
4800	25.150	55.450	44.940	90.300	- 46.646	- 53.587	0.848
4900	25.200	55.450	45.265	92.300	- 46.648	- 53.653	0.708
5000	25.250	55.450	45.580	94.300	- 46.650	- 53.715	0.568
5100	25.300	55.450	45.885	96.300	- 46.652	- 53.773	0.428
5200	25.350	55.450	46.180	98.300	- 46.654	- 53.827	0.288
5300	25.400	55.450	46.465	100.300	- 46.656	- 53.877	0.148
5400	25.450	55.450	46.740	102.300	- 46.657	- 53.923	0.008
5500	25.500	55.450	47.005	104.300	- 46.658	- 53.965	- 0.132
5600	25.550	55.450	47.260	106.300	- 46.659	- 54.003	- 0.272
5700	25.600	55.450	47.505	108.300	- 46.660	- 54.037	- 0.412
5800	25.650	55.450	47.740	110.300	- 46.661	- 54.067	- 0.552
5900	25.700	55.450	47.965	112.300	- 46.662	- 54.093	- 0.692
6000	25.750	55.450	48.180	114.300	- 46.663	- 54.115	- 0.832

Sept. 30, 1982; Dec. 31, 1982; June 30, 1985

TITANIUM DIBORIDE (TiB₂)

(LIQUID)

B₂Ti

MOL. WT. = 69.522

S_f^{298.15} = [13.455] cal. deg.⁻¹ mole⁻¹ΔH_f^{298.15} = [-44.99] kcal. mole⁻¹T_m = 3193°K.ΔH_m^{298.15} [24] kcal. mole⁻¹T_d = [4250]°K.

Heat of Formation.

ΔH_f^{298.15}(l) was calculated from ΔH_f^{298.15}(c) by adding ΔH_m^{298.15} and the difference between ΔH_m^{298.15} for crystal and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at 2100°K. C_p(l) at and below 2100°K. were assumed to be equal to those of TiB₂(c). Above 2100°K. the heat capacities were estimated to be constant. S_f^{298.15}(l) is calculated based on S_f^{298.15}(c) and an estimated ΔS_m^{298.15} = 2.5 cal. deg.⁻¹ gm. atom⁻¹.

Melting Data.

See TiB₂(c) table for details.

Decomposition Data.

T_d estimated from ΔP_{Td}^{298.15} = 0 for the reaction TiB₂(l) = Ti(g) + 2B(g).B₂Ti

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	III° - II° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	0.000	INFINITE	1.500	76.789	76.789	INFINITE
100	2.840	18.207	1.503	76.789	76.789	17.053
200	7.840	4.716	1.503	76.789	76.789	16.940
298	11.530	8.590	1.500	77.100	76.049	55.743
300	11.569	8.662	1.500	77.100	76.042	55.394
400	13.744	12.328	1.501	77.099	76.042	41.354
500	14.970	13.558	1.501	77.155	75.027	32.027
600	15.729	18.338	11.207	77.272	74.959	27.302
700	16.259	20.804	12.405	77.429	74.571	23.278
800	16.661	23.002	13.595	77.610	74.140	20.253
900	16.991	24.984	14.752	77.804	73.659	17.695
1000	17.245	26.788	15.867	78.016	73.225	16.003
1100	17.489	28.443	16.936	78.258	72.737	14.651
1200	17.733	29.975	17.959	78.472	72.174	13.144
1300	17.977	31.404	18.939	78.729	71.557	12.020
1400	18.221	32.745	19.878	79.095	70.897	10.970
1500	18.465	34.011	20.778	80.471	70.205	10.237
1600	18.709	35.210	21.643	80.553	69.582	9.504
1700	18.953	36.352	22.475	80.863	68.880	8.856
1800	19.197	37.442	23.276	81.134	68.178	8.278
1900	19.441	38.486	24.049	81.375	67.475	7.769
2000	19.685	39.490	24.797	81.710	66.708	7.289
2100	19.929	40.456	25.520	81.900	65.950	6.863
2200	20.173	41.389	26.220	87.164	65.015	6.458
2300	20.417	42.291	26.899	87.435	64.003	6.081
2400	20.661	43.165	27.550	87.691	62.975	5.734
2500	20.905	44.013	28.200	88.005	61.875	5.395
2600	21.149	44.838	28.824	88.612	60.242	5.064
2700	21.393	45.641	29.432	89.009	58.749	4.755
2800	21.637	46.423	30.025	89.253	57.253	4.460
2900	21.881	47.184	30.604	89.769	55.745	4.181
3000	22.125	47.933	31.169	90.497	54.242	3.951
3100	22.369	48.662	31.725	92.585	52.735	3.718
3200	22.613	49.376	32.262	94.765	51.221	3.498
3300	22.857	50.076	32.791	96.680	49.705	3.292
3400	23.101	50.766	33.311	98.680	48.180	3.097
3500	23.345	51.435	33.818	99.680	46.659	2.915
3600	23.589	52.096	34.317	100.643	45.164	2.742
3700	23.833	52.745	34.806	100.582	43.669	2.578
3800	24.077	53.384	35.287	100.496	42.135	2.423
3900	24.321	54.013	35.761	100.381	40.596	2.277
4000	24.565	54.632	36.223	100.240	39.058	1.003

Sept. 30, 1962; Mar. 31, 1963; June 30, 1965

ZIRCONIUM DIBORIDE (ZrB₂) (CRYSTAL)

MOL. WT. = 112.842

$\Delta H_f^0 = -76.8 \pm 1.6$ kcal. mole⁻¹
 $\Delta H_f^{298.15} = -77.1 \pm 1.6$ kcal. mole⁻¹
 $\Delta H_m^0 = [25]$ kcal. mole⁻¹
 $T_m = 3323^\circ K.$

Heat of Formation.

G. K. Johnson, Argonne National Laboratory, private communication, May 1965, reported ΔH_f^{298} (ZrB₂) = -76.7 ± 1.5 kcal. mole⁻¹. Their value was obtained by fluorine bomb calorimetry and was based on their recently redetermined value of $\Delta H_f^{298}(BF_3(g)) = -271.90 \pm 0.20$ kcal. mole⁻¹.
 G. M. Kibler, T. P. Lyon, M. J. Linavsky, and V. J. De Santis, General Electric Co., report No. WADD-TR-60-646, Part IV (August 1964) studied the vaporization of ZrB₂ by the Knudsen effusion method. Over the range 2260 to 2500°K., $\log K_p = 22.038 - \frac{10118}{T}$. For the reaction ZrB₂(s) = Zr(g) + 1.331 B(g), JANAP auxiliary data were used to calculate $\Delta H_f^{298} = 478.5 \pm 1.5$ kcal. mole⁻¹ by the 3rd law method and ΔH_f^{298} (ZrB₂(s)) = -76.7 ± 3.2 kcal. mole⁻¹.
 O. C. Trulsson and H. M. Goldstein, Union Carbide Res. Inat., report No. C-25 (October 1964), investigated the decomposition vapor pressure of the reaction ZrB₂(s) = Zr(g) + 2B(g) and reported ΔH_f^{298} (ZrB₂(s)) = -72.1 ± 5.3 kcal. mole⁻¹. They also reported ΔH_f^{298} = 289.7 kcal. mole⁻¹ for the reaction ZrB₂(s) + C(s) = ZrC(s) + 2B(g). Using the JANAP ΔH_f^{298} (ZrC(s)) = -47.0 ± 3 kcal. mole⁻¹, ΔH_f^{298} (ZrB₂(s)) = -76.1 ± 3 kcal. mole⁻¹ was calculated. JANAP values for ΔH_f^{298} B(g) and Zr(g) were not used since their independent determinations serve to cancel instrumental constants.
 From oxygen bomb calorimetry, E. J. Huber, Jr., E. L. Head, and C. E. Hollay, Jr., J. Phys. Chem. **68**, 3040 (1964) reported ΔH_f^{298} (ZrB₂(s)) = -77.2 ± 1.2 kcal. mole⁻¹.
 ΔH_f^{298} (ZrB₂(s)) = -77.1 ± 1.6 was chosen as a value representative of the above.

Heat Capacity and Entropy.

The heat capacity of ZrB₂(s) has been determined by the following investigators:

Investigator	Method	Temperature Range
Westrum and Feick ¹	Adiabatic calorimetry	5-350°K.
Valentine et al. ²	Copper-block drop calorimeter	410-1125°K.
Mazaki ³	Copper-block drop calorimeter	430-1170°K.
Prophet ⁴	Arc-furnace furnace	1300-2150°K.
Barriault et al. ⁵	Pulse-method	1740-2520°K.
Southern Research Institute ⁶	Drop type ica calorimeter	500-2500°K.

1. E. F. Westrum, Jr. and G. Feick, J. Chem. Eng. Data **8**(2), 183 (1963).
2. R. H. Valentine, T. P. Jambois, and J. L. Margrave, J. Chem. Eng. Data **9**(2), 182 (1964).
3. R. Mazaki, M. S. Thesis, University of Wisconsin (1961).
4. H. Prophet, Annual Report for 1962 of the Dow Chemical Co. to ARPA under Contract AF 04(611)7554.
5. R. J. Barriault et al., Thermodynamics of Certain Refractory Compounds, AVCO Corporation, report ASD-TR-61-260, Part I, Vol. 1, (May 1962).
6. D. Neel, C. Peers, and S. Oglesby, Southern Research Institute, report ASD-TRD-62-675 (August 1962).

Westrum and Feick's C_p values were adopted to 350°K. The disparities in heat capacities above room temperatures seem too great to be errors in measurement and are probably due to sample differences. Since the samples used by Westrum and Feick¹ and by Valentine et al.² were from the same batch, Valentine's data were used above 350°K. The two sets of data were fitted to a Shomate plot which was extrapolated to 4000°K. However, in consideration of the results of Mazaki³, Prophet⁴, and Southern Research Institute⁶, the C_p extrapolation ran somewhat higher than a direct extrapolation of Valentine's data would yield.

$S_{298.15}^{298.15}(ZrB_2) = 6.59$ cal. mole⁻¹ °K.⁻¹ was determined by Westrum¹.

Melting Data.

The melting point has been reported as 3313°, 3323°, and 3285°K. by P. Glaeser and B. Post, J. of Metals, **5**, 1117 (1953), B. Post, P. Glaeser, and D. W. Moskowitz, Acta. Met. **2**, 70 (1954) and H. Greenwood, Engineer **137**, 349 (1949) respectively. The heat of melting is derived from an estimated $\Delta S_m = 2.5$ cal. deg.⁻¹ g. atom⁻¹ at 3323°K. It should be pointed out that an error of 0.5 cal. deg.⁻¹ g. atom⁻¹ in the estimation of ΔS_m is 5 kcal. mole⁻¹ in ΔH_m^0 .

Zirconium Diboride (ZrB₂)

(Liquid) Mol. Wt. = 112.842

B₂Zr

MOL. WT. = 112.842

ZIRCONIUM DIBORIDE (ZrB₂)

(LIQUID)

$$\Delta H_f^{298.15} = [15.448] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^{298.15} = [25] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{298.15} = [15.448] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 3323^\circ\text{K.}$$

$$T_d = [4466]^\circ\text{K.}$$

Heat of Formation.

$\Delta H_f^{298.15}(l)$ was calculated from $\Delta H_f^{298.15}(c)$ by adding $\Delta H_m^{298.15}$ and the difference between $\Delta H_m^{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at 2200°K. $C_p(l)$ at and below 2200°K. were assumed to be equal to those of ZrB₂(c). Above 2200°K. the heat capacities were estimated to be constant. $S_{298.15}^{298.15}(c)$ and an estimated $\Delta S_m^{298.15} = 2.5 \text{ cal. deg.}^{-1} \text{ gm. atom}^{-1}$.

Melting Data.

See ZrB₂(c) table for details.

Decomposition Data.

T_d estimated from $\Delta F_{T_d}^{298.15} = 0$ for the reaction $\text{ZrB}_2(l) = \text{Zr}(g) + 2\text{B}(g)$.

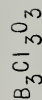
T, °K.	C _p ^o	S ^o	-(F ^o -H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _f
100							
200	11.530	15.448	15.448	.000	-54.194	-55.187	40.452
298	11.589	15.520	15.448	.021	-54.194	-55.194	40.207
300	11.590	15.520	15.448	.021	-54.194	-55.194	40.207
400	11.670	15.600	15.520	.080	-54.194	-55.194	39.938
500	11.750	15.680	15.600	.160	-54.194	-55.194	39.669
600	11.830	15.760	15.680	.240	-54.194	-55.194	39.400
700	11.910	15.840	15.760	.320	-54.194	-55.194	39.131
800	11.990	15.920	15.840	.400	-54.194	-55.194	38.862
900	12.070	16.000	15.920	.480	-54.194	-55.194	38.593
1000	12.150	16.080	16.000	.560	-54.194	-55.194	38.324
1100	12.230	16.160	16.080	.640	-54.194	-55.194	38.055
1200	12.310	16.240	16.160	.720	-54.194	-55.194	37.786
1300	12.390	16.320	16.240	.800	-54.194	-55.194	37.517
1400	12.470	16.400	16.320	.880	-54.194	-55.194	37.248
1500	12.550	16.480	16.400	.960	-54.194	-55.194	36.979
1600	12.630	16.560	16.480	1.040	-54.194	-55.194	36.710
1700	12.710	16.640	16.560	1.120	-54.194	-55.194	36.441
1800	12.790	16.720	16.640	1.200	-54.194	-55.194	36.172
1900	12.870	16.800	16.720	1.280	-54.194	-55.194	35.903
2000	12.950	16.880	16.800	1.360	-54.194	-55.194	35.634
2100	13.030	16.960	16.880	1.440	-54.194	-55.194	35.365
2200	13.110	17.040	16.960	1.520	-54.194	-55.194	35.096
2300	13.190	17.120	17.040	1.600	-54.194	-55.194	34.827
2400	13.270	17.200	17.120	1.680	-54.194	-55.194	34.558
2500	13.350	17.280	17.200	1.760	-54.194	-55.194	34.289
2600	13.430	17.360	17.280	1.840	-54.194	-55.194	34.020
2700	13.510	17.440	17.360	1.920	-54.194	-55.194	33.751
2800	13.590	17.520	17.440	2.000	-54.194	-55.194	33.482
2900	13.670	17.600	17.520	2.080	-54.194	-55.194	33.213
3000	13.750	17.680	17.600	2.160	-54.194	-55.194	32.944
3100	13.830	17.760	17.680	2.240	-54.194	-55.194	32.675
3200	13.910	17.840	17.760	2.320	-54.194	-55.194	32.406
3300	13.990	17.920	17.840	2.400	-54.194	-55.194	32.137
3400	14.070	18.000	17.920	2.480	-54.194	-55.194	31.868
3500	14.150	18.080	18.000	2.560	-54.194	-55.194	31.599
3600	14.230	18.160	18.080	2.640	-54.194	-55.194	31.330
3700	14.310	18.240	18.160	2.720	-54.194	-55.194	31.061
3800	14.390	18.320	18.240	2.800	-54.194	-55.194	30.792
3900	14.470	18.400	18.320	2.880	-54.194	-55.194	30.523
4000	14.550	18.480	18.400	2.960	-54.194	-55.194	30.254
4100	14.630	18.560	18.480	3.040	-54.194	-55.194	29.985
4200	14.710	18.640	18.560	3.120	-54.194	-55.194	29.716
4300	14.790	18.720	18.640	3.200	-54.194	-55.194	29.447
4400	14.870	18.800	18.720	3.280	-54.194	-55.194	29.178
4500	14.950	18.880	18.800	3.360	-54.194	-55.194	28.909
4600	15.030	18.960	18.880	3.440	-54.194	-55.194	28.640
4700	15.110	19.040	18.960	3.520	-54.194	-55.194	28.371
4800	15.190	19.120	19.040	3.600	-54.194	-55.194	28.102
4900	15.270	19.200	19.120	3.680	-54.194	-55.194	27.833
5000	15.350	19.280	19.200	3.760	-54.194	-55.194	27.564
5100	15.430	19.360	19.280	3.840	-54.194	-55.194	27.295
5200	15.510	19.440	19.360	3.920	-54.194	-55.194	27.026
5300	15.590	19.520	19.440	4.000	-54.194	-55.194	26.757
5400	15.670	19.600	19.520	4.080	-54.194	-55.194	26.488
5500	15.750	19.680	19.600	4.160	-54.194	-55.194	26.219
5600	15.830	19.760	19.680	4.240	-54.194	-55.194	25.950
5700	15.910	19.840	19.760	4.320	-54.194	-55.194	25.681
5800	15.990	19.920	19.840	4.400	-54.194	-55.194	25.412
5900	16.070	20.000	19.920	4.480	-54.194	-55.194	25.143
6000	16.150	20.080	20.000	4.560	-54.194	-55.194	24.874

Sept. 30, 1962; Dec. 31, 1962; June 30, 1965

B₂Zr

Boron Oxide Chloride, Trimeric ((BOCl)₃)₃

(Ideal Gas) Mol. Wt. = 186.831



BORON OXIDE CHLORIDE, TRIMERIC ((BOCl)₃)₃ (IDEAL GAS) MOL. WT. = 186.831

Point Group [D_{3h}]
 $\Delta H_f^\circ 0 = -389 \pm 2 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -390 \pm 2 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies		
ω_e, cm^{-1}	ω_e, cm^{-1}	ω_e, cm^{-1}
[807] (1)	[980] (2)	[600] (1)
[690] (1)	[1300] (2)	[140] (1)
[333] (1)	[920] (2)	[400] (2)
[1037] (1)	[390] (2)	[120] (2)
[400] (1)	[150] (2)	

Bond Distances: B-Cl = [1.75]Å B-O = [1.36]Å

Bond Angle: Cl-B-O = [120°] B-O-B = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [1.86850 \times 10^{-111}] \text{ g.}^3 \text{ cm.}^6$

$\sigma = 6$

Heat of Formation.

The equilibrium constants for the reaction $\text{B}_2\text{O}_3(1) + \text{BCl}_3(g) = (\text{BOCl})_3(g)$ were determined in the temperature range 536-825°K. by a transpiration method by J. Blauer and M. Farber, J. Chem. Phys. **39**, 158 (1963) and in the temperature range 1234-1309°K. by an effusion method by the same investigators, Trans. Faraday Soc. **50**, 301 (1964). Using the reported equilibrium constants, the enthalpy changes for this reaction were evaluated by both the second and third law methods. The results obtained are given in the following table.

Method Used	$\Delta H_f^\circ 298.15^\circ \text{ kcal. mole}^{-1}$	
	Third Law Value	Second Law Value
Transpiration	5.31	5.07 ± 0.4
Effusion	12.57	5.85 ± 3.3
*Based on the third law values		

By a mass spectroscopic method the enthalpy change, $\Delta H_f^\circ 1000 = 16.6 \pm 2.5 \text{ kcal. mole}^{-1}$, for the reaction $\text{BOCl}_3(g) + \text{B}_2\text{O}_3(1) = (\text{BOCl})_3(g)$ was determined by R. P. Porter and S. K. Gupta, J. Phys. Chem. **68**, 280 (1964). The $\Delta H_f^\circ 298.15$ value for $(\text{BOCl})_3(g)$ was derived as $-377 \pm 3 \text{ kcal. mole}^{-1}$. However, it is possible that the intensity of $\text{B}_2\text{O}_3\text{Cl}_3^+$ employed to plot the ion ratios $[(\text{B}_2\text{O}_3\text{Cl}_3^+)/(\text{BOCl}_2^+)]$ versus $\frac{1}{M}$ does not fully reflect the concentration of $\text{B}_2\text{O}_3\text{Cl}_3$ especially at the highest temperatures, due to changes in the fragmentation pattern with temperature.

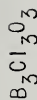
The value of $\Delta H_f^\circ 298.15$ adopted for $(\text{BOCl})_3(g)$ is $-390 \pm 2 \text{ kcal. mole}^{-1}$ derived from transpiration data. The effusion data were measured in the temperature range where Porter and Gupta, loc. cit. found the presence of $(\text{BOCl})_4(g)$. However, this point was not taken into consideration in the report. Hence, the corresponding $\Delta H_f^\circ 298.15$ value was not adopted.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with related molecules such as $\text{B}_2\text{O}_3(g)$ and $(\text{BH}_2\text{O})_3(g)$. The B-Cl bond distance was assumed to be the same as that in $\text{BOCl}_3(g)$. The B-O bond distance and all bond angles were estimated. The three principal moments of inertia are: $I_A = I_B = 9.7785 \times 10^{-38}$ and $I_C = 1.95517 \times 10^{-37} \text{ g. cm.}^2$

Dec. 31, 1960; Mar. 31, 1963; Sept. 30, 1963; June 30, 1964; Mar. 31, 1965

T. °K.	C _p	S°	$-(H^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	.000	INFINITE	- 6.057	- 388.778	- 388.778	- 388.778	INFINITE
100	16.750	65.733	114.858	- 4.912	- 389.314	- 389.314	837.693
200	25.139	80.088	94.052	- 2.793	- 389.994	- 376.742	411.664
298	31.436	91.367	.000	.000	- 390.000	- 370.238	271.379
300	31.538	91.562	.0098	- 389.999	- 370.117	- 370.117	269.617
400	36.250	101.318	3.461	- 389.874	- 363.505	- 363.505	198.600
500	39.618	109.792	95.262	- 389.685	- 356.933	- 356.933	156.008
600	41.975	117.236	98.317	- 389.456	- 350.402	- 350.402	127.628
700	43.646	123.639	15.637	- 389.204	- 343.912	- 343.912	107.569
800	44.894	129.750	104.669	- 388.930	- 337.463	- 337.463	92.186
900	45.747	135.087	107.757	- 388.660	- 331.045	- 331.045	80.385
1000	46.421	139.943	110.736	- 388.387	- 324.655	- 324.655	70.950
1100	46.940	144.393	113.497	- 388.134	- 318.298	- 318.298	63.237
1200	47.347	148.436	115.374	- 387.898	- 311.998	- 311.998	56.813
1300	47.672	152.259	118.938	- 387.687	- 305.640	- 305.640	51.380
1400	47.934	155.842	121.468	- 387.499	- 299.334	- 299.334	46.726
1500	48.149	159.156	123.871	- 387.343	- 293.045	- 293.045	42.695
1600	48.327	162.270	126.174	- 387.215	- 286.761	- 286.761	39.166
1700	48.476	165.200	128.385	- 387.115	- 280.483	- 280.483	36.069
1800	48.602	167.978	130.508	- 387.047	- 274.215	- 274.215	33.293
1900	48.709	170.606	132.550	- 387.001	- 267.946	- 267.946	30.819
2000	48.802	173.110	134.516	- 386.975	- 261.682	- 261.682	28.594
2100	48.881	175.593	136.411	- 386.966	- 255.417	- 255.417	26.580
2200	48.951	177.769	138.240	- 386.946	- 249.134	- 249.134	24.750
2300	49.012	179.946	140.006	- 386.940	- 242.888	- 242.888	23.079
2400	49.065	182.033	141.714	- 387.059	- 236.616	- 236.616	21.546
2500	49.113	184.037	143.367	- 387.059	- 230.321	- 230.321	20.108
2600	49.155	185.964	144.968	- 387.059	- 224.024	- 224.024	18.752
2700	49.193	187.820	146.588	- 387.059	- 217.724	- 217.724	17.480
2800	49.227	189.610	148.208	- 387.059	- 211.424	- 211.424	16.300
2900	49.257	191.337	149.842	- 387.059	- 205.124	- 205.124	15.223
3000	49.285	193.008	150.915	- 387.059	- 198.824	- 198.824	14.229
3100	49.310	194.634	152.299	- 387.059	- 192.524	- 192.524	13.281
3200	49.333	196.190	153.646	- 387.059	- 186.224	- 186.224	12.381
3300	49.353	197.709	154.959	- 387.059	- 179.924	- 179.924	11.535
3400	49.372	199.182	156.238	- 387.059	- 173.624	- 173.624	10.768
3500	49.389	200.614	157.485	- 387.059	- 167.324	- 167.324	10.026
3600	49.405	202.005	158.703	- 387.059	- 161.024	- 161.024	9.324
3700	49.419	203.359	159.892	- 387.059	- 154.724	- 154.724	8.660
3800	49.433	204.677	161.053	- 387.059	- 148.424	- 148.424	8.031
3900	49.445	205.961	162.188	- 387.059	- 142.124	- 142.124	7.435
4000	49.457	207.213	163.298	- 387.059	- 135.824	- 135.824	6.816
4100	49.468	208.435	164.384	- 387.059	- 129.524	- 129.524	6.242
4200	49.478	209.627	165.447	- 387.059	- 123.224	- 123.224	5.717
4300	49.487	210.791	166.488	- 387.059	- 116.924	- 116.924	5.230
4400	49.496	211.929	167.508	- 387.059	- 110.624	- 110.624	4.780
4500	49.504	213.041	168.508	- 387.059	- 104.324	- 104.324	4.363
4600	49.512	214.129	169.488	- 387.059	- 98.024	- 98.024	3.978
4700	49.519	215.194	170.449	- 387.059	- 91.724	- 91.724	3.623
4800	49.525	216.237	171.392	- 387.059	- 85.424	- 85.424	3.297
4900	49.532	217.258	172.317	- 387.059	- 79.124	- 79.124	2.999
5000	49.538	218.259	173.226	- 387.059	- 72.824	- 72.824	2.726
5100	49.543	219.240	174.119	- 387.059	- 66.524	- 66.524	2.477
5200	49.548	220.202	174.996	- 387.059	- 60.224	- 60.224	2.250
5300	49.553	221.144	175.858	- 387.059	- 53.924	- 53.924	2.044
5400	49.558	222.072	176.705	- 387.059	- 47.624	- 47.624	1.857
5500	49.562	222.982	177.538	- 387.059	- 41.324	- 41.324	1.686
5600	49.567	223.875	178.358	- 387.059	- 35.024	- 35.024	1.529
5700	49.571	224.752	179.164	- 387.059	- 28.724	- 28.724	1.385
5800	49.574	225.614	179.957	- 387.059	- 22.424	- 22.424	1.254
5900	49.578	226.462	180.739	- 387.059	- 16.124	- 16.124	1.134
6000	49.581	227.295	181.508	- 387.059	- 9.824	- 9.824	1.024

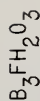


Monofluoroboroxin ($B_3O_3H_2F$)

(Ideal Gas) Mol. Wt. = 101.4554

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	+∞	+∞	INFINITE	-	4.273	-379.205	-379.205	INFINITE
100	11.162	57.652	91.583	3.393	-380.520	-375.559	-375.559	820.744
200	18.744	75.225	107.525	3.820	-382.000	-369.536	-369.536	156.742
298	22.764	75.225	75.225	0.000	-382.000	-364.731	-364.731	267.532
400	22.863	75.367	75.226	.042	-382.012	-364.625	-364.616	265.616
500	22.749	82.635	76.184	2.860	-382.586	-358.738	-358.738	195.996
600	31.713	89.269	78.147	5.561	-383.043	-352.721	-352.721	154.167
700	34.866	95.341	80.514	8.896	-383.381	-346.622	-346.622	126.251
800	37.367	100.911	83.036	12.512	-383.608	-340.475	-340.475	106.296
900	39.354	106.035	85.595	16.352	-383.739	-334.307	-334.307	91.324
1000	40.941	110.766	88.132	20.370	-383.790	-328.125	-328.125	79.676
1100	42.218	115.148	90.617	24.530	-383.786	-321.936	-321.936	70.356
1200	43.254	119.222	93.035	28.806	-383.753	-315.755	-315.755	62.732
1300	44.100	123.023	95.377	33.175	-383.695	-309.573	-309.573	56.378
1400	44.799	126.581	97.642	37.621	-383.632	-303.400	-303.400	51.004
1500	45.380	129.923	99.834	42.131	-383.567	-297.229	-297.229	46.397
1600	45.867	133.071	101.942	46.694	-383.515	-291.067	-291.067	42.406
1700	46.279	136.045	103.981	51.301	-383.477	-284.904	-284.904	38.914
1800	46.630	138.861	105.951	55.947	-383.455	-278.742	-278.742	35.833
1900	46.930	141.535	107.854	60.626	-383.453	-272.586	-272.586	33.095
2000	47.190	144.080	109.694	65.332	-383.466	-266.426	-266.426	30.645
2100	47.415	146.506	111.475	70.063	-383.491	-260.264	-260.264	28.443
2200	47.612	148.824	113.199	74.814	-383.531	-254.100	-254.100	26.443
2300	47.785	151.043	114.869	79.584	-383.588	-247.936	-247.936	24.629
2400	47.937	153.171	116.488	84.370	-383.657	-241.771	-241.771	22.972
2500	48.072	155.214	118.059	89.171	-383.746	-235.595	-235.595	21.453
2600	48.192	157.179	119.585	93.984	-400.013	-229.399	-229.399	20.027
2700	48.299	159.071	121.068	98.809	-400.108	-223.259	-223.259	18.682
2800	48.396	160.896	122.509	103.644	-400.209	-217.143	-217.143	17.446
2900	48.482	162.657	123.912	108.488	-400.316	-211.071	-211.071	16.279
3000	48.561	164.360	125.277	113.340	-400.429	-205.049	-205.049	15.201
3100	48.632	166.008	126.608	118.200	-400.549	-199.065	-199.065	14.195
3200	48.696	167.603	127.905	123.066	-400.673	-193.007	-193.007	13.254
3300	48.755	169.150	129.169	127.939	-400.806	-186.944	-186.944	12.371
3400	48.809	170.651	130.404	132.817	-400.946	-180.874	-180.874	11.541
3500	48.858	172.109	131.609	137.700	-401.092	-174.760	-174.760	10.760
3600	48.903	173.526	132.787	142.588	-401.246	-168.534	-168.534	10.024
3700	48.945	174.904	133.937	147.481	-401.406	-162.347	-162.347	9.327
3800	48.983	176.246	135.063	152.377	-401.576	-156.164	-156.164	8.669
3900	49.019	177.553	136.164	157.277	-401.750	-150.000	-150.000	8.044
4000	49.052	178.826	137.242	162.181	-401.933	-143.852	-143.852	7.452
4100	49.082	180.069	138.297	167.088	-402.125	-137.722	-137.722	6.897
4200	49.110	181.281	139.330	171.997	-402.327	-131.605	-131.605	6.377
4300	49.137	182.465	140.343	176.910	-402.536	-125.500	-125.500	5.887
4400	49.162	183.621	141.337	181.825	-402.750	-119.413	-119.413	5.426
4500	49.184	184.752	142.310	186.742	-402.968	-113.342	-113.342	4.991
4600	49.206	185.857	143.266	191.661	-403.190	-107.282	-107.282	4.579
4700	49.226	186.939	144.204	196.583	-403.416	-101.232	-101.232	4.187
4800	49.245	187.998	145.124	201.507	-403.646	-95.192	-95.192	3.822
4900	49.263	189.035	146.028	206.432	-403.880	-89.161	-89.161	3.483
5000	49.280	190.051	146.916	211.359	-404.118	-83.140	-83.140	3.167
5100	49.295	191.047	147.789	216.288	-404.360	-77.128	-77.128	2.872
5200	49.310	192.023	148.647	221.218	-404.606	-71.125	-71.125	2.596
5300	49.324	192.981	149.490	226.150	-404.856	-65.130	-65.130	2.338
5400	49.337	193.920	150.320	231.083	-405.110	-59.142	-59.142	2.094
5500	49.350	194.843	151.136	236.017	-405.368	-53.161	-53.161	1.863
5600	49.362	195.748	151.939	240.952	-405.630	-47.186	-47.186	1.644
5700	49.373	196.638	152.729	245.890	-405.896	-41.225	-41.225	1.436
5800	49.383	197.512	153.507	250.827	-406.166	-35.276	-35.276	1.238
5900	49.394	198.371	154.273	255.766	-406.440	-29.340	-29.340	1.050
6000	49.403	199.215	155.028	260.706	-406.718	-23.416	-23.416	0.872
6100	49.412	200.045	155.771	265.647	-407.000	-17.502	-17.502	0.704

Mar. 31, 1963; Sept. 30, 1963; Mar. 31, 1965; Dec. 31, 1965



MOL. WT. = 101.44554

(IDEAL GAS)

MONOFUOROBOROXIN ($B_3O_3H_2F$)

$\Delta H_f^0 = -379 \pm 6 \text{ kcal. mole}^{-1}$

$\Delta H_f^0 298.15 = -382 \pm 6 \text{ kcal. mole}^{-1}$

Point Group [C_{2v}]

$S_{298.15}^0 = [75.225] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies			
ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
[2100] (1)	[890] (1)	[350] (1)	
[870] (1)	[1460] (1)	[225] (1)	
[670] (1)	[520] (1)	[800] (1)	
[2200] (1)	[2230] (1)	[225] (1)	
[1390] (1)	[840] (1)	[840] (1)	
[1200] (1)	[1200] (1)	[800] (1)	
[890] (1)	[350] (1)	[260] (1)	

Bond Distances: B-O = [1.36] Å B-H = [1.18] Å B-F = [1.41] Å

Bond Angle: B-O-B = [120°] O-B-H = [120°] O-B-F = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [2.1654] \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$

$\sigma^- = [2]$

Heat of Formation.

The equilibrium constants (K), 1246-1396°K. for the two reactions $2B_3O_3 \cdot 2H_2(g) = B_3O_3 \cdot 2H_2(g) + B_3O_3 \cdot 2H_2(g)$ and $2B_3O_3 \cdot 2H_2(g) = B_3O_3 \cdot 2H_2(g) + B_3O_3 \cdot 2H_2(g)$ were reported by P. R. Porter and W. F. Sholette, J. Chem. Phys. 57, 198 (1962). The $\Delta H_f^0 298.15$ for $B_3O_3 \cdot 2H_2(g)$ adopted was evaluated by use of K values slightly outside the ranges given by Porter and Sholette. See the table for $B_3O_3 \cdot 2H_2(g)$ for details.

Heat Capacity and Entropy.

The structure was assumed to be a planar six membered ring structure of C_{2v} symmetry, which has 21 vibrations of the type B_{1g} , B_{2g} , $2A_{2g}$, and $4B_{2g}$. These frequencies were estimated from the values for boroxin and trifluoroboroxin, the symmetry being reduced from D_{3h} as follows: $2A_{1g} \rightarrow 3A_{1g}$, $2A_{2g} \rightarrow 2B_{1g}$, $5E_{1g} \rightarrow 5B_{1g}$, $2A_{2g} \rightarrow 2B_{2g}$ and $2E_{2g} \rightarrow 2A_{2g} + 2B_{2g}$.

The B-F distance was taken as approximately equal to that in $(CH_3)_2O \cdot BF_3$ reported by S. H. Bauer, O. R. Fendley and A. W. Leubengayer, J. Am. Chem. Soc. 57, 339 (1945). The other bond lengths and angles were taken equal to those in boroxin. The individual moments of inertia were calculated to be $I_A = 32.995 \times 10^{-39}$, $I_B = 13.973 \times 10^{-39}$, and $I_C = 46.968 \times 10^{-39} \text{ g. cm.}^2$.



Point Group [C_{2v}]
 $\Delta H_f^\circ = -472 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = -475 \pm 5 \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [78.6] \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}	ω_e, cm^{-1}
[1650] (1)	[660] (1)	[300] (1)
[830] (1)	[1370] (1)	[220] (1)
[610] (1)	[490] (1)	[710] (1)
[1800] (1)	[1840] (1)	[220] (1)
[1385] (1)	[1385] (1)	[780] (1)
[1080] (1)	[1080] (1)	[700] (1)
[680] (1)	[310] (1)	[230] (1)

Bond Distances: B-O = [1.36] Å B-H = [1.18] Å B-F = [1.41] Å
 Bond Angle: B-O-B = [120°] O-B-H = [120°] O-B-F = [120°]
 Product of the Moments of Inertia: $I_A I_B I_C = [7.5869] \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$

$\sigma^\circ = [2]$

Heat of Formation.

The stabilities of gaseous boroxin (B₃O₃H₃) and its fluoro derivatives have been studied by R. P. Porter and W. P. Sholette, J. Chem. Phys. 31, 198 (1959). From the mass spectra of the gaseous reaction products generated by reaction of an H₂-B₃O₃ mixture on B₂O₃ at 1250°K, the equilibrium constants (K) for the following proposed reactions were reported.

Reaction	Temperature, °K.	K	ΔH_f° , kcal. mole ⁻¹
(1) H ₂ (g) + B ₃ O ₃ H ₃ (g) = HF(g) + B ₃ O ₃ H ₂ (g)	1246 - 1326	4.2×10^{-3}	20.45 - 17.17
(2) 2B ₃ O ₃ H ₂ (g) = B ₃ O ₃ H ₂ (g) + B ₃ O ₃ H ₃ (g)	1246 - 1326	0.62 - 0.46	1.28 - 2.15
(3) 2B ₃ O ₃ H ₂ (g) = B ₃ O ₃ H ₂ (g) + B ₃ O ₃ H ₃ (g)	1246 - 1326	1.0 - 0.63	-2.56 - -1.51

Using these reported K values the corresponding enthalpy changes (ΔH_f° , 298.15°) were evaluated by the third law method. The results obtained are listed in the above table. Based on ΔH_f° , 298.15° = -565.3 and -64.8 kcal. mole⁻¹ for B₃O₃H₂(g) and HF(g), respectively, the value of ΔH_f° , 298.15° for B₃O₃H₃(g) was calculated from Reaction (1) as -482 kcal. mole⁻¹. From Reaction (2), the ΔH_f° , 298.15° value for B₃O₃H₂(g) was calculated as -397 kcal. mole⁻¹. However, employing ΔH_f° , 298.15° (B₃O₃H₃, g) = -591 kcal. mole⁻¹, the values of ΔH_f° , 298.15° for B₃O₃H₂(g) and B₃O₃H₃(g) thus obtained do not fit properly for Reaction (3). Therefore the ΔH_f° , 298.15° for B₃O₃H₂(g) and B₃O₃H₃(g) adopted were evaluated by use of K values slightly outside the ranges given by Porter and Sholette.

Heat Capacity and Entropy.

The vibrational frequencies were obtained by comparison with B₃O₃F₃(g) and B₃H₃O₃(g). The type of vibration and symmetry are identical to those given for B₃O₃F₃(g). The bond angles and lengths were taken equal to those for B₃O₃F₃(g). The individual moments of inertia were calculated to be $I_A = 22.051 \times 10^{-35}$, $I_B = 46.659 \times 10^{-35}$ and $I_C = 70.710 \times 10^{-35} \text{ g. cm.}^2$

T, °K.	C _p	S°	(-F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	Log K _p
0	0.000	INFINITE	-	4.571	-472.461	INFINITE
100	11.771	59.365	-	3.672	-468.147	1023.084
200	18.724	69.975	-	2.162	-474.435	505.117
300	24.744	78.608	-	0.000	-475.000	334.365
400	29.837	86.619	79.646	2.789	-475.009	332.219
500	33.785	93.719	81.762	5.979	-475.415	245.676
600	36.957	100.162	84.301	9.517	-475.910	193.712
700	39.230	106.030	86.992	13.327	-476.026	150.040
800	41.066	111.394	89.712	17.345	-476.059	134.283
900	42.495	116.316	92.398	21.526	-476.029	115.706
1000	43.618	120.854	95.020	25.834	-475.960	101.256
1100	44.512	125.055	97.562	30.242	-475.878	89.698
1200	45.230	128.960	100.018	34.731	-475.806	80.243
1300	45.814	132.604	102.386	39.284	-475.782	72.365
1400	46.294	136.017	104.667	43.860	-475.697	65.700
1500	46.692	139.225	106.865	48.500	-475.540	59.988
1600	47.026	142.250	108.983	53.226	-475.492	55.040
1700	47.308	145.109	111.025	57.943	-475.465	50.710
1800	47.548	147.820	112.994	62.686	-475.447	46.889
1900	47.755	150.397	114.896	67.452	-475.447	43.494
2000	47.933	152.851	116.733	72.236	-475.501	40.456
2100	48.088	155.193	118.509	77.038	-475.544	37.721
2200	48.223	157.434	120.228	81.853	-475.605	35.247
2300	48.342	159.580	121.892	86.682	-475.680	32.997
2400	48.448	161.640	123.506	91.521	-475.775	30.843
2500	48.541	163.619	125.071	96.371	-475.889	28.789
2600	48.625	165.525	126.590	101.229	-475.932	26.843
2700	48.699	167.361	128.067	106.095	-475.981	24.911
2800	48.766	169.134	129.502	110.969	-476.036	23.000
2900	48.827	170.846	130.898	115.848	-476.097	21.111
3000	48.882	172.502	132.257	120.734	-476.166	19.252
3100	48.931	174.106	133.582	125.625	-476.242	17.433
3200	48.976	175.660	134.872	130.520	-476.326	15.655
3300	49.018	177.168	136.131	135.420	-476.418	13.917
3400	49.055	178.632	137.360	140.323	-476.518	12.219
3500	49.088	180.054	138.560	145.231	-476.626	10.561
3600	49.122	181.437	139.732	150.141	-476.742	8.943
3700	49.151	182.784	140.877	155.055	-476.866	7.365
3800	49.178	184.095	141.997	159.972	-476.998	5.827
3900	49.204	185.373	143.093	164.861	-477.138	4.329
4000	49.227	186.619	144.166	169.712	-477.286	2.871
4100	49.248	187.834	145.216	174.536	-477.442	1.453
4200	49.269	189.021	146.245	179.336	-477.606	0.075
4300	49.287	190.181	147.253	184.110	-477.778	-1.259
4400	49.305	191.314	148.242	188.859	-477.958	-2.599
4500	49.321	192.423	149.211	193.584	-478.145	-3.943
4600	49.337	193.507	150.162	198.284	-478.339	-5.291
4700	49.351	194.568	151.096	202.959	-478.541	-6.643
4800	49.364	195.607	152.013	207.609	-478.750	-7.999
4900	49.376	196.625	152.913	212.234	-478.966	-9.359
5000	49.389	197.623	153.797	216.834	-479.189	-10.719
5100	49.400	198.601	154.666	221.409	-479.419	-12.079
5200	49.411	199.560	155.520	225.959	-479.656	-13.439
5300	49.421	200.502	156.360	230.484	-479.900	-14.799
5400	49.430	201.425	157.186	234.984	-480.150	-16.159
5500	49.439	202.332	158.000	239.459	-480.406	-17.519
5600	49.448	203.223	158.798	243.909	-480.668	-18.879
5700	49.456	204.099	159.585	248.334	-480.936	-20.239
5800	49.464	204.959	160.360	252.734	-481.210	-21.599
5900	49.472	205.804	161.123	257.109	-481.489	-22.959
6000	49.478	206.636	161.875	261.459	-481.774	-24.319

Mar. 31, 1965; Sept. 30, 1965; Mar. 31, 1965; Dec. 31, 1965

Boron Oxide Fluoride, Trimeric ((BOF)₃)

(Crystal) Mol. Wt. = 137.46

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0						
100						
200						
298						
300	30.085	52.000	52.000	-586.500	-557.166	408.394
400	31.000	52.186	52.001	-586.500	-556.986	408.744
500	31.000	52.372	52.001	-586.500	-556.806	409.094
600	31.000	52.558	52.001	-586.500	-556.626	409.444
700	31.000	52.744	52.001	-586.500	-556.446	409.794
800	31.000	52.930	52.001	-586.500	-556.266	410.144
900	31.000	53.116	52.001	-586.500	-556.086	410.494
1000	31.000	53.302	52.001	-586.500	-555.906	410.844
1100	31.000	53.488	52.001	-586.500	-555.726	411.194
1200	31.000	53.674	52.001	-586.500	-555.546	411.544
1300	31.000	53.860	52.001	-586.500	-555.366	411.894
1400	31.000	54.046	52.001	-586.500	-555.186	412.244
1500	31.000	54.232	52.001	-586.500	-555.006	412.594

BORON OXIDE FLUORIDE, TRIMERIC ((BOF)₃)

MOL. WT. = 137.46

ΔH_f⁰ 0 = Unknown
 ΔH_f⁰ 298.15 = -586.5 ± 3.0 kcal. mole⁻¹
 ΔH_f⁰ = Unknown
 ΔH_f⁰ 298.15 = 21.2 ± 3.2 kcal. mole⁻¹
 T_m = 353°K.

Heat of Formation.

The heats of solution of the compounds: B₂O₃(gl), BF₃(g) and (BOF)₃(c) in water and methanol, respectively, were reported by E. M. Magee, J. Inorg. Nucl. Chem. 22, 156 (1961). The corresponding enthalpy changes for the reaction B₂O₃(gl) + BF₃(g) = (BOF)₃(c) were derived as -19.8 and -14.4 kcal. mole⁻¹, yielding ΔH_f⁰ 298.15 for (BOF)₃(c) -589.18 and -585.78 kcal. mole⁻¹, respectively. The adopted value of ΔH_f⁰ 298.15 for (BOF)₃(c) is the average of these two values obtained.

Heat Capacity and Entropy.

The heat capacities (C_p) for (BOF)₃(c) were estimated from the C_p values for B₂O₃(c) and BF₃(g), according to the method suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York, 1958. S° 298.15 for (BOF)₃(c) was estimated by E. M. Magee, loc. cit.

Melting Data.

The value of T_m was reported by E. M. Magee, loc. cit.

Heat of Sublimation.

The heat of sublimation (ΔH_g⁰ 298.15) for (BOF)₃(c) is calculated as the difference between ΔH_f⁰ 298.15 for crystal and gas.

B₃F₃O₃

T. °K.	C _p	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	13.862	90.014	102.010	5.184	-563.331	-563.331	INFINITE
200	21.489	136.825	152.010	4.200	-564.676	-564.676	1219.713
298	27.489	161.825	181.825	4.000	-565.300	-565.300	390.373
300	27.490	81.995	81.995	.051	-565.305	-564.733	396.819
400	32.456	90.626	82.969	3.063	-565.480	-537.845	293.851
500	36.226	98.292	85.281	6.505	-565.584	-530.924	232.055
600	39.066	105.161	88.032	10.277	-565.618	-523.987	190.853
700	41.189	111.350	90.929	14.295	-565.591	-517.048	161.422
800	42.783	116.959	93.838	18.497	-565.520	-510.121	139.352
900	43.994	122.071	96.695	22.839	-565.411	-503.203	122.188
1000	44.927	126.757	99.470	27.259	-565.286	-496.295	108.460
1100	45.657	131.074	102.150	31.817	-565.164	-489.404	97.231
1200	46.237	135.073	104.729	36.413	-565.043	-482.520	87.875
1300	46.703	138.793	107.208	41.061	-564.937	-475.648	79.960
1400	47.083	142.268	109.589	45.751	-564.845	-468.781	73.176
1500	47.396	145.528	111.877	50.475	-564.776	-461.926	67.289
1600	47.657	148.595	114.077	55.228	-564.730	-455.068	62.156
1700	47.876	151.491	116.184	60.005	-564.708	-448.214	57.619
1800	48.062	154.233	118.232	64.802	-564.701	-441.366	53.587
1900	48.221	156.836	120.196	69.617	-564.736	-434.512	49.978
2000	48.358	159.313	122.050	74.446	-564.774	-427.655	46.750
2100	48.477	161.675	123.919	79.288	-564.830	-420.797	43.791
2200	48.581	163.931	125.687	84.141	-564.904	-413.938	41.119
2300	48.672	166.094	127.397	89.003	-564.993	-407.074	38.679
2400	48.750	168.168	129.058	93.875	-565.102	-399.204	36.442
2500	48.825	170.159	130.658	98.754	-565.230	-391.343	34.355
2600	48.886	172.075	132.214	103.639	-565.368	-383.488	32.400
2700	48.943	173.921	133.725	108.531	-565.520	-375.639	30.589
2800	48.994	175.702	135.192	113.427	-565.684	-367.792	28.908
2900	49.040	177.422	136.619	118.329	-565.860	-359.946	27.341
3000	49.081	179.086	138.007	123.245	-566.046	-352.100	25.860
3100	49.118	180.696	139.358	128.145	-566.242	-344.254	24.512
3200	49.153	182.256	140.675	133.059	-566.448	-336.408	23.230
3300	49.184	183.769	141.958	137.976	-566.664	-328.562	22.024
3400	49.212	185.237	143.209	142.895	-566.890	-320.716	20.889
3500	49.238	186.664	144.430	147.818	-567.124	-312.870	19.819
3600	49.262	188.052	145.623	152.743	-567.368	-305.023	18.808
3700	49.284	189.402	146.788	157.670	-567.622	-297.177	17.851
3800	49.305	190.716	147.927	162.600	-567.886	-289.331	16.944
3900	49.324	191.997	149.040	167.531	-568.160	-281.485	16.085
4000	49.341	193.246	150.115	172.465	-568.444	-273.639	15.270
4100	49.357	194.465	151.157	177.400	-568.738	-265.793	14.503
4200	49.373	195.654	152.261	182.336	-569.042	-257.947	13.779
4300	49.387	196.816	153.264	187.274	-569.356	-250.101	13.092
4400	49.400	197.952	154.267	192.213	-569.680	-242.255	12.445
4500	49.412	199.059	155.250	197.154	-569.999	-234.409	11.837
4600	49.424	200.148	156.214	202.096	-570.314	-226.563	11.260
4700	49.434	201.211	157.161	207.039	-570.624	-218.717	10.713
4800	49.444	202.252	158.069	211.983	-570.929	-210.871	10.196
4900	49.454	203.277	158.961	216.927	-571.229	-203.025	9.709
5000	49.463	204.277	159.836	221.871	-571.524	-195.179	9.252
5100	49.471	205.251	160.776	226.820	-571.814	-187.333	8.825
5200	49.479	206.211	161.661	231.768	-572.100	-179.487	8.428
5300	49.487	207.154	162.490	236.716	-572.381	-171.641	8.051
5400	49.494	208.082	163.264	241.664	-572.657	-163.795	7.694
5500	49.501	208.987	164.168	246.612	-572.929	-155.949	7.357
5600	49.507	209.879	164.957	251.565	-573.197	-148.103	7.040
5700	49.513	210.755	165.753	256.516	-573.461	-140.257	6.743
5800	49.519	211.617	166.536	261.468	-573.719	-132.411	6.466
5900	49.524	212.464	167.307	266.420	-573.972	-124.565	6.209
6000	49.529	213.298	168.067	271.372	-574.221	-116.719	5.972

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1962; Sept. 30, 1963; Mar. 31, 1965

BORON OXIDE FLUORIDE, TRIMERIC ((BOF)₃) (IDEAL GAS)

Point Group {D_{3h}}
S_{298.15}° = [81.8] cal. deg.⁻¹ mole⁻¹
Round State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies
 ω_j , cm.⁻¹ ω_j , cm.⁻¹ ω_j , cm.⁻¹

(1233) (1)	1450 (2)	714 (1)
(790) (1)	1381 (2)	(170) (1)
(570) (1)	966 (2)	(630) (2)
(1280) (1)	(420) (2)	(185) (2)
(440) (1)	(220) (2)	

Bond Distance: B-F = [1.3] Å B-O = [1.36] Å

Bond Angle: F-B-O = [120]° B-O-B = [120]° O-B-O = [120]°

Product of the Moments of Inertia: I_AI_BI_C = [1.9254 X 10⁻¹¹²] g.³ cm.⁶

Heat of Formation.

The enthalpy changes (ΔH_f°) of the reaction B₂O₃(l) + BF₃(g) = (BOF)₃(g) were derived by both the second and third law methods, using the equilibrium constant data reported by several investigators. The results are given as follows.

Investigator	Third Law Value	Second Law Value	ΔH _f ° 298.15° kcal. mole ⁻¹
Hildenbrand, et al. ¹	4.06	4.01 ± 0.3	-565.32 ± 1.0
Fisher, et al. ²	3.41	6.45 ± 0.6	-565.97 ± 1.5
Smith and Lawrence ³	4.03	—	-565.35 ± 1.3
Farber ⁴	5.25	—	-564.13 ± 2.0
Porter, et al. ⁵	—	7.58 ± 0.2	-565.82 ± 2.0
	—	4.33 ± 0.30	-565.05 ± 1.0

*Calculation based on the third law values available.

- 1 D. L. Hildenbrand, L. P. Theard and A. M. Saul, J. Chem. Phys. **39**, 1973 (1963).
- 2 H. D. Fisher, J. Kiehl and A. Cane, Report HTC-61-90, June 1961, Hughes Tool Company, Culver City, California.
- 3 D. D. Smith and R. W. Lawrence, Aerojet Report No. 1952, February 1961, Aerojet-General Corporation.
- 4 M. Farber, J. Chem. Phys. **35**, 661 (1962). The first ΔH_f° 298.15 value was evaluated based on K₁₀₀₀ = 11.8. The second ΔH_f° 298.15 values refer to the reaction B₂O₃(c) + BF₃(g) = (BOF)₃(g).
- 5 R. P. Porter, D. R. Biddisat and K. P. Watterson, J. Chem. Phys. **35**, 2104 (1962). The ΔH_f° 298.15 value was derived from ΔH_f° 700 = 3.46 ± 0.30 kcal. mole⁻¹.

The adopted value of ΔH_f° 298.15 for (BOF)₃(g) is the weighted average of the six ΔH_f° 298.15 values listed above.

Heat Capacity and Entropy.

The infra-red spectrum has been reported by D. D. Smith and R. L. Lawrence, loc. cit., and by H. D. Fisher, W. J. Lehmann, and I. Shapiro, J. Phys. Chem. **65**, 1166 (1961) who also made a partial assignment. The unassigned bands at 1280 and 1233 from Fisher, et al., can be assigned to the A₁ and A₂ species which may be observed if the selection rules are not rigorously obeyed in the solid. All the unobserved frequencies were estimated by comparison with B₂O₃(OH)₃, B₂O₃(OD)₃ from J. L. Parsons, J. Chem. Phys. **33**, 1860 (1960) and B₂O₃-H₂O from S. K. Gupta and R. P. Porter, J. Phys. Chem. **57**, 1286 (1953) and G. H. Lee, W. H. Bauer and S. E. Wiberley, J. Phys. Chem. **57**, 1742 (1953). The D_{3h} assumed symmetry has 14 vibrations of the type 3A₁, 2A₂, 5E₁, 2A₂ and 2E₁ which are given in order above. The B-F bond distance was assumed to be the same as that in BF₃. The B-O bond distance was estimated by comparison with other related compounds. The three principal moments of inertia are: I_A = I_B = 4.5832 X 10⁻³⁸ g. cm.²



MOL. WT. = 83.484



(Crystal) Mol. Wt. = 83.484

BOROXIN ($\text{B}_3\text{O}_3\text{H}_3$) (CRYSTAL)

$\Delta H_f^\circ 0$ = Unknown
 $\Delta H_f^\circ 298.15$ = -301.7 ± 10 kcal. mole⁻¹
 ΔH_g° = Unknown
 $\Delta H_g^\circ 298.15$ = 10.7 ± 0.5 kcal. mole⁻¹

$S^\circ 298.15$ = $[40 \pm 10]$ cal. deg.⁻¹ mole⁻¹
 T_m = Unknown

Heat of Formation.

The value of $\Delta H_f^\circ 298.15$ for $\text{B}_3\text{O}_3\text{H}_3(\text{c})$ was calculated from the $\Delta H_f^\circ 298.15$ for $\text{B}_3\text{O}_3\text{H}_3(\text{g})$ and $\Delta H_g^\circ 298.15$ for $\text{B}_3\text{O}_3\text{H}_3(\text{c})$ reported by R. P. Porter and S. K. Gupta, J. Phys. Chem. **68**, 280 (1964).

Heat Capacity and Entropy.

The heat capacities (C_p) were estimated from those for $\text{P}_2\text{O}_5(\text{c})$ and $1/2 \text{P}_2\text{H}_6(\text{g})$, according to the method suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York, 1958. The value of $S^\circ 298.15$ for $\text{B}_3\text{O}_3\text{H}_3(\text{c})$ was calculated based on $\Delta S_f^\circ 298.15 = 6.6$ cal. deg.⁻¹ mole⁻¹ for the reaction $\text{B}_3\text{O}_3\text{H}_3(\text{c}) = \text{P}_2\text{O}_5(\text{am}) + 1/2 \text{P}_2\text{H}_6(\text{g})$, which was obtained from the calculated $\Delta H_f^\circ 298.15$ and measured $\Delta H_f^\circ 298.15$ evaluated from the vapor pressure reported by W. P. Shollette and R. P. Porter, J. Phys. Chem. **67**, 177 (1963).

Heat of Sublimation.

$\Delta H_g^\circ 298.15$ was taken from R. P. Porter and S. K. Gupta, loc. cit.

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0							
100							
200							
298	23.500	40.000	40.000	0.000	-301.700	-276.498	202.649
300	23.600	40.146	40.000	0.044	-301.710	-276.343	201.306
400	28.700	47.631	40.987	2.658	-302.170	-267.813	146.319
500	33.900	54.598	43.019	5.784	-302.422	-259.190	113.286
600	38.900	61.234	45.506	9.437	-302.382	-250.561	91.255
700	43.000	67.546	48.208	13.537	-302.050	-241.921	75.528
800	46.500	73.525	51.002	18.018	-301.460	-233.373	63.751
900	49.138	79.160	53.821	22.805	-300.660	-224.808	54.612
1000	51.200	84.449	56.622	27.827	-299.711	-216.538	47.322
1100	52.517	89.392	59.379	33.014	-298.683	-208.272	41.378
1200	53.600	94.010	62.075	38.322	-297.605	-200.098	36.441
1300	54.203	98.324	64.699	43.713	-296.518	-192.018	32.280
1400	54.798	102.361	67.247	49.161	-295.438	-184.018	28.725
1500	55.203	106.154	69.715	54.658	-294.379	-176.099	25.656
1600	55.600	109.730	72.105	60.199	-293.340	-168.248	22.980
1700	55.928	113.111	74.419	65.776	-292.321	-160.459	20.627
1800	56.188	116.315	76.658	71.382	-291.329	-152.733	18.543
1900	56.378	119.398	78.826	77.011	-290.360	-145.059	16.685
2000	56.500	122.254	80.926	82.656	-289.415	-137.437	15.018



T, °K.	C _p	S°	cal. mole ⁻¹ H ₂₉₈ ⁻¹	cal. mole ⁻¹ H°	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	10.000	53.300	4.026	288.002	-288.002	-288.002	INFINITE
200	15.050	62.407	3.852	289.363	-289.363	-289.363	922.785
300	18.992	67.744	3.802	290.000	-290.000	-290.000	1011.366
400	21.084	69.874	3.809	291.015	-291.015	-291.015	201.326
500	23.706	72.440	3.816	292.346	-292.346	-292.346	200.012
600	32.920	88.490	8.302	292.817	-292.817	-292.817	146.951
700	35.514	93.767	11.729	293.158	-293.158	-293.158	115.041
800	37.614	98.651	15.389	293.389	-293.389	-293.389	93.728
900	38.326	103.183	18.607	293.526	-293.526	-293.526	78.482
1000	40.751	107.462	23.244	293.594	-293.594	-293.594	67.038
1100	41.891	111.340	27.377	293.620	-293.620	-293.620	58.130
1200	42.856	115.028	31.615	293.618	-293.618	-293.618	51.001
1300	43.664	118.491	35.943	293.594	-293.594	-293.594	45.169
1400	44.355	121.732	40.364	293.554	-293.554	-293.554	40.307
1500	44.923	124.832	44.808	293.529	-293.529	-293.529	36.194
1600	45.416	127.748	49.326	293.513	-293.513	-293.513	32.660
1700	45.839	130.514	53.869	293.508	-293.508	-293.508	29.616
1800	46.205	133.145	58.492	293.519	-293.519	-293.519	26.942
1900	46.523	135.651	63.129	293.543	-293.543	-293.543	24.583
2000	46.800	138.045	67.795	293.576	-293.576	-293.576	22.487
2100	47.044	140.334	72.487	293.622	-293.622	-293.622	20.611
2200	47.259	142.528	77.203	293.683	-293.683	-293.683	18.823
2300	47.446	144.634	81.938	293.755	-293.755	-293.755	17.295
2400	47.606	146.656	86.692	293.845	-293.845	-293.845	16.006
2500	47.748	148.603	91.461	293.911	-293.911	-293.911	14.738
2600	47.895	150.579	96.245	293.957	-293.957	-293.957	13.574
2700	48.026	152.590	101.042	293.980	-293.980	-293.980	12.476
2800	48.136	154.638	105.850	293.983	-293.983	-293.983	11.433
2900	48.226	156.729	110.667	293.972	-293.972	-293.972	10.467
3000	48.300	158.852	115.497	293.957	-293.957	-293.957	9.570
3100	48.360	161.003	120.334	293.930	-293.930	-293.930	8.734
3200	48.408	163.179	125.178	293.891	-293.891	-293.891	7.954
3300	48.443	165.383	130.030	293.837	-293.837	-293.837	7.224
3400	48.465	167.615	134.884	293.769	-293.769	-293.769	6.539
3500	48.475	169.875	139.741	293.688	-293.688	-293.688	5.890
3600	48.477	172.157	144.623	293.597	-293.597	-293.597	5.290
3700	48.476	174.461	149.529	293.498	-293.498	-293.498	4.718
3800	48.471	176.789	154.458	293.383	-293.383	-293.383	4.178
3900	48.463	179.141	159.417	293.255	-293.255	-293.255	3.667
4000	48.453	181.515	164.401	293.116	-293.116	-293.116	3.182
4100	48.440	183.911	169.413	292.967	-292.967	-292.967	2.722
4200	48.424	186.328	174.444	292.808	-292.808	-292.808	2.282
4300	48.405	188.766	179.494	292.640	-292.640	-292.640	1.864
4400	48.383	191.226	184.563	292.464	-292.464	-292.464	1.476
4500	48.359	193.707	189.650	292.281	-292.281	-292.281	1.103
4600	48.333	196.207	194.755	292.092	-292.092	-292.092	0.750
4700	48.305	198.726	199.879	291.898	-291.898	-291.898	0.418
4800	48.275	201.263	205.021	291.700	-291.700	-291.700	0.100
4900	48.243	203.817	210.181	291.500	-291.500	-291.500	0.000
5000	48.210	206.386	215.350	291.300	-291.300	-291.300	0.000
5100	48.176	208.960	220.529	291.100	-291.100	-291.100	0.000
5200	48.141	211.539	225.718	290.900	-290.900	-290.900	0.000
5300	48.105	214.123	230.917	290.700	-290.700	-290.700	0.000
5400	48.068	216.712	236.126	290.500	-290.500	-290.500	0.000
5500	48.030	219.306	241.345	290.300	-290.300	-290.300	0.000
5600	48.000	221.905	246.574	290.100	-290.100	-290.100	0.000
5700	47.969	224.509	251.813	289.900	-289.900	-289.900	0.000
5800	47.937	227.118	257.061	289.700	-289.700	-289.700	0.000
5900	47.904	229.732	262.319	289.500	-289.500	-289.500	0.000
6000	47.870	232.351	267.586	289.300	-289.300	-289.300	0.000

Mar. 31, 1963; Sept. 30, 1963; Mar. 31, 1965

(IDEAL GAS)

Point Group $[D_{3h}]$
 $\Delta H_f^0 = -288 \pm 10 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = -281 \pm 10 \text{ kcal. mole}^{-1}$
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
2530 (1)	2620 (2)	903 (1)	
[920] (1)	1404 (2)	[300] (1)	
[735] (1)	1335 (2)	1115 (2)	
[1560] (1)	940 (2)	[230] (2)	
[1550] (1)	[400] (2)		

Bond Distance: B-O = $1.36 \text{ \AA}$ B-H = $1.18 \text{ \AA}$

Bond Angle: B-O-B = 120° O-B-H = 120°

Product of the Moments of Inertia: $I_A I_B I_C = [5.4563] \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The equilibrium constants (1290-1461°K.) for the reaction (1) $3/2 \text{ H}_2(\text{g}) + \text{B(am)} + \text{B}_2\text{O}_3(\text{l}) = \text{B}_3\text{O}_3\text{H}_3(\text{g})$ were determined by W. P. Sholette and R. F. Porter, J. Phys. Chem. 67, 177 (1963). The equilibrium pressures of $\text{B}_3\text{O}_3\text{H}_3(\text{g})$ and $\text{B}_2\text{O}_3\text{H}_3(\text{g})$ for the reaction (2) $\text{B}_2\text{O}_3\text{H}_3(\text{g}) + \text{B}_2\text{O}_3(\text{c}) = 1/2 \text{ B}_3\text{O}_3\text{H}_3(\text{g}) + \text{B}_2\text{O}_3(\text{c})$ were measured at 300°K. by R. F. Porter and S. K. Gupta, J. Phys. Chem. 68, 280 (1964). The equilibrium constants (1246-1328°K.) for the reaction (3) $2\text{B}_3\text{O}_3\text{H}_3(\text{g}) = \text{B}_3\text{O}_3\text{H}_3(\text{g}) + \text{B}_2\text{O}_3\text{H}_3(\text{g})$ were reported by R. F. Porter and W. P. Sholette, J. Chem. Phys. 37, 198 (1962). Using these data the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented as follows.

Reaction	Third Law Value	Second Law Value	$\Delta H_f^{298.15^\circ}$ kcal. mole ⁻¹
(1)	-5.90	+6.52 ± 4.5	-304.0 ± 5.0
(2)**	-11.11	—	-287.6 ± 2.0
(3)	-2.0	—	-282.5 ± 2.0
			-314 ± 12.0

*Calculation based on the third law values.

**The initial system for the first set of measurements was $\text{B}_2\text{H}_6(\text{g}) + \text{B(OH)}_3(\text{c})$.

That for the second set was $\text{B}_2\text{H}_6(\text{g}) + \text{B}_2\text{O}_3(\text{g})$.

The value of $\Delta H_f^{298.15}$ for $\text{B}_3\text{O}_3\text{H}_3(\text{g})$ adopted is a weighted average of these $\Delta H_f^{298.15}$ values listed.

Heat Capacity and Entropy.

The infra-red spectrum of solid boroxin has been determined by S. K. Gupta and R. F. Porter, J. Phys. Chem. 67, 1286 (1963) and a partial assignment was made. The infra-red spectra of the gas has also been reported by G. H. Lee, W. H. Bauer, and S. E. Miberley, J. Phys. Chem. 67, 1742 (1963) and in an agreement with the solid. The assignment of the frequencies has been changed slightly due to the non-appearance of the band at 1115 cm.⁻¹ in the gas phase. The assumed D_{3h} symmetry has 14 vibrations of the type $3A_1$, $2A_2$, $5E$, $2A_2$, and $2E$, the 7 estimated frequencies were obtained by comparison with $\text{B}_3\text{O}_3\text{H}_3$ by J. L. Parsons, J. Chem. Phys. 33, 1860 (1960).

The point group, bond angles and bond lengths were assumed to be the same as for $\text{BOP}(\text{g})$. The B-H bond length was taken as the sum of the angle covalent radii of the atoms. The individual moments of inertia were calculated to be $I_A = I_B = 13.973 \times 10^{-39}$, and $I_C = 27.949 \times 10^{-39} \text{ g.}^2 \text{ cm.}^2$.

B₃H₃O₃

Metaboric Acid, Trimeric ((HBO₂)₃)
(Ideal Gas) Mol. Wt. = 131.484

B₃H₃O₆

T, °K.	C _p	S° -(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ⁰ keal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞
100	23.119	60.120	5.440	-538.303	INFINITE
200	23.148	71.939	4.530	-530.561	1159.485
298	32.807	83.047	0.000	-519.844	372.682
300	32.960	83.250	0.000	-519.844	372.682
400	32.960	83.250	0.000	-519.844	372.682
500	32.960	83.250	0.000	-519.844	372.682
600	32.960	83.250	0.000	-519.844	372.682
700	32.960	83.250	0.000	-519.844	372.682
800	32.960	83.250	0.000	-519.844	372.682
900	32.960	83.250	0.000	-519.844	372.682
1000	32.960	83.250	0.000	-519.844	372.682
1100	32.960	83.250	0.000	-519.844	372.682
1200	32.960	83.250	0.000	-519.844	372.682
1300	32.960	83.250	0.000	-519.844	372.682
1400	32.960	83.250	0.000	-519.844	372.682
1500	32.960	83.250	0.000	-519.844	372.682
1600	32.960	83.250	0.000	-519.844	372.682
1700	32.960	83.250	0.000	-519.844	372.682
1800	32.960	83.250	0.000	-519.844	372.682
1900	32.960	83.250	0.000	-519.844	372.682
2000	32.960	83.250	0.000	-519.844	372.682
2100	32.960	83.250	0.000	-519.844	372.682
2200	32.960	83.250	0.000	-519.844	372.682
2300	32.960	83.250	0.000	-519.844	372.682
2400	32.960	83.250	0.000	-519.844	372.682
2500	32.960	83.250	0.000	-519.844	372.682
2600	32.960	83.250	0.000	-519.844	372.682
2700	32.960	83.250	0.000	-519.844	372.682
2800	32.960	83.250	0.000	-519.844	372.682
2900	32.960	83.250	0.000	-519.844	372.682
3000	32.960	83.250	0.000	-519.844	372.682
3100	32.960	83.250	0.000	-519.844	372.682
3200	32.960	83.250	0.000	-519.844	372.682
3300	32.960	83.250	0.000	-519.844	372.682
3400	32.960	83.250	0.000	-519.844	372.682
3500	32.960	83.250	0.000	-519.844	372.682
3600	32.960	83.250	0.000	-519.844	372.682
3700	32.960	83.250	0.000	-519.844	372.682
3800	32.960	83.250	0.000	-519.844	372.682
3900	32.960	83.250	0.000	-519.844	372.682
4000	32.960	83.250	0.000	-519.844	372.682
4100	32.960	83.250	0.000	-519.844	372.682
4200	32.960	83.250	0.000	-519.844	372.682
4300	32.960	83.250	0.000	-519.844	372.682
4400	32.960	83.250	0.000	-519.844	372.682
4500	32.960	83.250	0.000	-519.844	372.682
4600	32.960	83.250	0.000	-519.844	372.682
4700	32.960	83.250	0.000	-519.844	372.682
4800	32.960	83.250	0.000	-519.844	372.682
4900	32.960	83.250	0.000	-519.844	372.682
5000	32.960	83.250	0.000	-519.844	372.682
5100	32.960	83.250	0.000	-519.844	372.682
5200	32.960	83.250	0.000	-519.844	372.682
5300	32.960	83.250	0.000	-519.844	372.682
5400	32.960	83.250	0.000	-519.844	372.682
5500	32.960	83.250	0.000	-519.844	372.682
5600	32.960	83.250	0.000	-519.844	372.682
5700	32.960	83.250	0.000	-519.844	372.682
5800	32.960	83.250	0.000	-519.844	372.682
5900	32.960	83.250	0.000	-519.844	372.682
6000	32.960	83.250	0.000	-519.844	372.682

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1964

METABORIC ACID, TRIMERIC ((HBO₂)₃) (IDEAL GAS)

Point Group C_{3h}
ΔH_f⁰ = [-538 ± 3] kcal. mole⁻¹
ΔH_f⁰ 298.15 = [-543 ± 3] kcal. mole⁻¹
Ground State Quantum Weight = 1

MOL. WT. = 131.484

Vibrational Frequencies and Degeneracies	
ω _e , cm. ⁻¹	ω _e , cm. ⁻¹
[550](1)	[250](1)
[1150](1)	[500](1)
[950](1)	[3500](2)
[3500](1)	[750](2)
[1100](1)	[900](2)
[1600](1)	[1300](2)
[500](1)	[1000](2)

Bond Distance: B-O = [1.36] Å O-H = [1.0] Å

Bond Angle: H-O-B = [120]° O-B-O = [120]° B-O-B = [120]°

Product of the Moments of Inertia: I_AI_BI_C = [1.7712 X 10⁻¹¹] g.³ cm.⁶

Heat of Formation.

The equilibrium constant, K_p 1451 = 0.9, for the reaction H₃BO₃(l) + B₂O₃(l) = (HBO₂)₃(g) was reported by D. J. Meschi, W. A. Chupka and J. Berkowitz, J. Chem. Phys. 33, 530 (1960), which was determined by means of mass spectrometry. The equilibrium constants of the reactions between water vapor and liquid B₂O₃ were determined at 1147°K. by J. A. Blauer and M. Farber, J. Phys. Chem. 68, 2357 (1964), by use of a transpiration method. From the reported value, 1.5 K₂ + 0.5 K₃ = 0.0342 ± 0.0095, the equilibrium constant, K₂, for the reaction 1.5 B₂O₃(l) + 1.5 H₂O(g) = (HBO₂)₃(g) was derived as 0.0168, using K₃ = 0.0181 for the reaction 0.5 B₂O₃(l) + 1.5 H₂O(g) = H₃BO₃(g) evaluated by use of JANAF values of ΔH_f⁰ for B₂O₃(l), H₂O(g) and H₃BO₃(g). Employing the equilibrium constants obtained the respective enthalpy changes (ΔH_f⁰ 298.15) for the two reactions were calculated by the third law method. The corresponding values of ΔH_f⁰ for (HBO₂)₃(g) were also derived. The results are presented as follows.

Investigator	Chemical Reaction	ΔH _f ⁰ 298.15 kcal. mole ⁻¹	ΔH _f ⁰ 298.15 kcal. mole ⁻¹
Meschi, et al.	H ₃ BO ₃ (l) + B ₂ O ₃ (l) = (HBO ₂) ₃ (g)	-7.31	-543.8
Blauer and Farber	1.5 B ₂ O ₃ (l) + 1.5 H ₂ O(g) = (HBO ₂) ₃ (g)	-6.67	-542.3

The adopted value of ΔH_f⁰ 298.15 for (HBO₂)₃(g) is the average of these two listed in the above table. The equilibrium constants for the same reactions between B₂O₃(l) and H₂O(g) were also determined by a transpiration method in the temperature region 1000°-1273°K. by S. F. Randall and J. L. Margrave, J. Inorg. Nucl. Chem. 15, 29 (1960). The reported value, ΔH_f⁰ = -537.5 ± 3 kcal. mole⁻¹ for (HBO₂)₃(g), is in good agreement with the value adopted.

Heat Capacity and Entropy.

All the molecular and spectroscopic constants were estimated by D. White, D. E. Mann, F. N. Walsh and A. Sommer, J. Chem. Phys. 32, 468 (1960). The three principal moments of inertia are: I_A = I_B = 4.4823 X 10⁻³⁸ and I_C = 8.9247 X 10⁻³⁸ g. cm.². The infrared absorption spectra for B₃O₃(OH)₃(c) in the 430 to 4000 cm.⁻¹ was reported by L. J. Parsons, J. Chem. Phys. 33, 1860 (1960). A partial Raman spectrum was also given.

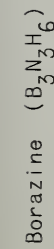
B₃H₃O₆



MOL. WT. = 80.532

(IDEAL GAS)

BORAZINE (B₃N₃H₆)



(Ideal Gas) Mol. Wt. = 80.532

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _P
0	0.000	INFINITE	0.000	-115.791	-115.791	INFINITE
100	9.046	83.060	3.947	-115.791	-115.791	INFINITE
200	23.146	61.358	7.065	-120.160	-107.080	111.543
298	23.146	68.083	8.000	-121.900	-92.829	68.042
300	23.307	69.127	8.043	-121.931	-92.850	67.492
400	30.302	76.821	8.734	-123.333	-82.667	45.165
500	35.507	84.215	9.058	-124.356	-72.373	31.635
600	40.486	91.187	9.869	-125.161	-61.800	22.542
700	44.137	97.712	10.427	-125.670	-51.300	16.016
800	47.140	103.808	10.895	-125.969	-40.655	11.106
900	49.645	109.506	11.316	-126.098	-29.981	7.280
1000	51.756	114.852	11.611	-126.095	-19.300	4.218
1100	53.554	119.872	11.879	-125.999	-8.626	1.714
1200	55.089	124.596	12.133	-125.826	2.041	-3.72
1300	56.407	129.062	12.369	-125.600	12.684	-2.132
1400	57.545	133.285	12.586	-125.335	23.314	-3.639
1500	58.531	137.289	12.784	-125.055	33.921	-4.942
1600	59.389	141.095	12.963	-124.765	44.509	-6.079
1700	60.138	144.718	13.124	-124.468	55.083	-7.081
1800	60.795	148.175	13.268	-124.170	65.631	-7.968
1900	61.367	151.487	13.400	-123.866	76.151	-8.761
2000	61.885	154.659	13.518	-123.554	86.643	-9.473
2100	62.338	157.669	13.629	-123.262	97.108	-10.115
2200	62.742	160.579	13.734	-122.963	107.689	-10.697
2300	63.102	163.376	13.836	-122.666	118.164	-11.228
2400	63.426	166.064	13.924	-122.364	128.544	-11.713
2500	63.716	168.664	14.000	-122.060	138.807	-12.168
2600	63.978	171.168	14.065	-121.751	149.005	-12.601
2700	64.215	173.587	14.123	-121.445	159.111	-13.020
2800	64.430	175.926	14.175	-121.144	169.144	-13.427
2900	64.630	178.184	14.223	-120.846	179.105	-13.820
3000	64.803	180.384	14.266	-120.550	189.000	-14.191
3100	64.956	182.517	14.305	-120.260	198.844	-14.511
3200	65.115	184.577	14.340	-119.974	208.644	-14.812
3300	65.272	186.563	14.371	-119.693	218.400	-15.094
3400	65.426	188.484	14.400	-119.414	228.124	-15.358
3500	65.494	190.429	14.426	-119.136	237.824	-15.606
3600	65.602	192.276	14.448	-118.861	247.500	-15.841
3700	65.701	194.075	14.467	-118.588	257.154	-16.062
3800	65.793	195.828	14.483	-118.316	266.789	-16.272
3900	65.878	197.534	14.497	-118.046	276.405	-16.469
4000	65.958	199.207	14.508	-117.778	286.000	-16.659
4100	66.033	200.837	14.517	-117.511	295.574	-16.841
4200	66.102	202.429	14.524	-117.246	305.129	-17.014
4300	66.167	203.985	14.529	-116.983	314.674	-17.180
4400	66.227	205.507	14.533	-116.724	324.200	-17.338
4500	66.284	206.996	14.536	-116.466	333.714	-17.489
4600	66.337	208.453	14.538	-116.211	343.214	-17.634
4700	66.387	209.881	14.539	-115.958	352.700	-17.774
4800	66.436	211.279	14.540	-115.706	362.174	-17.909
4900	66.482	212.646	14.541	-115.456	371.639	-18.040
5000	66.521	213.992	14.542	-115.208	381.094	-18.166
5100	66.560	215.310	14.543	-114.961	390.539	-18.288
5200	66.597	216.603	14.544	-114.716	399.974	-18.406
5300	66.633	217.874	14.545	-114.472	409.400	-18.520
5400	66.666	219.118	14.546	-114.230	418.814	-18.631
5500	66.698	220.341	14.547	-113.989	428.219	-18.738
5600	66.728	221.543	14.548	-113.750	437.614	-18.841
5700	66.756	222.725	14.549	-113.512	447.000	-18.940
5800	66.783	223.887	14.550	-113.276	456.374	-19.036
5900	66.809	225.028	14.551	-113.041	465.739	-19.129
6000	66.834	226.151	14.552	-112.808	475.094	-19.219

Dec. 31, 1960; Mar. 31, 1965

Point Group D_{3h}

S_{298.15}^o = 68.983 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH_f^o 0 = -115.8 ± 3 kcal. mole⁻¹

ΔH_f^o 298.15 = -121.9 ± 3 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

ω_j, cm.⁻¹

Bond Distances: B-N = 1.44 Å B-H = 1.20 Å H-N = 1.02 Å

Bond Angle: N-B-N = 120° B-N-B = 120° N-B-H = 120°

Product of Moments of Inertia: I_AI_BI_C = 0.3303 X 10⁻¹⁴ g.³ cm.⁶

Heat of Formation.

The heat of combustion for the reaction B₃N₃H₆(l) + 15/4 O₂(g) + 3/2 H₂O(l) = 3 H₃BO₃(c) + 3/2 N₂(g) was reported to be -552.9 ± 3.0 kcal. mole⁻¹ by M. V. Kilday, W. H. Johnson and E. J. Prosen, J. Res. Natl. Bur. Std. 65A, 101 (1961). ΔH_f^o 298.15 H₂O(l) = -68.317 kcal. mole⁻¹ from Natl. Bur. Std. Circ. 500, "Selected Values of Chemical Thermodynamic Properties", 1952 and ΔH_f^o 298.15 H₃BO₃(c) = -261.47 kcal. mole⁻¹ from JANAF tables were used to calculate ΔH_f^o 298.15 B₃N₃H₆(l) = -129.0 ± 3.0 kcal. mole⁻¹. Vapor pressure data on B₃N₃H₆(l) reported by A. Stock and E. Pohland, Ber. 59, 2215 (1926) were fitted to a linear least squares. ΔC_p(1-g) for borazine was approximated by benzene to calculate a 2nd law ΔH_v 298 = 7.1 ± 0.1 kcal. mole⁻¹.

Heat Capacity and Entropy.

The fundamental frequency assignment was made by B. L. Crawford, Jr. and J. T. Edsall, J. Chem. Phys. 7, 223 (1939). The three frequencies enclosed by brackets are calculated values. The moments of inertia were calculated from molecular constants given by S. H. Bauer, J. Am. Chem. Soc. 80, 524 (1958). The three principal moments of inertia are: I_A = I_B = 16.09 X 10⁻³⁹ and I_C = 32.18 X 10⁻³⁹ g. cm.².



Dipotassium Tetraborate ($K_2B_4O_7$)

(Crystal) Mol. Wt. = 233.44

$B_4K_2O_7$

MOL. WT. = 233.44

DIPOTASSIUM TETRABORATE ($K_2B_4O_7$)

(CRYSTAL)

T. °K.	C _p	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$-(F^* - H_{298}^*)/T$	$H^* - H_{298}^*$ kcal. mole ⁻¹	ΔH_f^*	ΔF_f^*	Log K _p
0							
100							
200							
298							
300	40.750	49.800	49.800	0.000	-796.900	-749.734	549.543
400	40.950	50.053	49.801	0.076	-796.916	-749.440	545.940
500	49.300	63.092	51.522	4.628	-798.828	-733.276	400.624
600	55.640	74.813	55.028	9.893	-799.288	-716.829	313.311
700	59.880	85.364	59.221	15.686	-799.485	-700.314	255.077
800	62.700	94.937	63.063	21.424	-799.500	-682.739	207.448
900	66.300	111.059	72.434	34.763	-799.621	-650.688	158.001
1000	67.700	118.118	76.654	41.464	-799.664	-634.137	136.584
1100	68.901	124.629	80.723	48.296	-797.935	-615.953	122.289
1200	69.708	130.699	84.637	55.127	-797.716	-597.240	106.703
1300	70.313	136.369	88.370	61.958	-797.320	-577.240	90.657
1400	71.313	141.560	92.008	68.773	-836.320	-555.140	77.956
1500	71.720	146.495	95.478	76.526	-835.945	-535.068	
1600	72.279	151.142	98.813	83.727	-835.588	-515.023	70.346
1700	72.713	155.509	102.022	90.279	-835.584	-494.024	57.663
1800	73.153	159.700	105.075	96.275	-834.894	-472.994	47.663
1900	73.467	163.673	108.000	105.607	-834.574	-455.011	52.336
2000	73.700	167.448	110.965	112.966	-834.265	-435.043	47.537

$\Delta H_f^* O = \text{Unknown}$

$\Delta H_f^* 298.15 = -796.9 \text{ kcal. mole}^{-1}$

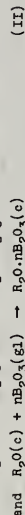
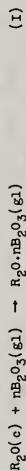
$\Delta H_m^* = 24.9 \pm 1 \text{ kcal. mole}^{-1}$

$S_{298.15}^* = [49.8 \pm 1.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_m = 1098^\circ K.$

Heat of Formation.

$\Delta H_f^* 298.15$ was recalculated from the experimental data of L. Shartais and W. Capps, J. Am. Ceram. Soc. **37**, 27-32 (1954). They studied the heat of solution of various alkali borates in 2N nitric acid. Average molecular weights were used for physical mixtures of the oxides B_2O_3 and R_2O (where R is either Li, Na, or K) rather than for the borate compounds $R_2O \cdot nB_2O_3$ present. These incorrect molecular weights led to spurious correlations and faulty conclusions. In reinterpreting the data, the steps followed were: (1) The calculation of the correct molecular weights and molar heats of reaction; (2) The establishment that the heat of formation of the borates from the oxides is linear with the mole fraction of B_2O_3 in the total original moles of oxides for the reactions



with the heat of formation being zero at 100 percent R_2O ; (3) The evaluation of the least square fit of the line through the heat of reaction data for reaction I and for reaction II; (4) The use of the proper weighting factors in applying least squares to adjust for both the sample size and the molecular weight of the mixture of borates used in each solution experiment.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic. 59-2916, in the range 298-973°K were smoothed graphically and were used to obtain a smooth set of C_p data. The heat capacity was extrapolated smoothly above this region. The entropy at 298°K was estimated from that of $Na_2B_4O_7(c)$ by using an average entropy change of $4.5 \pm 1.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ on substituting Na by K.

Melting Data.

T_m was given by A. P. Rollet, Comp. Rend. **200**, 1763 (1955). The heat of melting was obtained from the heats of formation of the crystal and glass at 298°K combined with the enthalpy differences between 298 and 1098°K. This involves a slight extrapolation of the crystal data and an uncertainty of about 1.0 kcal. mole⁻¹.

$B_4K_2O_7$

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100						
200						
298						
400	40.750	56.700	56.700	0.000	-740.001	543.135
500	40.950	56.953	56.701	0.076	-740.710	530.581
600	40.950	56.953	56.701	0.076	-740.710	530.581
700	40.950	56.953	56.701	0.076	-740.710	530.581
800	40.950	56.953	56.701	0.076	-740.710	530.581
900	40.950	56.953	56.701	0.076	-740.710	530.581
1000	40.950	56.953	56.701	0.076	-740.710	530.581
1100	40.950	56.953	56.701	0.076	-740.710	530.581
1200	40.950	56.953	56.701	0.076	-740.710	530.581
1300	40.950	56.953	56.701	0.076	-740.710	530.581
1400	40.950	56.953	56.701	0.076	-740.710	530.581
1500	40.950	56.953	56.701	0.076	-740.710	530.581
1600	40.950	56.953	56.701	0.076	-740.710	530.581
1700	40.950	56.953	56.701	0.076	-740.710	530.581
1800	40.950	56.953	56.701	0.076	-740.710	530.581
1900	40.950	56.953	56.701	0.076	-740.710	530.581
2000	40.950	56.953	56.701	0.076	-740.710	530.581
2100	40.950	56.953	56.701	0.076	-740.710	530.581
2200	40.950	56.953	56.701	0.076	-740.710	530.581
2300	40.950	56.953	56.701	0.076	-740.710	530.581
2400	40.950	56.953	56.701	0.076	-740.710	530.581
2500	40.950	56.953	56.701	0.076	-740.710	530.581
2600	40.950	56.953	56.701	0.076	-740.710	530.581
2700	40.950	56.953	56.701	0.076	-740.710	530.581
2800	40.950	56.953	56.701	0.076	-740.710	530.581
2900	40.950	56.953	56.701	0.076	-740.710	530.581
3000	40.950	56.953	56.701	0.076	-740.710	530.581

$S_{298.15}^o = [56.7 \pm 2.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = -786.1 \text{ kcal. mole}^{-1}$
 $\Delta F_f^o = -740.0 \text{ kcal. mole}^{-1}$
 $T_m = 1088^\circ\text{K.}$

Heat of Formation.

The heat of formation was obtained from reaction (1) given on the crystal table.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1375°K on the glass and liquid were smoothed graphically and used to determine C_p . There is a discontinuity (glass transition) in the C_p curve at 678°K. Above 1375°K the C_p values were extrapolated smoothly.

The entropy at 298°K was obtained from that of the crystal by adding ΔS_m^o and the difference between S_{1088}^o for crystal and liquid.

Melting Data.

See the crystal table.

Dilithium Tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$)
(Crystal) Mol. Wt. = 169.1178



MOL. WT. = 169.1178

(CRYSTAL)

DILITHIUM TETRABORATE ($\text{Li}_2\text{B}_4\text{O}_7$)

T, °K	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
100						
200						
298	43.750	37.200	0.000	- 803.600	- 757.734	555.408
300	43.761	37.201	0.081	- 803.607	- 757.452	551.777
400	47.239	38.053	4.616	- 804.090	- 741.998	405.390
500	52.567	42.194	9.608	- 806.144	- 726.257	317.431
600	57.625	46.446	15.124	- 806.597	- 710.231	258.689
700	61.950	50.715	21.108	- 806.800	- 694.151	216.713
800	65.586	55.023	27.489	- 806.776	- 678.053	185.229
900	68.766	59.285	34.208	- 806.552	- 661.985	160.744
1000	71.803	63.460	41.234	- 806.140	- 645.937	141.163
1100	75.052	67.529	48.578	- 805.525	- 629.948	125.153
1200	78.198	71.459	56.248	- 804.663	- 614.021	111.823
1300	81.344	75.342	64.218	- 803.613	- 598.176	100.558
1400	84.490	79.091	72.509	- 802.403	- 582.417	90.915
1500	87.636	82.870	81.116	- 800.755	- 566.770	82.574
1600	90.782	86.303	90.036	- 798.958	- 551.222	75.290
1700	93.928	89.779	99.272	- 797.004	- 535.145	68.537
1800	97.074	93.175	108.822	- 794.939	- 518.581	62.354
1900	100.220	96.498	118.687	- 792.766	- 501.513	56.840
2000	103.366	99.752	128.866	- 789.521	- 474.927	51.895

ΔH_f° 0 = Unknown

ΔH_f° 298.15 = -803.6 ± 1.5 kcal. mole⁻¹

ΔH_m° = 28.8 ± 1.5 kcal. mole⁻¹

S° 298.15 = [37.2 ± 1.0] cal. deg.⁻¹ mole⁻¹

T_m = 1190 ± 2°K.

Heat of Formation.

The heat of formation was calculated from ΔH_f° 298 = -12.2 kcal. for the reaction $\text{Li}_2\text{B}_4\text{O}_7(\text{c}) + 2\text{HNO}_3(\text{aq.}) + 5\text{H}_2\text{O}(\text{l.}) = 4\text{H}_3\text{BO}_3(\text{aq.}) + 2\text{LiNO}_3(\text{aq.})$. The heat of solution (ΔH_f°) was interpolated from the heat of solution data of L. Shartels and W. Ceppa, J. Am. Ceram. Soc. 37, 27 (1954). Auxiliary data are from National Bureau of Standards Circular 500 (1952).

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph. D. Thesis, Penn. State Univ., Jan. 1953, L. C. Card No. Mic 59-2916 in the range 298 to 1190°K. were smoothed graphically and used to determine C_p. A linear extrapolation of C_p was used from 1190 to 2000°K.

S° 298 was estimated by three routes: (1) S° 298 ($\text{Li}_2\text{B}_4\text{O}_7$) = 37.3 cal. mole⁻¹ deg.⁻¹ based on JANAP S° 298 ($\text{Na}_2\text{B}_4\text{O}_7$) = 45.3 and ΔS° 298 (2Na-2Li) = 8 cal. deg.⁻¹ from W. M. Latimer, J. Am. Chem. Soc. 73, 1490 (1951); (2) S° 298 ($\text{Li}_2\text{B}_4\text{O}_7$) = 36.7 cal. mole⁻¹ deg.⁻¹ in a similar manner based on ΔS° 298 (2Na-2Li) = 8.6 cal. deg.⁻¹ from K. K. Kelley, Bureau of Mines, private communication, June 1960; and (3) S° 298 ($\text{Li}_2\text{B}_4\text{O}_7$) = 37.6 cal. mole⁻¹ deg.⁻¹ based on addition of the JANAP entropies for 2LiBO₂ and B₂O₃. The value adopted is an average of these estimates.

Melting Data.

The value for T_m is from B. S. R. Sastry and P. A. Hummel, J. Am. Chem. Soc. 42, 216 (1959). A. P. Rollet and R. Bousziz, Compt. rend. 240, 2417 (1955) earlier reported T_m = 1188°K. ΔH_m = 28.8 kcal. mole⁻¹ is from G. S. Smith loc. cit.



T, °K	C _p	S° -(H°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	Log K _f
0					
100					
200					
298	43.295	41.564	+0.000	- 748.226	948.438
300	43.400	41.565		- 748.226	948.438
400	49.050	45.001	4.080	- 782.797	944.856
500	54.701	48.893	9.890	- 795.052	933.683
600	60.332	51.045	15.643	- 795.268	925.757
700	66.003	56.844	21.961	- 795.137	914.378
800	109.155	98.205	30.538	- 782.917	871.253
900	104.585	115.064	35.004	- 784.060	859.349
1000	110.595	122.708	70.204	- 641.870	140.274
1100	111.175	123.212	75.464	- 621.866	124.740
1200	111.845	122.674	80.691	- 779.704	111.865
1300	112.515	121.993	85.832	- 771.063	99.999
1400	113.185	121.264	90.973	- 762.475	83.842
1500	113.728	120.492	95.721	- 758.106	76.917
1600	114.315	119.500	100.508	- 824.016	70.501
1700	114.918	118.249	105.125	- 814.732	60.411
1800	115.527	116.772	109.669	- 805.374	54.739
1900	116.142	115.170	114.142	- 800.663	50.536
2000	116.822	201.274	118.170	- 805.374	46.737
2100	117.488	206.990	122.264	- 805.374	40.187
2200	118.170	212.471	126.241	- 805.374	37.236
2300	118.868	217.739	130.105	- 805.374	34.528
2400	119.583	222.709	133.750	- 805.374	32.036
2500	120.310	227.400	137.200	- 805.374	27.607
2600	121.055	232.442	141.080	- 805.374	25.634
2700	121.816	237.025	144.569	- 805.374	
2800	122.594	241.232	147.705	- 805.374	
2900	123.386	245.078	151.232	- 805.374	
3000	124.115	249.081	154.444	- 805.374	

DILITHIUM TETRABORATE (Li₂B₄O₇) (LIQUID)

MOL. WT. = 169.1178

$S_{298.15}^{\circ} = [41.564 \pm 1.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^{\circ} 298.15 = -792.79 \pm 1.5 \text{ kcal. mole}^{-1}$

$\Delta H_m^{\circ} = 26.3 \pm 1.5 \text{ kcal. mole}^{-1}$

$T_m = 1190 \pm 2^{\circ}\text{K.}$

Heat of Formation.

$\Delta H_f^{\circ} 298.15(1)$ was calculated from $\Delta H_f^{\circ} 298.15(c)$ by adding ΔH_m° and the difference between H_m° and H_f° for crystal and liquid.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph. D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. M1c 58-2918 in the range 298 to 1373°K. were smoothed graphically and used to determine C_p . The C_p data have a discontinuity at about 756°K. A linear extrapolation of C_p was used from 1373 to 3000°K.

The entropy at 298°K. is set so that ΔP is equal at T_m for the crystal and liquid.

Melting Data.

See crystal table for details.

Magnesium Tetraboride (MgB_4)
(Crystal) Mol. Wt. = 67.60

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	0.000	INFINITE	-2.275	-25.011	-25.011	INFINITE
100	4.120	1.920	23.300	-2.138	-25.052	-25.052	94.601
200	11.060	6.860	13.775	-1.383	-25.179	-25.179	27.289
298	16.810	12.410	12.410	0.000	-25.100	-24.797	18.176
300	16.900	12.514	12.410	0.031	-25.100	-24.796	18.063
400	19.000	17.671	13.099	1.829	-25.204	-24.685	13.487
500	20.800	22.104	14.467	3.820	-25.507	-24.523	10.718
600	22.500	26.053	16.075	5.947	-25.909	-24.290	8.647
700	24.000	29.570	17.940	8.285	-26.317	-23.817	6.852
800	25.270	32.697	19.850	10.766	-26.792	-23.417	5.452
900	26.540	35.959	21.117	13.357	-27.226	-23.196	4.453
1000	27.660	38.814	22.785	16.069	-29.773	-22.540	4.026
1100	28.610	41.496	24.322	18.881	-30.177	-21.602	3.231
1200	29.430	43.937	25.755	21.767	-30.586	-20.709	2.567
1300	30.144	46.167	27.095	24.767	-31.000	-19.882	2.047
1400	30.800	48.165	28.268	27.814	-31.470	-19.124	1.642
1500	31.450	50.813	30.194	30.928	-31.797	-18.524	1.305
1600	32.000	52.861	31.547	34.101	-31.813	-17.755	1.026
1700	32.500	54.674	32.659	37.321	-31.650	-16.869	0.794
1800	32.800	56.352	33.582	40.584	-31.442	-15.882	0.599
1900	33.200	58.440	35.345	43.881	-31.184	-14.854	0.440
2000	33.600	60.173	36.543	47.221	-31.848	-13.853	0.353

MAGNESIUM TETRABORIDE (MgB_4)
(CRYSTAL)

MOL. WT. = 67.60

$$\Delta F_f^\circ 0 = -25.0 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^\circ 298.15 = -25.1 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$S^\circ_{298.15} = 12.41 \pm 0.06 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_d = [1100]^\circ\text{K.}$$

Heat of Formation.

The equilibrium pressures (1169-1177°K.) of the reaction $\text{MgB}_4(\text{c}) \rightarrow \text{Mg}(\text{g}) + 4\text{B}(\text{c})$ were measured by M. Wright and P. N. Walsh, "The Vaporization of $\text{MgB}_4(\text{c})$ ", Technical Research Report OMCC-HEF-55, Jan. 9, 1958, Ohio State University Research Foundation. The third law value of $\Delta H_f^\circ 298.15$ for this reaction was derived as 60.40 ± 1.5 kcal. mole⁻¹. This leads to a $\Delta F_f^\circ 298.15 = -25.1 \pm 2.0$ kcal. mole⁻¹ for $\text{MgB}_4(\text{c})$. The unit of equilibrium pressures reported should be in atmosphere not in mm Hg as printed. The diameter of the hole drilled through the center of the lid served as the effusion orifice should be 1/16 inch rather than the reported value 1/8 inch.

Heat Capacity and Entropy.

The low temperature (17.34-299.53°K.) heat capacities were measured by R. M. Swift and D. White, J. Am. Chem. Soc. 79, 3641 (1957). Above 298.15°K. the C_p values were estimated by comparison with those of other related borides. $S^\circ_{298.15}$ was reported by R. M. Swift and D. White, loc. cit., using $S^\circ_{20}(\text{extrap.}) = 0.022 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Temperature of Decomposition.

T_d was estimated from the decomposition reaction reported by M. Wright and P. N. Walsh, loc. cit.

B_4Mg

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ ^o)/T	H° - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	18.290	12.145	76.054	-778.009	-778.009	INFINITE
200	33.400	20.772	40.027	-766.799	-766.799	1676.758
298	44.640	28.289	0.000	-751.763	-751.763	821.449
300	44.801	28.289	0.000	-751.763	-751.763	821.449
400	51.100	35.546	-983	-736.230	-736.230	536.318
500	54.621	41.172	-50.701	-704.284	-704.284	307.827
600	57.720	45.111	15.811	-688.061	-688.061	250.614
700	60.396	48.515	59.486	-671.785	-671.785	200.731
800	62.822	51.236	108.236	-655.471	-655.471	170.039
900	64.872	53.536	162.880	-639.115	-639.115	146.059
1000	66.850	55.470	213.437	-622.794	-622.794	136.105
1100	68.734	57.031	260.000	-606.459	-606.459	120.486
1200	70.574	58.287	302.574	-590.105	-590.105	107.304
1300	72.374	59.287	341.152	-573.732	-573.732	95.655
1400	74.134	60.052	375.727	-557.340	-557.340	85.555
1500	75.850	60.602	406.299	-540.929	-540.929	77.012
1600	77.526	61.052	432.869	-524.500	-524.500	69.452
1700	79.156	61.411	455.436	-508.053	-508.053	62.759
1800	80.734	61.684	474.000	-491.587	-491.587	56.759
1900	82.256	61.874	488.569	-475.102	-475.102	51.587
2000	83.730	62.000	500.000	-458.597	-458.597	46.837

$\Delta H_f^o = -778.31 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o \text{ 298.15} = -793.16 \pm 2.0 \text{ kcal. mole}^{-1}$
 $\Delta H_m^o = 19.4 \pm 1.5 \text{ kcal. mole}^{-1}$
 $T_m = 1015.6^\circ \text{K}$

Heat of Formation.

The heat of the reaction $\text{Na}_2\text{O}(c) + 2\text{B}_2\text{O}_3(l) \rightarrow \text{Na}_2\text{B}_4\text{O}_7(c)$ was reported by L. Spatola and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAP values for $\text{B}_2\text{O}_3(l)$ (Dec. 31, 1964) and for $\text{Na}_2\text{O}(c)$ (June 30, 1962). The above $\Delta H_f^o = -85.2 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

In the low temperature region (5-344°K) the C_p values are those determined by E. P. Westrum, Jr., and O. Grenier, J. Am. Chem. Soc. 79, 1799 (1957). The enthalpy measurements of O. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic S9-2916 in the range 298 to 1015.6°K were smoothed graphically and used to determine C_p ; the values did not join smoothly with those of Westrum and Grenier and the low temperature values were given greater weight. Above T_m the heat capacity was extrapolated. $S_{298.15}^o$ was derived from low temperature heat capacities.

Melting.

The value for T_m is from O. W. Morey and H. E. Merwin, J. Am. Chem. Soc. 59, 2248 (1936). Other reported values for T_m are: 1008 ± 5°K by S. S. Coles, S. R. Scholtes, and C. R. Amberg, J. Am. Ceram. Soc. 19, 58 (1935); 1011°K by H. Menzel, Z. anorg. Chem., 224, 1 (1935); 1005°K by J. P. Ponomareff, Z. anorg. Chem. 89, 383 (1924); 1015°K by A. L. Day and E. T. Allen, "The Isomorphism and Thermal Properties of the Feldspars", Carnegie Inst. of Washington, Publ. No. 31 (1905) p. 23; and 1064°K by C. H. Burgeas and A. Holt, Proc. Roy. Soc. (London) 74, 285 (1904). ΔH_m^o was obtained from the values of ΔH_f^o for $\text{Na}_2\text{B}_4\text{O}_7(c)$ and $\text{Na}_2\text{B}_2\text{O}_5(l)$ at 298°K as described above and the difference between $H_{1015.6}^o$ and H_{298}^o for crystal and liquid.

Disodium Tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$)
(Liquid) Mol. Wt. = 201.262

T, °K.	C_p	S°	$-(F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K_p
0						
100						
200						
298	44.800	47.513	47.513	0.000	-732.383	536.825
300	44.967	47.791	47.514	-0.083	-732.098	533.307
400	53.000	61.873	49.379	4.997	-716.527	391.473
500	59.100	74.374	53.152	10.611	-700.664	306.245
600	64.200	85.601	57.640	16.777	-684.809	249.430
700	69.200	95.874	62.378	23.447	-669.009	208.864
800	106.330	107.921	67.260	32.529	-653.374	178.485
900	106.330	120.445	72.487	43.162	-638.217	154.973
1000	106.330	131.668	77.853	53.795	-623.509	136.261
1100	106.330	141.783	83.212	64.428	-609.211	121.033
1200	106.330	151.035	88.468	75.061	-594.337	108.238
1300	106.330	159.545	93.627	85.694	-579.137	96.957
1400	106.330	167.425	98.620	96.327	-563.494	87.337
1500	106.330	174.761	103.455	106.960	-547.520	79.041
1600	106.330	181.424	108.128	117.593	-531.313	71.817
1700	106.330	188.070	112.643	128.226	-514.699	65.474
1800	106.330	194.148	117.004	138.859	-497.752	59.864
1900	106.330	199.897	121.217	149.492	-479.057	54.867
2000	106.330	205.351	125.288	160.125	-461.166	50.391
2100	106.330	210.538	129.225	170.758	-442.795	46.360
2200	106.330	215.485	133.034	181.391	-423.988	42.713
2300	106.330	220.212	136.723	192.024	-404.699	39.399
2400	106.330	224.737	140.296	202.657	-384.953	36.373
2500	106.330	229.077	143.761	213.290	-364.761	33.566
2600	106.330	233.248	147.124	223.923	-344.196	30.948
2700	106.330	237.261	150.388	234.556	-323.241	28.535
2800	106.330	241.128	153.560	245.189	-301.921	26.304
2900	106.330	244.859	156.644	255.822	-280.255	24.235
3000	106.330	248.464	159.645	266.455	-258.282	22.314

$\text{B}_4\text{Na}_{207}$
MOL. WT. = 201.262

DISODIUM TETRABORATE ($\text{Na}_2\text{B}_4\text{O}_7$) (LIQUID)

$$S_{298.15}^\circ = 47.513 \pm 1.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad \Delta H_f^\circ 298.15 = -778.36 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = 19.4 \pm 1.5 \text{ kcal. mole}^{-1}$$

$$T_m = 1015.6^\circ\text{K.}$$

Heat of Formation.

The heat of reaction $\text{Na}_2\text{O}(c) + 2\text{B}_2\text{O}_3(l) \rightarrow \text{Na}_2\text{B}_4\text{O}_7(l)$ was reported by L. Shartala and W. Capps, J. Am. Ceram. Soc. 57, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $\text{B}_2\text{O}_3(l)$ (Dec. 31, 1964) and for $\text{Na}_2\text{O}(c)$ (June 30, 1962). The above $\Delta H_f^\circ = -80.4 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916, in the range 298 to 1373°K, were smoothed graphically and used to determine C_p . These were joined smoothly with the low temperature data of E. P. Westrum and G. Grenier, J. Am. Chem. Soc. 79, 1799 (1957). At 743°K a glass transition was observed and above this temperature the C_p adopted as constant.

The entropy at 298°K obtained from that of the crystal by adding ΔS_m° and the difference between S_{1015}° and S_{298}° for crystal and liquid.

Melting.

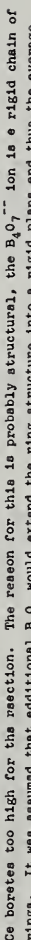
See the crystal for details.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° = (F° - H° ₂₉₈)/T eu	H° - H° ₂₉₈ kcal. mole ⁻¹	ΔF° _f	Log K _p
0					
100					
200					
298	40.200	39.900	+ 0.000	- 683.000	- 637.470
300	40.400	39.901	- 0.075	- 683.003	- 637.188
400	46.400	44.700	- 4.700	- 682.487	- 606.706
500	51.020	48.085	- 8.085	- 681.684	- 591.016
600	53.470	50.875	- 10.875	- 681.728	- 576.499
700	56.030	53.844	- 13.844	- 680.344	- 561.561
800	57.780	56.504	- 16.504	- 676.013	- 532.241
900	58.880	58.880	- 18.880	- 674.960	- 517.873
1000	59.400	60.900	- 20.900	- 672.887	- 503.679
1100	60.140	62.635	- 22.635	- 670.746	- 489.666
1200	61.000	64.100	- 24.100	- 668.540	- 475.828
1300	61.980	65.387	- 25.387	- 666.280	- 462.131
1400	63.000	66.500	- 26.500	- 663.980	- 448.583
1500	64.180	67.459	- 27.459	- 661.664	- 435.176
1600	65.420	68.271	- 28.271	- 659.240	- 421.901
1700	66.720	68.941	- 28.941	- 656.718	- 408.764
1800	68.080	69.470	- 29.470	- 654.100	- 395.761
1900	69.500	69.860	- 29.860	- 651.390	- 382.880
2000	71.000	70.110	- 30.110	- 648.600	- 370.120

Heat of Formation. See lead diborate table for the complete writeup. W. H. Evans in NBS Report 7192, July 1, 1981, analysed the heats of formation of the lead borate system based upon Shertels and Newman's heats of solution and Mazzetti and DeCarli's phase studies. From the Shertels and Newman paper Evans obtained the following:
 $PbO(c) + 2B_2O_3(ql.) \rightarrow PbO \cdot 2B_2O_3(c)$ $\Delta H_f^\circ = -11.9$ kcal. mole⁻¹
end estimated a ΔH_{298}° of 11.4 kcal. mole⁻¹ for the conversion to the $PbO \cdot 2B_2O_3$ (crystal). With auxiliary JANAF values the ΔH_f° 298.15 was calculated to be -683.00 kcal./mole.

Heat Capacity and Entropy. The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities of the constituent oxides.

The entropy at 298.15 was obtained from a consideration of the entropies of sodium and calcium borates and those of the constituent oxides, as given by K. K. Kelley and E. O. King, Bureau of Mines Bull. 592 (1961). These indicate for the reaction:



that the simple addition of entropies will give values at least 2.7 e.u. in the case of Na borates and 5.7 e.u. for Ca borates too high for the reaction. The reason for this is probably structural, the $B_4O_7^{--}$ ion is a rigid chain of rings. It was assumed that additional B_2O_3 would extend the ring structure into a rigid plane and thus the average entropy difference of 4.2 for the reaction was assumed to hold for each additional mole of B_2O_3 . Therefore the entropy at 298.15 was obtained from $S_{298.15}^\circ$ for PbB_2O_4 and B_2O_3 and the subtraction of 4.2 e.u.

Pentaborane (B₅H₉)

(Liquid) Mol. Wt. = 63.172

T, °K.	C _p ^a	S° ^b	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^c	ΔF _f ^c	Log K _f
0							
100	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
200	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
300	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
400	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
500	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
600	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
700	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
800	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
900	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
1000	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
1100	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
1200	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
1300	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
1400	36.172	44.056	44.056	0.000	10.240	41.067	-30.102
1500	36.172	44.056	44.056	0.000	10.240	41.067	-30.102



MOL. WT. = 63.172

(LIQUID)

PENTABORANE (B₅H₉)

$$\Delta H_f^{298.15} = 10.240 \pm 1.6 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 1.466 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{\circ} = 6.79 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{\circ} = 44.056$$

$$T_m = 226.34^{\circ}\text{K.}$$

$$T_b = 335^{\circ}\text{K.}$$

Heat of Formation.

The vapor pressures of B₅H₉(l) were measured by H. E. Wirth and E. D. Palmer, J. Phys. Chem. 60, 914 (1956) and H. L. Johnston, E. C. Kerr, J. T. Clarke and N. C. Hallett, "Calorimetric Investigation with the Condensed Gas Calorimeter. IV. The Heat Capacities, Latent Heats and Entropies of Pentaborane from 13 to 298°K.; Heats of Transition, Fusion and Vaporization; Vapor Pressures of the Liquid", TR-6, July 8, 1949, The Ohio State University. By use of both the second and third law methods, the respective heats of vaporization (ΔH_v^{298.15}) were evaluated. The ΔH_f^{298.15} values for B₅H₉(l) were calculated from ΔH_f^{298.15} for B₅H₉(g) and ΔH_v^{298.15} for B₅H₉(l) obtained previously. The results are presented as follows.

Investigator	ΔH _f ^{298.15} , kcal. mole ⁻¹	ΔH _f ^{298.15} , kcal. mole ⁻¹
	Second Law Value	Third Law Value
Wirth and Palmer	7.26 ± 0.02	7.26
Johnston, et al.	7.23 ± 0.04	7.25

*Calculation based on the third law ΔH_f^{298.15} values.

The adopted value is the average of the two ΔH_f^{298.15} values obtained.

Heat Capacity and Entropy.

The heat capacities (C_p), 231.34 - 290.19°K., for B₅H₉(l) were measured by Johnston, Kerr, Clarke and Hallett, loc. cit. The C_p values above 290.19°K. were estimated by graphical extrapolation of the C_p curve plotted using the experimental data. The value of S_{298.15}[°] was derived based on the low temperature C_p, 13.29 - 221.61°K., and ΔH_m[°] for B₅H₉(c) reported by Johnston, Kerr, Clarke and Hallett, loc. cit. and C_p values, 226.34 - 298.15°K., for B₅H₉(l), using S_{13.29}[°] = 0.236 cal. deg.⁻¹ mole⁻¹ for B₅H₉(c).

Melting Data.

The values of T_m and ΔH_m[°] were taken from Johnston, Kerr, Clarke and Hallett, loc. cit.

Vaporization Data.

The boiling point (T_b) is calculated as the temperature at which the free energy change of the reaction B₅H₉(l) - B₅H₉(g) becomes zero. The enthalpy change of the reaction at T_b is heat of vaporization (ΔH_v[°]).





MOL. WT. = 63.172

(IDEAL GAS)

PENTABORANE (B_5H_9)

Pentaborane (B_5H_9)

(Ideal Gas) Mol. Wt. = 63.172

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	8.286	51.031	79.877	24.444	24.444	24.444	INFINITE
200	18.286	51.031	79.877	21.799	21.799	21.799	60.425
298	22.423	65.803	85.803	17.500	17.500	17.500	30.671
300	22.588	65.943	85.943	17.458	17.458	17.458	30.590
400	31.120	67.783	87.783	15.418	15.418	15.418	27.584
500	38.456	69.137	88.939	13.702	13.702	13.702	25.988
600	44.841	69.000	88.000	12.357	12.357	12.357	25.039
700	50.047	66.316	84.657	11.370	11.370	11.370	24.423
800	54.342	63.284	80.888	10.695	10.695	10.695	23.991
900	57.882	60.901	77.800	10.278	10.278	10.278	23.673
1000	60.485	58.212	74.212	9.971	9.971	9.971	23.427
1100	63.227	55.068	69.387	9.749	9.749	9.749	23.228
1200	65.245	51.551	64.512	9.587	9.587	9.587	23.064
1300	66.936	47.694	59.512	9.476	9.476	9.476	22.932
1400	68.361	43.594	54.512	9.404	9.404	9.404	22.821
1500	69.569	39.272	49.272	9.366	9.366	9.366	22.720
1600	70.600	34.764	43.764	9.350	9.350	9.350	22.627
1700	71.486	30.100	39.100	9.353	9.353	9.353	22.543
1800	72.250	25.321	34.321	9.370	9.370	9.370	22.466
1900	72.914	20.456	29.456	9.400	9.400	9.400	22.394
2000	73.484	15.531	24.531	9.442	9.442	9.442	22.333
2100	74.002	10.548	19.548	9.496	9.496	9.496	22.281
2200	74.450	5.513	14.513	9.562	9.562	9.562	22.237
2300	74.847	0.421	9.421	9.639	9.639	9.639	22.200
2400	75.199	-4.704	4.296	9.726	9.726	9.726	22.168
2500	75.514	-9.860	-0.456	9.822	9.822	9.822	22.140
2600	75.796	-15.000	-5.600	9.926	9.926	9.926	22.115
2700	76.050	-20.113	-10.713	10.036	10.036	10.036	22.092
2800	76.279	-25.200	-15.800	10.150	10.150	10.150	22.070
2900	76.486	-30.256	-20.856	10.266	10.266	10.266	22.049
3000	76.674	-35.281	-25.881	10.382	10.382	10.382	22.029
3100	76.845	-40.274	-30.874	10.498	10.498	10.498	22.010
3200	77.001	-45.234	-35.834	10.614	10.614	10.614	21.992
3300	77.144	-50.159	-40.759	10.729	10.729	10.729	21.975
3400	77.275	-55.049	-45.649	10.844	10.844	10.844	21.959
3500	77.396	-59.894	-50.494	10.958	10.958	10.958	21.943
3600	77.507	-64.694	-55.294	11.071	11.071	11.071	21.927
3700	77.609	-69.449	-60.049	11.183	11.183	11.183	21.911
3800	77.704	-74.159	-64.759	11.294	11.294	11.294	21.895
3900	77.792	-78.824	-69.424	11.404	11.404	11.404	21.879
4000	77.874	-83.444	-74.044	11.513	11.513	11.513	21.863
4100	77.950	-88.019	-78.619	11.621	11.621	11.621	21.847
4200	78.021	-92.549	-83.149	11.728	11.728	11.728	21.831
4300	78.087	-97.029	-87.629	11.834	11.834	11.834	21.815
4400	78.148	-101.459	-92.059	11.939	11.939	11.939	21.799
4500	78.205	-105.834	-96.434	12.043	12.043	12.043	21.783
4600	78.258	-110.154	-100.754	12.146	12.146	12.146	21.767
4700	78.311	-114.419	-105.019	12.248	12.248	12.248	21.751
4800	78.359	-118.629	-109.229	12.349	12.349	12.349	21.735
4900	78.404	-122.779	-113.379	12.449	12.449	12.449	21.719
5000	78.446	-126.869	-117.469	12.548	12.548	12.548	21.703
5100	78.486	-130.904	-121.504	12.646	12.646	12.646	21.687
5200	78.524	-134.884	-125.484	12.743	12.743	12.743	21.671
5300	78.559	-138.809	-129.409	12.839	12.839	12.839	21.655
5400	78.593	-142.679	-133.279	12.934	12.934	12.934	21.639
5500	78.625	-146.494	-137.094	13.028	13.028	13.028	21.623
5600	78.655	-150.254	-140.854	13.121	13.121	13.121	21.607
5700	78.684	-153.959	-144.559	13.213	13.213	13.213	21.591
5800	78.711	-157.609	-148.209	13.304	13.304	13.304	21.575
5900	78.736	-161.204	-151.804	13.394	13.394	13.394	21.559
6000	78.759	-164.744	-155.344	13.483	13.483	13.483	21.543

Dec. 31, 1960; Mar. 31, 1965

Point Group C_{4v}
 $\Delta H_f^o = 65.803 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = 17.5 \pm 1.6 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
2600 (1)	[1450] (1)	[1500] (1)	1449 (2)
2600 (1)	[500] (1)	[1100] (1)	1034 (2)
1844 (1)	1870 (1)	739 (1)	882 (2)
1413 (1)	1387 (1)	470 (1)	700 (2)
1126 (1)	[900] (1)	2599 (2)	605 (2)
985 (1)	782 (1)	1802 (2)	568 (2)
799 (1)	2600 (1)	1621 (2)	

Bond Distance: B-B = $1.800 \pm 0.003 \text{ \AA}$ B-B_{apex} = $1.687 \pm 0.005 \text{ \AA}$
 B-H = B_{apex}-H = $1.22 \text{ \AA}$ B-H_{bridge} = $1.35 \pm 0.02 \text{ \AA}$

Bond Angle: B_{apex}-B-H = $136^\circ 10' + 30'$ H-B_{apex}-B = $131^\circ \text{ \AA}$
 B-H_{bridge}-B = $83^\circ 37'$ B-B_{apex}-B = 90°

Angle between B_{apex}B plane and B_H bridge plane = $136 \pm 2^\circ$
 Product of the Moments of Inertia: $I_A I_B I_C = 2.3693 \times 10^{-114} \text{ g. cm.}^2$

Heat of Formation

The enthalpy change (ΔH_f^o) of the reaction $\text{B}_5\text{H}_9(\text{g}) \rightarrow 5\text{B}(\text{am.}) + 9/2 \text{ H}_2(\text{g})$ was reported to be -12.99 ± 0.39 and $-9.9 \pm 1 \text{ kcal. mole}^{-1}$ by E. J. Prosen, W. H. Johnson and P. V. Pergiel, J. Res. Natl. Bur. Std. 61, 247 (1958) and S. R. Omm and L. O. Green, J. Phys. Chem. 65, 2175 (1961), respectively. Using ΔH_f^o 298.15 = $1.2 \pm 0.4 \text{ kcal. mole}^{-1}$ for the reaction $\text{B}(\text{c}) \rightarrow \text{B}(\text{am.})$, the corresponding ΔH_f^o 298.15 values for $\text{B}_5\text{H}_9(\text{g})$ were derived as 18.99 and 15.9 kcal. mole⁻¹. The adopted value is the average of these two.

Heat Capacity and Entropy

The molecular structure, a tetragonal pyramid of boron atoms, and constants were obtained from H. J. Hrostowski and R. J. Myers, J. Chem. Phys. 22, 262 (1954). The vibrational frequencies were reported by H. J. Hrostowski and O. C. Finantel, J. Am. Chem. Soc. 76, 998 (1954). The earlier models of pentaborane were assumed to have a hydrocarbon - like structure of low symmetry by S. H. Bauer and L. Pauling, J. Am. Chem. Soc. 58, 2403 (1936) and K. S. Pitzer, J. Am. Chem. Soc. 67, 1126 (1945). However, the electron diffraction and X-ray data by K. Hedberg, M. E. Jones and V. Schomaker, Proc. Natl. Acad. Sci., U. S. 39, 679 (1952) and W. J. Dulmage and W. N. Lipscomb, Acta Cryst. 5, 260 (1952) revealed an unusual pyramidal structure of C_{4v} symmetry. The Raman spectrum of liquid B_5H_9 and the infrared spectrum of the gas B_5H_9 from 3 to 25 microns have been obtained by W. J. Taylor, C. W. Beckett, J. Y. Rung, R. B. Holden and H. L. Johnson, Phys. Rev. 79, 234 (1950). The near infrared spectrum of $\text{B}_5\text{H}_9(\text{l})$ have been examined at high resolution by F. R. Pondy and H. C. Beechell, J. Chem. Phys. 25, 238 (1956). Ten bands were observed. The three principal moments of inertia are: $I_A = I_B = 1.18344 \times 10^{-38} \text{ g. cm.}^2$ and $I_C = 1.69172 \times 10^{-38} \text{ g. cm.}^2$



Dipotassium Hexaborate ($K_2B_{10}O_{10}$)
(Crystal) Mol. Wt. = 303.12

T. °K.	C _p ^o	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$\int_0^T C_p dT$ S° - (F° - H ₂₉₈ °)/T	$\frac{H^\circ - H_{298}^\circ}{T}$ kcal. mole ⁻¹	ΔF°	Log K _p
100						
200						
298	62.600	60.000	60.000	0.000	-1040.549	762.707
300	62.700	60.389	60.001	6.116	-1040.136	767.702
400	67.600	70.000	70.000	0.000	-1040.136	795.470
500	73.680	95.019	95.019	13.768	-994.470	834.662
600	78.900	108.916	73.252	21.398	-971.412	853.820
700	84.000	121.461	79.257	28.343	-948.292	866.056
800	89.100	133.053	85.253	38.199	-925.159	872.730
900	94.200	143.800	91.250	50.000	-902.000	877.730
1000	98.670	153.942	96.949	64.000	-878.945	882.084
1100	101.170	163.490	102.571	81.012	-853.887	886.644
1200	102.790	172.365	108.021	100.212	-827.333	890.671
1300	104.130	180.646	113.293	121.599	-800.593	894.636
1400	105.450	188.472	118.472	145.000	-774.742	898.545
1500	106.450	195.712	123.288	169.621	-748.294	899.021
1600	107.520	202.616	128.042	195.320	-722.116	898.632
1700	108.580	209.167	132.623	221.125	-696.030	897.476
1800	109.650	215.452	137.050	247.000	-670.018	896.178
1900	110.730	221.392	141.250	272.945	-644.178	894.702
2000	111.600	227.055	145.276	300.000	-618.209	893.551

B_6K_{20}
MOL. WT. = 303.12

(CRYSTAL)

DIPOTASSIUM HEXABORATE ($K_2B_{10}O_{10}$)

$\Delta H_f^\circ 0$ = Unknown

$\Delta H_f^\circ 298.15 = -1,107.44 \pm 2.4$ kcal. mole⁻¹

$T_D = 1098^\circ K$

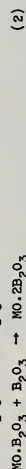
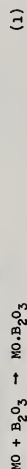
Heat of Formation.

The heat of reaction $K_2O(c) + 3B_2O_3(l) \rightarrow K_2B_{10}O_{10}(c)$ was reported by L. Shwarts and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and for $K_2O(c)$ (June 30, 1963). The above $\Delta H_f^\circ = -122.8$ kcal. mole⁻¹.

Heat Capacity and Entropy.

The enthalpy measurements of O. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Cerd No. Mic 59-2916 in the range 288 to 973°K were graphically smoothed and used to determine C_p . Above this range C_p was extrapolated.

The entropy at 298°K was obtained from a consideration of the entropies of sodium end calcium borates and those of the constituent oxides, as given by K. K. Kelley and E. G. King, Bureau of Mines Bull. 592 (1961). These indicate that for the reactions



the simple addition of entropies will give values at least 2.7 e.u. too low for reaction (1) and at least 2.7 e.u. too high for reaction (2). The reason for this is probably structural, the $B_2O_4^{--}$ ion being a flexible chain while the $B_4O_7^{--}$ ion probably is a rigid chain of rings. It was assumed that additional B_2O_3 would extend the ring structure into a rigid plane and thus the entropy difference for reaction (2) was assumed to hold for each additional mole of B_2O_3 added. Thus a value for $MO \cdot B_2O_3$ was estimated to be 55.5 ± 1.5 and then using an average value of 4.5 ± 1.5 e.u. for the difference between K_2 and Na_2 gave 60 ± 3 e.u. for the entropy of $K_2B_{10}O_{10}$.

Decomposition Temperature.

The incongruent melting point was given by A.-P. Rollat, Comp. rend. 200, 1763 (1935), the decomposition products being $K_2B_4O_7(l)$ and $K_2B_{10}O_{13}(c)$.

B_6K_{20}

Dilithium Hexaborate ($\text{Li}_2\text{B}_6\text{O}_{10}$)
(Crystal) Mol. Wt. = 238.80

$\text{B}_6\text{Li}_2\text{O}_{10}$

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K_p
		cal. mole ⁻¹ deg ⁻¹	keal. mole ⁻¹		
0					
100					
200					
298	70.080	45.000	-0.000	-1113.740	-1047.448
300	70.180	45.434	1.130	-1113.727	-1047.039
400	75.590	66.378	7.423	-1113.163	-1024.899
500	80.440	83.779	53.319	-1114.325	-1002.723
600	84.610	98.824	59.677	-1114.117	-980.419
700	88.050	112.132	66.238	-1113.866	-958.156
800	90.940	124.083	72.734	-1113.557	-935.939
900	93.390	134.939	79.052	-1113.185	-913.759
1000	95.500	144.890	85.145	-1112.764	-891.614
1100	97.145	154.069	90.989	-1112.327	-869.526
1200	98.777	162.561	96.614	-1111.862	-847.470
1300	100.305	170.557	101.999	-1111.370	-825.461
1400	101.819	178.046	107.166	-1110.835	-803.483
1500	103.290	185.121	112.129	-1110.266	-781.536
1600	104.717	191.833	116.903	-1109.651	-759.655
1700	106.101	198.223	121.500	-1109.083	-735.145
1800	107.441	204.326	125.933	-1117.015	-709.063
1900	108.737	210.170	130.214	-1176.893	-683.039
2000	109.990	215.760	134.353	-1175.706	-657.082

Mar. 31, 1962; Dec. 31, 1962; Mar. 31, 1965

DILITHIUM HEXABORATE ($\text{Li}_2\text{B}_6\text{O}_{10}$)

(CRYSTAL)

MOL. WT. = 238.80

$\Delta H_f^\circ 0$ = Unknown

$\Delta H_f^\circ 298.15$ = -1,113.74 $\pm$ 2.40 kcal. mole⁻¹

$S_{298.15}^\circ$ = [45.0 $\pm$ 1.0] cal. deg.⁻¹ mole⁻¹

T_d = 1107 $\pm$ 4°K.

Heat of Formation.

The heat of reaction $\text{Li}_2\text{O}(c) + 3\text{B}_2\text{O}_3(l) \rightarrow \text{Li}_2\text{B}_6\text{O}_{10}(c)$ was reported by L. Shartais and W. Capps, J. Am. Ceram. Soc. 37, 21-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $\text{B}_2\text{O}_3(l)$ (Dec. 31, 1964) and $\text{Li}_2\text{O}(c)$ (March 31, 1964). The above ΔH_f° = -72.80 kcal. mole⁻¹.

Heat Capacity and Entropy.

The enthalpy measurement of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 823°K. were used to determine C_p . Above this range C_p is extrapolated. Entropy at 298°K. is estimated from that of the component oxides and the difference from the oxides observed for twice $\text{LiBO}_2(c)$.

Temperature of Decomposition.

The incongruent melting point reported by E. S. R. Sastry and P. A. Hummel, J. Am. Ceram. Soc. 42, 216-8 (1959) is used here.

$\text{B}_6\text{Li}_2\text{O}_{10}$

Disodium Hexaborate ($\text{Na}_2\text{B}_6\text{O}_{10}$)
(Crystal) Mol. Wt. = 270.902

T, °K.	C _p	S°	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
	cal. mole ⁻¹ deg. ⁻¹			cal. mole ⁻¹			
0							
100							
200							
298	56.4200	55.5500	55.500	+0.00	-1094.760	-1078.411	753.810
300	58.4000	55.5601	55.504	+1.08	-1094.771	-1078.400	748.862
400	67.6800	73.9944	57.904	6.416	-1096.638	-1079.551	549.381
500	76.4480	90.0005	62.745	13.630	-1097.039	-1082.775	429.528
600	84.5500	104.673	68.527	21.687	-1097.089	-959.852	349.609
700	92.5600	118.927	73.827	30.518	-1096.715	-917.275	269.735
800	98.5600	131.900	78.027	40.519	-1096.150	-875.215	206.745
900	104.2500	142.937	81.160	50.159	-1094.431	-831.667	216.516
1000	109.0000	154.176	83.305	60.871	-1092.784	-869.214	189.958
1100	112.6800	164.745	99.324	71.962	-1090.994	-866.957	168.267
1200	117.5300	183.994	110.401	95.674	-1132.756	-798.106	134.167
1300	123.1400	205.764	125.891	121.858	-1130.118	-772.461	120.581
1400	129.1400	232.786	141.921	159.822	-1127.456	-747.014	108.835
1500	126.3300	261.030	121.805	118.638	-1127.456	-747.014	108.835
1600	121.1800	288.824	127.002	130.915	-1124.796	-721.731	98.579
1700	116.9300	316.191	122.034	145.087	-1122.156	-696.619	89.552
1800	113.5600	343.146	117.594	161.507	-1119.594	-671.852	81.401
1900	112.7400	369.790	114.921	177.559	-1116.990	-646.852	74.401
2000	113.1200	396.100	112.821	193.221	-1114.447	-622.179	67.985

DISODIUM HEXABORATE ($\text{Na}_2\text{B}_6\text{O}_{10}$)

(CRYSTAL)

$$\text{B}_6\text{Na}_{20}\text{I}_0$$

MOL. WT. = 270.902

 $\Delta H_f^\circ = \text{Unknown}$
$$S_{298.15}^{\circ} = [55.5 \pm 1.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

-1, -1, -1

$$T_A = 1039^\circ\text{K}.$$

Heat of Formation.

The heat of reaction $\text{Na}_2\text{O}(c) + 3\text{B}_2\text{O}_3(l) \rightarrow \text{Na}_2\text{B}_6\text{O}_{10}(c)$ was reported by L. Shartais and W. Osppas, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $\text{B}_2\text{O}_3(l)$ (Dec. 31, 1954) and for $\text{Na}_2\text{O}(c)$ (June 30, 1952). The above $\Delta H_f^\circ = -97.52$ kcal./mole.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. M1c 59-2916 in the range 298 to 1039°K were smoothed graphically and used to determine C_p . Above this range C_p was extrapolated. Entropy at 298°K was estimated as described in detail for $K_2PbO_1(c)$.

Decomposition Temperature.

The incongruent melting point was reported by G. W. Morey and H. E. Merwin, J. Am. Chem. Soc. **58**, 2248 (1936), the products are $\text{Na}_2\text{B}_4\text{O}_{11}$ (1) and $\text{Na}_2\text{B}_8\text{O}_{13}$ (c).

 $B_6Na_{20}^{10}$

LEAD HEXABORATE (PbB₆O₁₀) (CRYSTAL)

T, °K.	C _p	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	ΔH_f°	ΔF_f°	Log K _p
0					
100					
200					
298	55.200	48.600	48.600	-937.311	687.034
300	55.400	48.942	48.942	-936.905	682.502
400	68.400	66.696	50.934	-914.894	606.835
500	76.880	83.221	55.758	-892.906	590.270
600	89.680	98.678	61.637	-871.122	517.291
700	106.230	124.532	71.699	-859.931	465.176
800	111.630	139.770	81.046	-850.258	425.504
900	115.590	151.746	87.525	-842.826	394.915
1000	118.420	162.904	93.476	-836.009	371.774
1100	121.370	182.060	100.066	-829.520	352.087
1200	121.470	191.060	106.066	-824.314	335.734
1300	121.590	191.060	111.063	-820.438	321.162
1400	121.630	191.060	115.516	-817.717	308.162
1500	122.320	200.409	124.339	-816.285	295.987
1600	122.640	208.310	136.582	-816.051	284.111
1700	122.740	215.740	147.058	-816.017	272.304
1800	122.880	222.765	158.127	-816.028	260.477
1900	122.990	229.411	168.138	-816.104	248.217
2000	123.080	235.722	185.724	-816.317	235.680

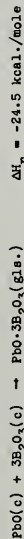
Mar. 31, 1962; Dec. 31, 1962; Mar. 31, 1965

$\Delta H_f^{\circ} = \text{Unknown}$
 $\Delta H_f^{\circ} 298.15 = -1003 \pm 2.0 \text{ kcal mole}^{-1}$

$S^{\circ} 298.15 = \{48.6 \pm 3\} \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Heat of Formation.

See lead diborate table for the complete writeup. W. H. Evans in NBS Report 7192, July 1, 1961, analysed the heats of formation of the lead borate system based upon Shartsis and Newman's heats of solution and Mazzetti and De Carli's phase studies. From the Shartsis and Newman paper Evans obtained the following:



and estimated a ΔH_f° of 16.0 kcal. mole⁻¹ for the conversion to the $\text{PbO} \cdot 3\text{B}_2\text{O}_3(\text{crystal})$. With auxiliary JANAF values the $\Delta H_f^{\circ} 298.15$ was calculated to be -1003.00 kcal./mole.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of heat capacities of the constituent oxides.

The entropy at 298.15 was obtained in the manner described in the $\text{PbB}_6\text{O}_{10}$ table from $S_{298.15}^{\circ}$ for $\text{PbB}_6\text{O}_{10}$ and B_2O_3 and the subtraction of 4.2 e.u.

Dipotassium Octaborate ($K_2B_8O_{13}$)
(Crystal) Mol. Wt. = 372.76

Dipotassium Octaborate ($K_2B_8O_{13}$)
(Crystal) Mol. Wt. = 372.76

T, °K	C _p	cal. mole ⁻¹ deg ⁻¹	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	cal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0								
100								
200								
298								
76.700		70.200		0.000	-1420.920	-1334.318		976.035
76.970		70.676		.142	-1420.928	-1333.783		971.614
86.160		94.086		8.302	-1422.594	-1304.441		712.670
500		94.960		17.356	-1423.082	-1274.844		557.207
600	104.000	132.371		27.307	-1423.290	-1245.167		453.530
700	112.680	149.077		38.156	-1423.058	-1215.489		370.475
800	119.600	164.587		48.778	-1422.407	-1185.687		323.054
900	125.500	179.023		62.041	-1421.387	-1156.380		280.764
1000	130.500	192.518		78.853	-1420.072	-1126.992		246.262
1100	134.000	205.122		98.081	-1418.404	-1098.715		217.688
1200	137.200	216.671		120.643	-1416.300	-1063.003		193.591
1300	140.100	228.019		146.511	-1413.869	-1030.496		173.234
1400	142.700	238.499		175.653	-1411.112	-998.150		155.811
1500	145.000	248.424		208.397	-1408.068	-965.960		140.738
1600	147.000	257.848		244.643	-1404.744	-933.978		127.569
1700	148.700	266.812		284.431	-1401.166	-902.136		115.072
1800	150.100	275.353		327.701	-1397.358	-870.449		103.682
1900	151.200	283.459		374.425	-1393.332	-838.804		93.461
2000	152.000	291.276		424.603	-1389.091	-807.497		84.235

ΔH_f° = Unknown
 ΔH_f° 298.15 = -1,420.92 ± 1.4 kcal. mole⁻¹
 ΔH_m° = 29.9 ± 1.0 kcal. mole⁻¹
 T_m = 1130°K.
 $S_{298.15}^\circ$ = [70.2 ± 4] cal. deg.⁻¹ mole⁻¹

Heat of Formation.
 The heat of reaction $K_2O(c) + 4B_2O_3(l) \rightarrow K_2B_8O_{13}(c)$ was reported by L. Shartala and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and for $K_2O(c)$ (June 30, 1963). The above ΔH_f° = -137.00 kcal. mole⁻¹.

Heat Capacity and Entropy.
 The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1130°K were smoothed graphically and used to determine C_p . Above this range C_p is extrapolated.
 The entropy at 298°K was obtained by estimating the entropy of $Na_2B_8O_{13}(c)$ as 65.7 ± 2.5 e.u., as described on the table for $K_2B_8O_{10}(c)$ and then using an average value of 4.5 ± 1.5 e.u. for the replacement of Na_2 by K_2 .

Melting Data.
 T_m is given by A.-P. Rollet, Comp. rend., 200, 1763 (1935). ΔH_m° was obtained from the values of ΔH_f° for $K_2B_8O_{13}(c)$ and $K_2B_8O_{13}(l)$ at 298°K reported above and the enthalpy of the crystal and liquid at T_m .

$B_8K_{20}^{13}$

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0									
100									
200									
298	77.220	71.295	71.295		.000	-1403.570	-1317.295		965.557
300	77.560	71.774			.143	-1403.577	-1316.762		959.214
400	96.120	96.428			8.453	-1404.193	-1287.767		916.568
500	107.000	110.517			18.901	-1404.196	-1256.330		849.089
600	113.000	130.279			30.024	-1403.223	-1229.245		747.731
700	158.100	158.560			42.597	-1401.267	-1200.336		674.744
800	158.100	179.571			58.407	-1396.428	-1171.076		570.154
900	158.100	198.592			74.841	-1391.568	-1144.456		444.685
1000	158.100	214.590			90.037	-1387.549	-1116.901		244.687
1100	158.100	230.018			109.937	-1421.298	-1087.994		216.154
1200	158.100	243.775			121.647	-1416.946	-1057.680		182.657
1300	158.100	256.430			137.457	-1412.773	-1028.135		152.857
1400	158.100	268.456			156.640	-1408.842	-999.549		124.857
1500	158.100	279.054			169.077	-1404.982	-969.549		141.296
1600	158.100	289.257			184.887	-1401.151	-940.639		128.479
1700	158.100	298.842			200.697	-1397.450	-911.971		117.236
1800	158.100	307.597			216.307	-1393.794	-883.241		107.248
1900	158.100	315.627			231.717	-1390.076	-854.241		98.490
2000	158.100	324.536			246.127	-1387.418	-827.144		90.382
2100	158.100	332.250			263.937	-1384.214	-799.200		83.170
2200	158.100	339.604			279.747	-1381.102	-771.418		76.630
2300	158.100	346.633			295.557	-1378.060	-743.621		70.672
2400	158.100	353.447			311.367	-1375.000	-715.793		65.242
2500	158.100	359.915			327.177	-1415.323	-688.003		60.142
2600	158.100	366.016			342.987	-1412.447	-658.562		55.388
2700	158.100	371.983			358.797	-1409.622	-630.030		50.995
2800	158.100	377.783			374.607	-1406.844	-601.218		46.925
2900	158.100	383.459			390.417	-1404.116	-572.142		43.147
3000	158.100	388.940			406.227	-1401.422	-543.847		39.617

$S_{298.15}^{\circ} = [71.295] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = -1,403.57 \pm 2.4 \text{ kcal. mole}^{-1}$
 $\Delta H_m = 29.9 \pm 1.0 \text{ kcal. mole}^{-1}$
 $T_m = 1130^{\circ}\text{K.}$

Heat of Formation.

The heat of reaction $K_2O(c) + 4B_2O_3(l) \rightarrow K_2B_8O_{13}(l)$ was reported by L. Shartais and W. Ceppa, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxida have been converted to the heats of formation using JANAP values for $B_2O_3(l)$ (Dec. 31, 1964) and for $K_2O(c)$ (June 30, 1963). The above $\Delta H_f^{\circ} = -119.65 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2910 in the range 298 to 1373°K on the glass and liquid were smoothed graphically and used to determine C_p . There is a discontinuity in the C_p curve, a glass transition at about 873°K. Above 873°K the C_p values were estimated to be constant.

The entropy was obtained from that of the crystal by adding ΔS_m° and the difference between $S_{1130-298}$ for crystal and liquid.

Melting Data.

See the crystal table.

Lithium Octaborate ($\text{Li}_2\text{B}_8\text{O}_{13}$)
(Crystal) Mol. Wt. = 308.44

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔH_f°	ΔF_f°	Log K_f
0						
100						
200						
298	77.800	63.400	63.400	-1413.570	-1390.011	974.878
300	78.100	63.882	63.401	-1413.572	-1329.496	968.490
400	89.300	88.577	64.465	-1413.591	-1301.481	711.042
500	102.430	110.437	73.281	-1414.669	-1273.398	556.575
600	108.320	120.656	81.189	-1414.653	-1245.310	453.549
700	112.720	126.692	89.284	-1413.680	-1217.117	379.583
800	116.320	131.986	97.432	-1413.654	-1189.095	324.830
900	119.200	135.858	105.387	-1412.475	-1161.135	281.949
1000	121.570	138.542	113.078	-1411.869	-1133.229	247.665
1100	123.480	200.235	120.426	-1411.871	-1105.402	219.613
1200	125.988	211.557	127.476	-1411.871	-1077.574	191.613
1300	127.131	221.152	134.303	-1410.040	-1049.803	176.435
1400	128.828	230.646	140.933	-1409.413	-1022.207	159.566
1500	130.480	239.591	147.215	-1408.763	-994.584	144.904
1600	132.087	248.093	153.235	-1408.081	-966.983	132.077
1700	133.648	256.118	159.071	-1407.281	-939.402	120.878
1800	135.164	263.600	164.678	-1406.352	-911.847	110.447
1900	136.635	271.148	170.089	-1405.307	-884.319	100.447
2000	138.060	278.193	175.320	-1404.146	-856.826	91.967

Li_2O

(CRYSTAL)

LITHIUM OCTABORATE ($\text{Li}_2\text{B}_8\text{O}_{13}$)

MOL. WT. = 308.44

ΔH_f° = UNKNOWN

ΔH_f° 298.15 = -1413.57 ± 2.50 kcal. mole⁻¹

$S_{298.15}^\circ$ = [63.4 ± 1.0] cal. deg.⁻¹ mole⁻¹

T_d = 908 ± 10°K.

Heat of Formation.

The heat of the reaction $\text{Li}_2\text{O}(c) + 4\text{B}_2\text{O}_3(l) \rightarrow \text{Li}_2\text{B}_8\text{O}_{13}(c)$ was reported by L. Shartsis and V. Cappe, J. Am. Ceram. Soc. 51, 27-32 (1964) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAP values for $\text{B}_2\text{O}_3(l)$ (Dec. 51, 1964) and for $\text{Li}_2\text{O}(c)$ (March 51, 1964). The above ΔH_f° = -73.35 kcal. mole⁻¹.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1968, L. C. Card No. Mic 59-2316 in the range of 298 to 823°K. were used to determine C_p . Above this range C_p is extrapolated. Entropy at 298°K. is estimated from that of the component oxides and the difference from the oxides observed for twice $\text{LiB}_2\text{O}_4(c)$.

Temperature of Decomposition. The incongruent melting point reported by B. S. R. Sastry and P. A. Hummel, J. Am. Ceram. Soc. 42, 216-8 (1959) is used here.

Li_2O

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔF ₂₉₈ ^o	Log K _p
0	-0.00	INFINITE	- 6.742	3.426	INFINITE
100	13.294	12.718	- 1.226	14.654	- 32.025
200	20.490	26.225	- 6.001	31.652	- 34.566
298	52.092	42.200	- 0.000	49.634	- 36.527
300	52.411	42.524	- 0.007	50.183	- 36.546
400	72.900	70.400	- 6.944	68.813	- 38.578
500	78.000	77.559	- 14.023	89.207	- 38.991
600	87.200	92.614	- 22.295	109.211	- 39.778
700	95.000	106.680	- 31.516	129.416	- 40.403
800	100.750	119.729	- 41.210	149.720	- 40.900
900	105.750	131.820	- 51.343	169.481	- 41.308
1000	110.000	143.290	- 61.925	189.481	- 41.628
1100	113.500	153.914	- 73.516	210.667	- 41.893
1200	116.250	163.913	- 85.010	231.256	- 42.115
1300	118.250	173.302	- 96.741	251.611	- 42.298
1400	120.000	182.182	- 107.882	271.682	- 42.448
1500	120.000	190.392	- 120.018	292.310	- 42.568

$\Delta H_f^{\circ} 0 = 3.4 \pm 4.5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = -6.9 \pm 4.5 \text{ kcal. mole}^{-1}$
 $\Delta H_m^{\circ} = 5.25 \pm 0.01 \text{ kcal. mole}^{-1}$
 $\Delta H_g^{\circ} 298 = 19.2 \pm 0.2 \text{ kcal. mole}^{-1}$

$S_{298.15}^{\circ} = 42.20 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 371.93^{\circ}\text{K}$

Heat of Formation.
The enthalpy change ($\Delta H_f^{\circ} 298.15$) of the reaction $B_{10}H_{14}(c) \rightarrow 10B(am) + 7H_2(g)$ was reported to be 19.8 ± 1.4 and $18.0 \pm 1.0 \text{ kcal. mole}^{-1}$ by W. H. Johnson, M. V. Kilday and E. J. Prosen, *J. Res. Natl. Bur. Std.* **54A**, 521 (1960) and G. L. Gal'chenko, B. I. Timofeev and S. M. Shursov, *Doklady Akademii Nauk. USSR*, **142**, 1077 (1962), respectively. Using $\Delta H_f^{\circ} 298.15 = 1.2 \pm 0.4 \text{ kcal. mole}^{-1}$ for the reaction $B(c) \rightarrow B(am)$, the corresponding $\Delta H_f^{\circ} 298.15$ values for $B_{10}H_{14}(c)$ were calculated to be -7.8 and $-6.0 \text{ kcal. mole}^{-1}$. The adopted value of $\Delta H_f^{\circ} 298.15$ for $B_{10}H_{14}(c)$ is the average of these two.

Heat Capacity and Entropy.
 C_p (60° to 371.93°K.) was given by G. T. Furukawa and R. P. Park, *J. Res. Natl. Bur. Standards*, **55**, 255 (1955). The heat capacity above 371.93° was estimated by comparison with that of the liquid decaborane. Heat capacity (14° to 205°K.) was also reported by E. C. Kerr, N. C. Hallett and H. L. Johnston, *J. Am. Chem. Soc.*, **73**, 1117 (1951). The value of $S_{298.15}^{\circ}$ was taken from G. T. Furukawa and R. P. Park, loc. cit.

Melting Data.
 T_m and ΔH_m° were obtained from G. T. Furukawa and R. P. Park, loc. cit.

Heat of Sublimation.
 $\Delta H_g^{\circ} 298.15$ was calculated from free energy functions and vapor pressure reported by G. T. Furukawa and R. P. Park, loc. cit. See $B_{10}H_{14}(g)$ table for details.

Decaborane (B₁₀H₁₄)
(Liquid) Mol. Wt. = 122.312

T. °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0						
100	52.870	56.299	56.299	0.000	1.700	50.630
200	53.280	56.627	56.627	0.000	1.743	37.258
300	53.600	56.955	56.955	0.000	1.787	37.263
400	53.920	57.283	57.283	0.000	1.831	37.268
500	54.240	57.611	57.611	0.000	1.875	37.273
600	54.560	57.939	57.939	0.000	1.919	37.278
700	54.880	58.267	58.267	0.000	1.963	37.283
800	55.200	58.595	58.595	0.000	2.007	37.288
900	55.520	58.923	58.923	0.000	2.051	37.293
1000	55.840	59.251	59.251	0.000	2.095	37.298
1100	56.160	59.579	59.579	0.000	2.139	37.303
1200	56.480	59.907	59.907	0.000	2.183	37.308
1300	56.800	60.235	60.235	0.000	2.227	37.313
1400	57.120	60.563	60.563	0.000	2.271	37.318
1500	57.440	60.891	60.891	0.000	2.315	37.323

B₁₀H₁₄
MOL. WT. = 122.312

DECABORANE (B₁₀H₁₄) (LIQUID)

S_{298.15} = 56.299 cal. deg.⁻¹ mole⁻¹
 T_m = 371.93°K.
 T_b = [492]°K.

Heat of Formation.

ΔH_f° 298.15 was calculated from ΔH_f° 298.15 for B₁₀H₁₄(c) and ΔH_m° reported by G. T. Furukawa and R. P. Park, J. Res. Natl. Bur. Standards, 55, 255 (1955) and the difference H_m° - H_f° 298.15 for crystal and liquid.

Heat Capacity and Entropy.

C_p (371.93° to 380°K) was measured by G. T. Furukawa and R. P. Park, J. Res. Natl. Bur. Standards, 55, 255 (1955). Heat capacities below 371.93° and above 380°K. were estimated by comparison with that of the gaseous decaborane. S_{298.15} was calculated from that of crystal in a manner analogous to that of the heat of formation.

Melting and Vaporization Data.

T_m and ΔH_m° were obtained from G. T. Furukawa and R. P. Park, loc. cit. T_b and ΔH_v° were calculated from functions for B₁₀H₁₄(l) and B₁₀H₁₄(g), respectively.

B₁₀H₁₄

T, °K	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	- 5.937	22.451	22.451	INFINITE
100	10.998	49.315	110.076	- 5.076	17.959	17.959	- 65.725
200	21.996	98.630	220.152	- 4.216	13.467	13.467	- 54.465
298	42.920	84.147	0.000	0.000	11.300	95.327	- 40.701
300	43.250	84.414	0.080	0.080	11.239	95.799	- 40.647
400	52.738	92.182	86.030	86.334	7.109	38.850	- 38.850
500	73.238	112.017	90.185	112.956	5.984	8.082	- 38.082
600	84.050	128.362	10.811	103.478	4.219	103.478	- 37.600
700	92.719	141.994	101.044	28.665	2.999	120.131	- 37.505
800	99.711	154.848	106.974	38.269	2.241	137.401	- 37.401
900	105.389	166.931	112.972	48.564	1.462	153.773	- 37.339
1000	110.051	178.284	118.941	58.342	1.764	170.604	- 37.297
1100	113.852	188.956	124.826	67.542	1.842	187.947	- 37.260
1200	117.019	199.002	130.593	82.081	2.063	204.430	- 37.230
1300	119.663	208.476	136.223	93.929	2.353	221.273	- 37.198
1400	121.895	217.428	141.707	106.009	2.685	238.111	- 37.169
1500	123.766	225.803	147.040	118.494	2.998	254.907	- 37.139
1600	125.369	233.943	152.222	131.753	3.281	271.691	- 37.109
1700	126.743	241.584	157.256	143.361	3.530	288.465	- 37.083
1800	127.929	248.865	162.145	156.006	3.736	305.209	- 37.056
1900	128.957	255.809	166.693	168.941	3.909	321.956	- 37.032
2000	129.854	262.447	171.100	181.983	4.056	338.698	- 37.009
2100	130.641	268.802	175.989	194.708	4.163	355.430	- 36.988
2200	131.334	274.896	180.347	208.008	4.239	372.156	- 36.968
2300	131.947	280.748	184.386	221.172	4.280	388.873	- 36.950
2400	132.485	286.325	188.171	234.175	4.295	405.581	- 36.934
2500	132.978	291.704	191.727	247.040	4.287	422.280	- 36.912
2600	133.414	297.018	195.038	260.089	4.267	442.933	- 36.893
2700	133.805	302.260	198.150	274.350	4.235	464.546	- 36.874
2800	134.158	307.433	201.066	288.748	4.191	486.125	- 36.857
2900	134.478	311.447	203.811	303.281	4.136	507.670	- 36.841
3000	134.768	315.211	206.403	317.963	4.070	529.189	- 36.826
3100	135.032	320.634	214.785	336.936	4.000	550.681	- 36.812
3200	135.273	324.725	218.160	361.649	4.000	572.148	- 36.800
3300	135.493	329.091	221.459	385.167	4.000	593.581	- 36.790
3400	135.693	333.641	224.681	407.581	4.000	614.981	- 36.781
3500	135.881	337.079	227.839	429.826	4.000	636.356	- 36.773
3600	136.053	340.504	230.927	451.923	4.000	657.707	- 36.766
3700	136.211	344.635	233.950	473.866	4.000	679.032	- 36.760
3800	136.357	348.270	236.914	495.656	4.000	700.332	- 36.754
3900	136.493	351.514	239.812	517.301	4.000	721.607	- 36.749
4000	136.618	354.271	242.653	538.807	4.000	742.857	- 36.744
4100	136.735	356.644	245.443	560.178	4.000	764.082	- 36.740
4200	136.845	361.842	248.178	581.423	4.000	785.282	- 36.736
4300	136.946	365.163	250.861	602.546	4.000	806.457	- 36.732
4400	137.041	368.514	253.495	623.546	4.000	827.607	- 36.728
4500	137.130	371.394	256.081	644.423	4.000	848.732	- 36.724
4600	137.214	374.408	258.621	665.178	4.000	869.832	- 36.720
4700	137.292	377.360	261.116	685.807	4.000	890.907	- 36.716
4800	137.366	380.252	263.568	706.312	4.000	911.957	- 36.712
4900	137.436	383.082	265.948	726.697	4.000	932.982	- 36.708
5000	137.500	385.862	268.248	747.062	4.000	953.982	- 36.704
5100	137.561	388.585	270.679	767.307	4.000	974.957	- 36.700
5200	137.619	391.257	272.972	787.432	4.000	995.907	- 36.696
5300	137.674	393.879	275.229	807.447	4.000	1016.832	- 36.692
5400	137.727	396.451	277.451	827.351	4.000	1037.732	- 36.688
5500	137.775	398.980	279.637	847.146	4.000	1058.607	- 36.684
5600	137.822	401.463	281.790	866.832	4.000	1079.457	- 36.680
5700	137.866	403.903	283.911	886.417	4.000	1100.282	- 36.676
5800	137.908	406.301	285.991	905.902	4.000	1121.082	- 36.672
5900	137.948	408.657	288.031	925.287	4.000	1141.857	- 36.668
6000	137.986	410.978	290.039	944.572	4.000	1162.607	- 36.664

Dec. 31, 1960; Sept. 30, 1962; June 30, 1963; Dec. 31, 1964

DECABORANE (B₁₀H₁₄)

(IDEAL GAS)

MOL. WT. = 122.312

Point Group C_{2v}ΔH_f⁰ = 22.5 ± 4.5 kcal. mole⁻¹ΔH_f⁰ 298.15 = 11.3 ± 4.5 kcal. mole⁻¹S° 298.15 = 84.147 cal. deg.⁻¹ mole⁻¹

Ground State Multiplicity (1)

Vibrational Frequencies and Degeneracies

Wavenumber, cm. ⁻¹	Degeneracy
230(1)	295(1)
230(1)	344(1)
230(1)	350(1)
230(1)	387(1)
230(1)	434(1)
230(1)	446(1)
230(1)	452(1)
484(1)	508(1)
484(1)	588(1)
484(1)	618(1)
484(1)	635(1)
484(1)	651(1)
484(1)	690(1)
709(1)	720(1)
709(1)	747(1)
709(1)	752(1)
709(1)	787(1)
709(1)	814(1)
709(1)	822(1)
832(1)	859(1)
832(1)	862(1)
832(1)	903(1)
832(1)	915(1)
832(1)	924(1)
832(1)	938(1)
942(1)	980(1)
942(1)	987(1)
942(1)	1008(1)
942(1)	1037(1)
942(1)	1060(1)
942(1)	1104(1)
1160(1)	1190(1)
1160(1)	1210(1)
1160(1)	1250(1)
1160(1)	1300(1)
1160(1)	1360(1)
1160(1)	1390(1)
1160(1)	1410(1)
1460(1)	1500(1)
1460(1)	1555(1)
1460(1)	1590(1)
1460(1)	1620(1)
1460(1)	1665(1)
1460(1)	1880(2)
2550(2)	2576(2)
2550(2)	2585(2)
2550(2)	2618(2)

Bond Distances: B-B = 1.762 Å

Bond Angle: B-B-B = 108°

B-B-bridge = 1.394 Å

B-bridge-B = 59° 34'

B-bridge-B-bridge = 67° 42'

B-bridge-B-center-H = 120°

Product of the Moments of Inertia: I_AI_BI_C = 8.6710 X 10⁻¹¹⁵ g.³ cm.⁶

Heat of Formation.

The vapor pressures of decaborane (B₁₀H₁₄) were measured by O. T. Furukawa and R. P. Park, J. Res. Natl. Bur. Std. 55, 255 (1955) and O. A. Miller, J. Phys. Chem. 57, 1353 (1953). The heats of vaporization (ΔH_v⁰) were derived by both the second and third law methods. Using the average value of ΔH_v⁰, the respective heats of formation (ΔH_f⁰ 298.15) for B₁₀H₁₄(g) were calculated. The results are presented as follows.

Investigator

Furukawa and Park

Miller

The adopted value of ΔH_f⁰ 298.15 for B₁₀H₁₄(g) is the weighted average of the three ΔH_f⁰ 298.15 values listed in the above table.

Heat Capacity and Entropy.

The molecular structure of B₁₀H₁₄(c) were reported by J. S. Kasper, C. M. Lucht and D. Harker, Acta Cryst. 3, 436 (1950); E. B. Moore, Jr., R. E. Dickerson and W. N. Lipscomb, J. Chem. Phys. 21, 209 (1957) and W. N. Lipscomb, Boron Hydrides, W. A. Benjamin, Inc., New York, 1953. For the calculation of the moments of inertia for B₁₀H₁₄(g) a simplified molecular model is adopted. The molecule is assumed to be composed of two regular pentagonal pyramids with a common base edge. The angle between the base planes of these pyramids is 73° 30'. Each of 10 H atoms is attached to a single B atom above the base plane. The remaining 4 H atoms, each bridge two B atoms. The vibrational frequencies were obtained from W. H. Evans, National Bureau of Standards Report 7033 (Jan. 1, 1961), which were derived based on the infrared and Raman spectra reported by J. E. Stewart, National Bureau of Standards, private communication, 1957 and W. E. Kaller and H. L. Johnston, J. Chem. Phys. 20, 1749 (1952). The three principal moments of inertia are I_A = 4.53925 X 10⁻³⁸, I_B = 3.51508 X 10⁻³⁸ and I_C = 5.43559 X 10⁻³⁸ g.² cm.²

Dilead Decaborate ($\text{Pb}_2\text{B}_{10}\text{O}_{17}$)
(Crystal) Mol. Wt. = 794.62

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	ΔH°_f	ΔF°_f	Log K_p
0						
100						
200						
298	97.200	84.300	0.000	-1694.000	-1591.528	1159.236
300	97.600	84.902	0.180	-1694.004	-1590.034	1151.581
400	127.600	116.453	11.111	-1693.601	-1543.134	084.069
500	137.600	144.097	24.034	-1692.407	-1503.634	036.081
600	153.400	171.511	38.023	-1690.366	-1468.453	534.858
700	166.100	196.135	54.013	-1689.489	-1431.296	446.849
800	176.100	217.318	72.003	-1688.734	-1394.596	390.967
900	184.100	234.435	91.993	-1688.089	-1358.856	336.085
1000	193.400	248.436	108.941	-1687.534	-1322.612	289.043
1100	199.100	279.149	152.259	-1672.465	-1267.375	255.766
1200	203.200	296.060	172.737	-1667.118	-1252.592	228.117
1300	206.100	310.458	188.467	-1661.484	-1238.117	204.117
1400	207.400	323.349	198.755	-1655.176	-1224.370	184.800
1500	208.200	342.683	202.277	-1650.775	-1210.869	167.673
1600	209.000	356.148	211.478	-1645.474	-1197.706	152.664
1700	209.800	368.842	220.365	-1640.259	-1184.878	139.464
1800	210.600	380.840	228.980	-1635.130	-1172.280	127.064
1900	211.400	392.267	237.268	-1630.087	-1160.030	117.936
2000	212.200	403.128	245.272	-1625.093	-1148.159	107.976

$\text{B}_{10}\text{O}_{17}\text{Pb}_2$
MOL. WT. = 794.62

DILEAD DECARBORATE ($\text{Pb}_2\text{B}_{10}\text{O}_{17}$) (CRYSTAL)

$S^\circ_{298.15} = [84.3 \pm 3] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^\circ_f 0 = \text{Unknown}$
 $\Delta H^\circ_f 298.15 = -1694 \pm 3 \text{ kcal. mole}^{-1}$

Heat of Formation.

See lead diborate for the complete writeup. W. H. Evans in NBS. Report 7192, July 1, 1961, analysed the heats of formation of the lead borate system based upon Sharvats and Newman's heats of solution and Mazzetti and DeCarli's phase studies. From the Sharvats and Newman paper Evans obtained the following:

$2\text{PbO}(c) + 5\text{B}_2\text{O}_3(c) \rightarrow 2\text{PbO} \cdot 5\text{B}_2\text{O}_3(c)$ $\Delta H^\circ_f = -45.2 \text{ kcal./mole}$
and estimated a ΔH°_{298} of 28.8 kcal. mole⁻¹ for the conversion to the $2\text{PbO} \cdot 5\text{B}_2\text{O}_3(\text{crystal})$. With auxiliary JANAF values the $\Delta H^\circ_f 298.15$ was calculated to be -1694.00 kcal./mole.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities of the constituent oxides.

The entropy at 298.15 was obtained in the manner described in the $\text{Pb}_2\text{B}_{10}\text{O}_{17}$ table from $S^\circ_{298.15}$ of $\text{Pb} \cdot 2\text{B}_2\text{O}_3$ and $\text{Pb} \cdot 3\text{B}_2\text{O}_3$ and the subtraction of 4.2 e.u.

$\text{B}_{10}\text{O}_{17}\text{Pb}_2$

(Reference State) Mol. Wt. = 9.013

MOL. WT. = 9.013

(REFERENCE STATE)

BERYLLIUM (Be)

Be

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	.000	INFINITE	=	.468	.000	.000	.000
100	2.437	1.130	2.412	=	.320	.000	.000	.000
200	2.926	2.280	2.280	=	.000	.000	.000	.000
300	3.950	2.304	2.280	.007	.000	.000	.000	.000
400	4.770	3.561	2.446	.466	.000	.000	.000	.000
500	5.254	4.684	2.784	.950	.000	.000	.000	.000
600	5.579	5.671	3.184	1.492	.000	.000	.000	.000
700	5.636	6.552	3.604	2.054	.000	.000	.000	.000
800	6.065	7.346	4.022	2.659	.000	.000	.000	.000
900	6.287	8.073	4.433	3.276	.000	.000	.000	.000
1000	6.517	8.741	4.831	3.916	.000	.000	.000	.000
1100	6.765	9.360	5.216	4.580	.000	.000	.000	.000
1200	7.003	9.979	5.588	5.269	.000	.000	.000	.000
1300	7.242	10.549	5.948	5.981	.000	.000	.000	.000
1400	7.481	11.094	6.298	6.717	.000	.000	.000	.000
1500	7.719	11.618	6.634	7.477	.000	.000	.000	.000
1600	7.901	13.495	7.010	11.016	.000	.000	.000	.000
1700	8.052	14.315	7.428	11.709	.000	.000	.000	.000
1800	7.004	14.714	7.821	12.407	.000	.000	.000	.000
1900	7.055	15.094	8.194	13.110	.000	.000	.000	.000
2000	7.108	15.457	8.548	13.818	.000	.000	.000	.000
2100	7.158	15.805	8.884	14.531	.000	.000	.000	.000
2200	7.209	16.139	9.208	15.249	.000	.000	.000	.000
2300	7.250	16.461	9.516	15.972	.000	.000	.000	.000
2400	7.320	16.771	9.812	16.700	.000	.000	.000	.000
2500	7.380	17.070	10.098	17.434	.000	.000	.000	.000
2600	7.400	17.360	10.370	18.172	.000	.000	.000	.000
2700	7.440	17.640	10.634	18.914	.000	.000	.000	.000
2800	4.997	43.675	11.285	90.691	.000	.000	.000	.000
2900	5.007	43.851	12.405	91.191	.000	.000	.000	.000
3000	5.021	44.021	13.458	91.693	.000	.000	.000	.000
3100	5.037	44.185	14.445	92.196	.000	.000	.000	.000
3200	5.057	44.346	15.377	92.700	.000	.000	.000	.000
3300	5.081	44.502	16.257	93.207	.000	.000	.000	.000
3400	5.109	44.654	17.090	93.717	.000	.000	.000	.000
3500	5.142	44.802	17.880	94.229	.000	.000	.000	.000
3600	5.179	44.948	18.630	94.745	.000	.000	.000	.000
3700	5.221	45.090	19.343	95.265	.000	.000	.000	.000
3800	5.268	45.230	20.022	95.790	.000	.000	.000	.000
3900	5.319	45.366	20.678	96.318	.000	.000	.000	.000
4000	5.376	45.503	21.288	96.854	.000	.000	.000	.000
4100	5.440	45.636	21.862	97.395	.000	.000	.000	.000
4200	5.508	45.768	22.449	97.942	.000	.000	.000	.000
4300	5.581	45.899	22.993	98.496	.000	.000	.000	.000
4400	5.656	46.028	23.515	99.058	.000	.000	.000	.000
4500	5.741	46.156	24.018	99.628	.000	.000	.000	.000
4600	5.828	46.283	24.499	100.207	.000	.000	.000	.000
4700	5.919	46.409	24.964	100.794	.000	.000	.000	.000
4800	6.014	46.535	25.412	101.391	.000	.000	.000	.000
4900	6.113	46.660	25.844	101.997	.000	.000	.000	.000
5000	6.215	46.785	26.262	102.613	.000	.000	.000	.000
5100	6.320	46.909	26.666	103.240	.000	.000	.000	.000
5200	6.428	47.032	27.056	103.877	.000	.000	.000	.000
5300	6.538	47.156	27.434	104.526	.000	.000	.000	.000
5400	6.650	47.279	27.799	105.186	.000	.000	.000	.000
5500	6.763	47.402	28.158	105.852	.000	.000	.000	.000
5600	6.877	47.525	28.501	106.538	.000	.000	.000	.000
5700	6.993	47.648	28.835	107.231	.000	.000	.000	.000
5800	7.109	47.761	29.156	107.936	.000	.000	.000	.000
5900	7.226	47.874	29.472	108.652	.000	.000	.000	.000
6000	7.340	48.015	29.785	109.381	.000	.000	.000	.000

September 30, 1981

Solid state to the melting point 1556°K.
Liquid state from 1556°K. to the boiling point 2757°K.
Ideal monatomic gas state above 2757°K.

See Crystal, Liquid, Ideal Monatomic gas for details.

Beryllium (Be)

(Crystal) Mol. Wt. = 9.013

T, °K.	C_p	S° - (F°-H ₂₉₈)/T	H° - H ₂₉₈	ΔH_f°	ΔF_f°	Log K _p
0	.000	INFINITE	INFINITE	.000	.000	INFINITE
100	2.437	1.130	4.712	.456	.000	.000
200	2.400	1.010	2.610	.320	.000	.000
298	3.932	2.280	.000	.000	.000	.000
300	3.950	2.304	.007	.000	.000	.000
400	4.770	3.561	2.446	.446	.000	.000
500	5.294	4.664	2.764	.950	.000	.000
600	5.579	5.671	3.144	1.492	.000	.000
700	5.731	6.551	3.404	2.046	.000	.000
800	5.845	7.346	4.022	2.659	.000	.000
900	6.267	8.073	4.433	3.276	.000	.000
1000	6.517	8.747	4.831	3.916	.000	.000
1100	6.745	9.360	5.216	4.500	.000	.000
1200	7.003	9.979	5.566	5.099	.000	.000
1300	7.242	10.549	5.946	5.717	.000	.000
1400	7.461	11.094	6.296	6.334	.000	.000
1500	7.719	11.616	6.747	.000	.000	.000
1600	7.956	12.124	7.191	7.255	.076	.011
1700	8.174	12.619	7.649	7.900	.086	.032
1800	8.435	13.049	8.091	8.576	.097	.051
1900	8.674	13.551	8.591	9.256	.107	.066
2000	8.913	14.002	9.165	10.736	.112	.079
2100	9.152	14.443	9.772	11.635	.116	.090
2200	9.429	14.874	10.429	12.536	.120	.100
2300	9.629	15.297	11.147	13.447	.123	.107
2400	9.866	15.712	11.929	14.361	.126	.112
2500	10.106	16.120	12.764	15.391	.129	.116
2600	10.345	16.521	13.643	16.390	.132	.119
2700	10.582	16.905	14.569	17.413	.135	.120
2800	10.822	17.305	15.539	18.459	.138	.123
2900	11.060	17.669	16.577	19.529	.141	.126
3000	11.299	18.068	17.620	20.623	.144	.129
				21.741	.147	.132
				22.882	.150	.135
				24.044	.153	.138
				25.229	.156	.141
				26.437	.159	.144
				27.669	.162	.147
				28.924	.165	.150
				30.204	.168	.153
				31.509	.171	.156
				32.839	.174	.159
				34.194	.177	.162
				35.574	.180	.165
				36.979	.183	.168
				38.409	.186	.171
				39.864	.189	.174
				41.344	.192	.177
				42.849	.195	.180
				44.379	.198	.183
				45.934	.201	.186
				47.514	.204	.189
				49.119	.207	.192
				50.749	.210	.195
				52.404	.213	.198
				54.084	.216	.201
				55.789	.219	.204
				57.519	.222	.207
				59.274	.225	.210
				61.054	.228	.213
				62.859	.231	.216
				64.689	.234	.219
				66.544	.237	.222
				68.424	.240	.225
				70.329	.243	.228
				72.259	.246	.231
				74.214	.249	.234
				76.194	.252	.237
				78.199	.255	.240
				80.229	.258	.243
				82.284	.261	.246
				84.364	.264	.249
				86.469	.267	.252
				88.599	.270	.255
				90.754	.273	.258
				92.934	.276	.261
				95.139	.279	.264
				97.369	.282	.267
				99.624	.285	.270
				101.904	.288	.273
				104.209	.291	.276
				106.539	.294	.279
				108.894	.297	.282
				111.274	.300	.285
				113.679	.303	.288
				116.109	.306	.291
				118.564	.309	.294
				121.044	.312	.297
				123.549	.315	.300
				126.079	.318	.303
				128.634	.321	.306
				131.214	.324	.309
				133.819	.327	.312
				136.449	.330	.315
				139.094	.333	.318
				141.764	.336	.321
				144.459	.339	.324
				147.179	.342	.327
				149.924	.345	.330
				152.694	.348	.333
				155.489	.351	.336
				158.309	.354	.339
				161.154	.357	.342
				164.024	.360	.345
				166.919	.363	.348
				169.839	.366	.351
				172.784	.369	.354
				175.754	.372	.357
				178.749	.375	.360
				181.769	.378	.363
				184.814	.381	.366
				187.884	.384	.369
				190.979	.387	.372
				194.099	.390	.375
				197.244	.393	.378
				200.414	.396	.381
				203.609	.399	.384
				206.829	.402	.387
				210.074	.405	.390
				213.344	.408	.393
				216.639	.411	.396
				219.959	.414	.399
				223.304	.417	.402
				226.674	.420	.405
				230.069	.423	.408
				233.489	.426	.411
				236.934	.429	.414
				240.404	.432	.417
				243.899	.435	.420
				247.419	.438	.423
				250.964	.441	.426
				254.534	.444	.429
				258.129	.447	.432
				261.749	.450	.435
				265.394	.453	.438
				269.064	.456	.441
				272.759	.459	.444
				276.479	.462	.447
				280.224	.465	.450
				284.004	.468	.453
				287.809	.471	.456
				291.639	.474	.459
				295.494	.477	.462
				299.374	.480	.465
				303.279	.483	.468
				307.209	.486	.471
				311.164	.489	.474
				315.144	.492	.477
				319.149	.495	.480
				323.179	.498	.483
				327.234	.501	.486
				331.314	.504	.489
				335.419	.507	.492
				339.549	.510	.495
				343.704	.513	.498
				347.884	.516	.501
				352.089	.519	.504
				356.319	.522	.507
				360.574	.525	.510
				364.854	.528	.513
				369.159	.531	.516
				373.489	.534	.519
				377.844	.537	.522
				382.224	.540	.525
				386.629	.543	.528
				391.059	.546	.531
				395.514	.549	.534
				400.004	.552	.537
				404.519	.555	.540
				409.059	.558	.543
				413.624	.561	.546
				418.214	.564	.549
				422.829	.567	.552
				427.469	.570	.555
				432.134	.573	.558
				436.824	.576	.561
				441.539	.579	.564
				446.279	.582	.567
				451.044	.585	.570
				455.834	.588	.573
				460.649	.591	.576
				465.489	.594	.579
				470.354	.597	.582
				475.244	.600	.585
				480.159	.603	.588
				485.099	.606	.591
				490.064	.609	.594
				495.054	.612	.597
				500.069	.615	.600
				505.109	.618	.603
				510.174	.621	.606
				515.264	.624	.609
				520.379	.627	.612
				525.519	.630	.615
				530.684	.633	.618
				535.874	.636	.621
				541.089	.639	.624
				546.329	.642	.627
				551.594	.645	.630
				556.884	.648	.633
				562.199	.651	.636
				567.539	.654	.639
				572.904	.657	.642
				578.294	.660	.645
				583.709	.663	.648
				589.149	.666	.651
				594.614	.669	.654
				600.104	.672	.657
				605.619	.675	.660
				611.159	.678	.663
				616.724	.681	.666
				622.314	.684	.669
				627.929	.687	.672
				633.569	.690	.675
				639.234	.693	.678
				644.924	.696	.681
				650.639	.699	.684
				656.379	.702	.687
				662.144	.705	.690
				667.934	.708	.693
				673.749	.711	.696
				679.589	.714	.699
				685.454	.717	.702
				691.344	.720	.705
				697.259	.723	.708
				703.199	.726	.711
				709.164	.729	.714
				715.154	.732	.717
				721.169	.735	.720
				727.209	.738	.723
				733.274		

(Liquid) Mol. Wt. = 9.013

BERYLLIUM (Be) (LIQUID) MOL. WT. = 9.013

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0						
100	3.805	3.934	.000	2.881	2.381	-1.746
200	3.637	3.978	.007	2.881	2.376	-1.733
300	3.497	4.027	.039	2.894	2.310	-1.207
400	3.387	4.073	.096	2.927	2.036	-.890
500	3.297	4.122	.176	2.971	1.653	-.675
600	3.227	4.173	.283	3.012	1.164	-.519
700	3.173	4.227	.416	3.044	1.469	-.401
800	3.131	4.283	.573	3.064	1.271	-.309
900	3.098	4.340	.753	3.069	1.071	-.234
1000	3.073	4.398	.956	3.059	.872	-.173
1100	3.054	4.457	1.183	3.032	.674	-.123
1200	3.040	4.517	1.434	2.990	.479	-.081
1300	3.030	4.577	1.708	2.930	.287	-.043
1400	3.023	4.637	2.004	2.852	.101	-.015
1500	3.018	4.697	2.321	.000	.000	.000
1600	3.014	4.757	2.658	.000	.000	.000
1700	3.011	4.817	3.015	.000	.000	.000
1800	3.008	4.877	3.392	.000	.000	.000
1900	3.006	4.937	3.789	.000	.000	.000
2000	3.004	5.000	4.206	.000	.000	.000
2100	3.002	5.063	4.643	.000	.000	.000
2200	3.000	5.126	5.099	.000	.000	.000
2300	3.000	5.189	5.574	.000	.000	.000
2400	3.000	5.252	6.068	.000	.000	.000
2500	3.000	5.315	6.581	.000	.000	.000
2600	3.000	5.378	7.113	.000	.000	.000
2700	3.000	5.441	7.664	.000	.000	.000
2800	3.000	5.504	8.234	.000	.000	.000
2900	3.000	5.567	8.823	.000	.000	.000
3000	3.000	5.630	9.431	.000	.000	.000
3100	3.000	5.693	10.058	.000	.000	.000
3200	3.000	5.756	10.704	.000	.000	.000
3300	3.000	5.819	11.369	.000	.000	.000
3400	3.000	5.882	12.053	.000	.000	.000
3500	3.000	5.945	12.756	.000	.000	.000
3600	3.000	6.008	13.478	.000	.000	.000
3700	3.000	6.071	14.219	.000	.000	.000
3800	3.000	6.134	14.979	.000	.000	.000
3900	3.000	6.197	15.758	.000	.000	.000
4000	3.000	6.260	16.556	.000	.000	.000
4100	3.000	6.323	17.373	.000	.000	.000
4200	3.000	6.386	18.209	.000	.000	.000
4300	3.000	6.449	19.064	.000	.000	.000
4400	3.000	6.512	19.938	.000	.000	.000
4500	3.000	6.575	20.831	.000	.000	.000
4600	3.000	6.638	21.743	.000	.000	.000
4700	3.000	6.701	22.674	.000	.000	.000
4800	3.000	6.764	23.624	.000	.000	.000
4900	3.000	6.827	24.593	.000	.000	.000
5000	3.000	6.890	25.581	.000	.000	.000
5100	3.000	6.953	26.589	.000	.000	.000
5200	3.000	7.016	27.616	.000	.000	.000
5300	3.000	7.079	28.662	.000	.000	.000
5400	3.000	7.142	29.727	.000	.000	.000
5500	3.000	7.205	30.811	.000	.000	.000
5600	3.000	7.268	31.914	.000	.000	.000
5700	3.000	7.331	33.036	.000	.000	.000
5800	3.000	7.394	34.177	.000	.000	.000
5900	3.000	7.457	35.337	.000	.000	.000
6000	3.000	7.520	36.516	.000	.000	.000

September 30, 1961

 ΔH_f^o 238.15 = [2.881] kcal. mole⁻¹ ΔH_m^o = 2800 ± 500 cal. mole⁻¹ ΔH_v^o = 71.137 kcal. mole⁻¹ $S_{298.15}^o$ = [3.954] cal. deg.⁻¹ mole⁻¹ T_m = 1556°K. T_b = 2757°K.

Heat of Formation.

Obtained from ΔH_m 1556°K.

Heat Capacity and Extrapolation.

Heat capacity from T_m to 2200°K. taken from P. B. Kantor, R. M. Krasovitskaya and A. N. Kisel, Fiz. Metal. i Metalloved., Akad. Nauk S.S.S.R. 10, 635 (1960). C_p values below T_m and above 2200°K. were extrapolated.

Entropy.

Third law entropies between T_m and T_b extrapolated in both directions by means of extrapolated heat capacities.

Vaporization Phenomena.

 T_b and ΔH_v derived from a third law analysis of the vapor pressure data of E. A. Gulbransen and K. F. Andrews, J. Electrochem. Soc. 97, 363 (1952), and of R. B. Holden, R. Speiser, and H. L. Johnston, J. Am. Chem. Soc. 70, 3897 (1948).

A mass spectrometric study and review undertaken by O. T. Mikitin and L. N. Gorokhov, Zhur. Neorg. Khim. 8, 224 (1961), on the composition of beryllium vapor reveals that beryllium vaporizing both below and above the melting point, 1556°K., consists only of monatomic Be.

Beryllium (Be)

(Ideal Gas) Mol. Wt. = 9.013

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	cal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	4.968	21.000	INFINITE	77.241	75.824	INFINITE
100	4.968	20.561	32.999	76.087	72.177	-78.667
200	4.968	20.121	32.545	76.255	69.231	-50.745
298	4.968	20.000	32.545	76.257	69.175	-50.392
300	4.968	20.000	32.545	76.257	69.175	-50.392
400	4.968	19.576	32.108	76.307	63.093	-27.376
500	4.968	19.152	31.671	76.307	60.053	-21.873
600	4.968	18.728	31.234	76.307	57.024	-17.803
700	4.968	18.304	30.797	76.307	54.007	-14.753
800	4.968	17.880	30.360	76.307	51.000	-11.723
900	4.968	17.456	29.923	76.307	48.000	-8.713
1000	4.968	17.032	29.486	76.307	45.000	-5.723
1100	4.968	16.608	29.049	76.307	42.000	-2.753
1200	4.968	16.184	28.612	76.307	39.000	0.217
1300	4.968	15.760	28.175	76.307	36.000	3.187
1400	4.968	15.336	27.738	76.307	33.000	6.157
1500	4.968	14.912	27.301	76.307	30.000	9.127
1600	4.968	14.488	26.864	76.307	27.000	12.097
1700	4.968	14.064	26.427	76.307	24.000	15.067
1800	4.968	13.640	25.990	76.307	21.000	18.037
1900	4.968	13.216	25.553	76.307	18.000	20.997
2000	4.968	12.792	25.116	76.307	15.000	23.957
2100	4.968	12.368	24.679	76.307	12.000	26.917
2200	4.968	11.944	24.242	76.307	9.000	29.877
2300	4.968	11.520	23.805	76.307	6.000	32.837
2400	4.968	11.096	23.368	76.307	3.000	35.797
2500	4.968	10.672	22.931	76.307	0.000	38.757
2600	4.968	10.248	22.494	76.307	-3.000	41.717
2700	4.968	9.824	22.057	76.307	-6.000	44.677
2800	4.968	9.400	21.620	76.307	-9.000	47.637
2900	4.968	8.976	21.183	76.307	-12.000	50.597
3000	4.968	8.552	20.746	76.307	-15.000	53.557
3100	4.968	8.128	20.309	76.307	-18.000	56.517
3200	4.968	7.704	19.872	76.307	-21.000	59.477
3300	4.968	7.280	19.435	76.307	-24.000	62.437
3400	4.968	6.856	18.998	76.307	-27.000	65.397
3500	4.968	6.432	18.561	76.307	-30.000	68.357
3600	4.968	6.008	18.124	76.307	-33.000	71.317
3700	4.968	5.584	17.687	76.307	-36.000	74.277
3800	4.968	5.160	17.250	76.307	-39.000	77.237
3900	4.968	4.736	16.813	76.307	-42.000	80.197
4000	4.968	4.312	16.376	76.307	-45.000	83.157
4100	4.968	3.888	15.939	76.307	-48.000	86.117
4200	4.968	3.464	15.502	76.307	-51.000	89.077
4300	4.968	3.040	15.065	76.307	-54.000	92.037
4400	4.968	2.616	14.628	76.307	-57.000	94.997
4500	4.968	2.192	14.191	76.307	-60.000	97.957
4600	4.968	1.768	13.754	76.307	-63.000	100.917
4700	4.968	1.344	13.317	76.307	-66.000	103.877
4800	4.968	0.920	12.880	76.307	-69.000	106.837
4900	4.968	0.496	12.443	76.307	-72.000	109.797
5000	4.968	0.072	12.006	76.307	-75.000	112.757
5100	4.968	-0.352	11.569	76.307	-78.000	115.717
5200	4.968	-0.776	11.132	76.307	-81.000	118.677
5300	4.968	-1.200	10.695	76.307	-84.000	121.637
5400	4.968	-1.624	10.258	76.307	-87.000	124.597
5500	4.968	-2.048	9.821	76.307	-90.000	127.557
5600	4.968	-2.472	9.384	76.307	-93.000	130.517
5700	4.968	-2.896	8.947	76.307	-96.000	133.477
5800	4.968	-3.320	8.510	76.307	-99.000	136.437
5900	4.968	-3.744	8.073	76.307	-102.000	139.397
6000	4.968	-4.168	7.636	76.307	-105.000	142.357

Be

MOL. WT. = 9.013

(IDEAL GAS)

BERYLLIUM (Be)

ΔH_f⁰ 298.15 = 78.25 ± 0.5 kcal. mole⁻¹
 S_{298.15} = 32.545 cal. deg.⁻¹ mole⁻¹

ΔH_f⁰ = 77.241 kcal. mole⁻¹
 Ground State Configuration 1s.

Electronic Levels and Multiplicities

Electronic Level	g ₁	Electronic Level	g ₁
0-0	1	67943	15
21980	9	68781	5
42565	3	69009	3
52082	3	69322	1
54677	1	69834	9
56432	15	70806	15
58791	9	71002	3
59698	3	71162	3
60187	3	71320	1
62054	15	71483	9
64428	5	71499	15
64507	3	72030	15
65245	1	72251	5
65949	9	72355	3
67228	3	72448	1
		72882	15
		73017	5

Heat of Formation

Derived from a third law analysis of the vapor pressure data. See Be crystal for references.

Heat Capacity and Entropy

Electronic levels and multiplicities from C. E. Moore, Natl. Bur. Standards Circ. 467 (1949).

Beryllium Unipositive Ion (Be⁺)
(Ideal Gas) Mol. Wt. = 9.01165

Be⁺

BERYLLIUM UNIPosITIVE ION (Be⁺) (IDEAL GAS)
MOL. WT. = 9.01165
Ground State Configuration 2s^{1/2}
ΔH_f⁰ = 292.2 ± .5 kcal/mole
ΔH_f⁰ 298.15 = 294.7 ± .5 kcal/mole

Electronic Levels and Quantum Weight

E_i , cm. ⁻¹	g_i
0.0	2
31928.8	2
31935.4	4
80231.2	2
96496.4	2
96498.2	4
98053.2	10

Heat of Formation.

The heat of formation was calculated from the equation: Be(g) + e⁻ → Be⁺(g) with the JANAP auxiliary value for Be(g) using an I.P. = 7.519229 X 10⁶ cm⁻¹ (215.001 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore loc. cit. The electronic levels above 1 X 10⁶ cm⁻¹ were omitted because their contribution is negligible below 6000°K. The H⁺-H⁺ value at 0°K. is -1.481 kcal./mole.

June 30, 1965

Be⁺

T, °K.	C _v ⁰	S ⁰	-(F ⁰ -H ₂₉₈)/T	H ⁰ -H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0				0.000	294.700	283.779	-208.005
100	4.968	33.922	33.922	0.009	294.711	283.711	-206.673
200	4.968	34.117	34.117	1.006	295.266	279.056	-192.955
300	4.968	34.485	34.485	1.500	295.756	276.074	-180.086
400	4.968	34.897	34.897	1.500	296.208	272.094	-99.105
500	4.968	35.311	35.311	1.506	296.628	268.040	-83.682
600	4.968	35.709	35.709	2.493	297.027	263.930	-72.099
700	4.968	36.088	36.088	3.487	297.408	259.781	-62.464
800	4.968	36.455	36.455	4.481	297.768	255.569	-53.852
900	4.968	36.815	36.815	5.471	298.108	251.336	-46.933
1000	4.968	37.168	37.168	6.468	298.427	247.072	-40.813
1100	4.968	37.515	37.515	7.461	298.725	242.782	-35.413
1200	4.968	37.857	37.857	8.455	299.003	238.466	-30.713
1300	4.968	38.194	38.194	9.449	299.262	234.126	-26.613
1400	4.968	38.527	38.527	10.443	299.503	229.772	-23.103
1500	4.968	38.855	38.855	11.436	299.727	225.412	-20.015
1600	4.968	39.178	39.178	12.429	299.935	221.042	-17.263
1700	4.968	39.496	39.496	13.423	300.127	216.662	-14.847
1800	4.968	39.809	39.809	14.417	300.303	212.272	-12.663
1900	4.968	40.117	40.117	15.411	300.465	207.872	-10.713
2000	4.968	40.421	40.421	16.405	300.613	203.462	-8.903
2100	4.968	40.721	40.721	17.399	300.747	199.042	-7.323
2200	4.968	41.017	41.017	18.393	300.867	194.612	-5.963
2300	4.968	41.310	41.310	19.387	300.973	190.172	-4.803
2400	4.968	41.600	41.600	20.381	301.065	185.722	-3.823
2500	4.968	41.887	41.887	21.375	301.143	181.262	-3.003
2600	4.968	42.171	42.171	22.369	301.207	176.792	-2.323
2700	4.968	42.452	42.452	23.363	301.257	172.312	-1.773
2800	4.968	42.730	42.730	24.357	301.293	167.822	-1.333
2900	4.968	43.005	43.005	25.351	301.315	163.322	-1.003
3000	4.968	43.277	43.277	26.345	301.325	158.812	-0.773
3100	4.969	43.546	43.546	27.339	301.323	154.292	-0.633
3200	4.969	43.812	43.812	28.333	301.308	149.762	-0.583
3300	4.969	44.075	44.075	29.327	301.280	145.222	-0.533
3400	4.970	44.336	44.336	30.321	301.239	140.672	-0.483
3500	4.970	44.594	44.594	31.315	301.185	136.112	-0.433
3600	4.971	44.849	44.849	32.309	301.117	131.542	-0.383
3700	4.972	45.101	45.101	33.303	301.035	126.962	-0.333
3800	4.973	45.350	45.350	34.297	300.939	122.372	-0.283
3900	4.974	45.596	45.596	35.291	300.829	117.772	-0.233
4000	4.976	45.839	45.839	36.285	300.705	113.162	-0.183
4100	4.978	46.079	46.079	37.279	300.567	108.542	-0.133
4200	4.981	46.316	46.316	38.273	300.415	103.912	-0.083
4300	4.984	46.550	46.550	39.267	300.249	99.272	-0.033
4400	4.987	46.781	46.781	40.261	300.069	94.622	0.017
4500	4.991	47.009	47.009	41.255	299.875	89.962	0.067
4600	4.995	47.234	47.234	42.249	299.667	85.292	0.117
4700	5.000	47.456	47.456	43.243	299.445	80.612	0.167
4800	5.006	47.675	47.675	44.237	299.209	75.922	0.217
4900	5.013	47.891	47.891	45.231	298.959	71.222	0.267
5000	5.020	48.104	48.104	46.225	298.695	66.512	0.317
5100	5.027	48.314	48.314	47.219	298.417	61.792	0.367
5200	5.036	48.520	48.520	48.213	298.125	57.062	0.417
5300	5.045	48.723	48.723	49.207	297.819	52.322	0.467
5400	5.055	48.923	48.923	50.201	297.500	47.572	0.517
5500	5.066	49.120	49.120	51.195	297.167	42.812	0.567
5600	5.078	49.314	49.314	52.189	296.821	38.042	0.617
5700	5.090	49.505	49.505	53.183	296.461	33.262	0.667
5800	5.104	49.693	49.693	54.177	296.087	28.472	0.717
5900	5.118	49.877	49.877	55.171	295.700	23.662	0.767
6000	5.133	50.057	50.057	56.165	295.300	18.832	0.817

T, °K.	C _p	S° - (R°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _f
0	6.063	46.099	10.012	2.135	10.012	10.012	10.012
100	6.063	46.099	10.012	2.135	10.012	10.012	10.012
200	7.235	51.859	10.012	2.135	10.012	10.012	10.012
298	7.719	54.839	10.012	2.135	10.012	10.012	10.012
300	7.727	54.839	10.012	2.135	10.012	10.012	10.012
400	8.110	57.165	10.012	2.135	10.012	10.012	10.012
500	8.365	59.005	10.012	2.135	10.012	10.012	10.012
600	8.534	60.546	10.012	2.135	10.012	10.012	10.012
700	8.650	61.870	10.012	2.135	10.012	10.012	10.012
800	8.729	62.921	10.012	2.135	10.012	10.012	10.012
900	8.783	63.713	10.012	2.135	10.012	10.012	10.012
1000	8.813	64.303	10.012	2.135	10.012	10.012	10.012
1100	8.822	64.738	10.012	2.135	10.012	10.012	10.012
1200	8.813	65.032	10.012	2.135	10.012	10.012	10.012
1300	8.783	65.187	10.012	2.135	10.012	10.012	10.012
1400	8.729	65.213	10.012	2.135	10.012	10.012	10.012
1500	8.650	65.122	10.012	2.135	10.012	10.012	10.012
1600	8.534	64.811	10.012	2.135	10.012	10.012	10.012
1700	8.365	64.287	10.012	2.135	10.012	10.012	10.012
1800	8.110	63.563	10.012	2.135	10.012	10.012	10.012
1900	7.719	62.563	10.012	2.135	10.012	10.012	10.012
2000	7.235	61.335	10.012	2.135	10.012	10.012	10.012
2100	6.727	59.845	10.012	2.135	10.012	10.012	10.012
2200	6.189	58.089	10.012	2.135	10.012	10.012	10.012
2300	5.623	56.089	10.012	2.135	10.012	10.012	10.012
2400	5.034	53.835	10.012	2.135	10.012	10.012	10.012
2500	4.429	51.287	10.012	2.135	10.012	10.012	10.012
2600	3.811	48.481	10.012	2.135	10.012	10.012	10.012
2700	3.183	45.453	10.012	2.135	10.012	10.012	10.012
2800	2.549	42.259	10.012	2.135	10.012	10.012	10.012
2900	1.911	38.951	10.012	2.135	10.012	10.012	10.012
3000	1.271	35.583	10.012	2.135	10.012	10.012	10.012
3100	0.630	32.111	10.012	2.135	10.012	10.012	10.012
3200	0.000	28.583	10.012	2.135	10.012	10.012	10.012
3300		25.000	10.012	2.135	10.012	10.012	10.012
3400		21.383	10.012	2.135	10.012	10.012	10.012
3500		17.750	10.012	2.135	10.012	10.012	10.012
3600		14.111	10.012	2.135	10.012	10.012	10.012
3700		10.453	10.012	2.135	10.012	10.012	10.012
3800		6.783	10.012	2.135	10.012	10.012	10.012
3900		3.111	10.012	2.135	10.012	10.012	10.012
4000		-0.555	10.012	2.135	10.012	10.012	10.012
4100		-4.183	10.012	2.135	10.012	10.012	10.012
4200		-7.779	10.012	2.135	10.012	10.012	10.012
4300		-11.335	10.012	2.135	10.012	10.012	10.012
4400		-14.859	10.012	2.135	10.012	10.012	10.012
4500		-18.353	10.012	2.135	10.012	10.012	10.012
4600		-21.811	10.012	2.135	10.012	10.012	10.012
4700		-25.233	10.012	2.135	10.012	10.012	10.012
4800		-28.611	10.012	2.135	10.012	10.012	10.012
4900		-31.944	10.012	2.135	10.012	10.012	10.012
5000		-35.233	10.012	2.135	10.012	10.012	10.012
5100		-38.481	10.012	2.135	10.012	10.012	10.012
5200		-41.683	10.012	2.135	10.012	10.012	10.012
5300		-44.853	10.012	2.135	10.012	10.012	10.012
5400		-47.983	10.012	2.135	10.012	10.012	10.012
5500		-51.083	10.012	2.135	10.012	10.012	10.012
5600		-54.153	10.012	2.135	10.012	10.012	10.012
5700		-57.183	10.012	2.135	10.012	10.012	10.012
5800		-60.183	10.012	2.135	10.012	10.012	10.012
5900		-63.153	10.012	2.135	10.012	10.012	10.012
6000		-66.083	10.012	2.135	10.012	10.012	10.012

Dec. 31, 1961; Sept. 30, 1964

Ground State Configuration $2s^2 +$ $S_{298.15}^{\circ} = [54.84] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^{\circ} 0 = [10.1 \pm 5.0] \text{ kcal. mole}^{-1}$ $\Delta H_f^{\circ} 298.15 = [6.6 \pm 5.0] \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$$\frac{\epsilon_1 \text{ cm.}^{-1}}{0} = \frac{\epsilon_2}{2}$$

 $\omega_2 = [743] \text{ cm.}^{-1}$ $\omega_2 = [4.08] \text{ cm.}^{-1}$ $\sigma = 1$ $B_0 = [0.55780] \text{ cm.}^{-1}$ $\omega_e = [0.00293] \text{ cm.}^{-1}$ $r_e = [1.97] \text{ \AA}$

Heat of Formation.

The dissociation energy was estimated from the experimental energies for BeF(g), BeCl(g), and the gaseous lithium halides. The resulting value, 97.1 kcal. mole⁻¹, was combined with JANAF heats of formation for Be(g) and Br(g) in arriving at $\Delta H_f^{\circ} 298.15^{\circ}$.

Heat Capacity and Entropy.

The vibrational frequency was estimated from those of BeF(g), BeCl(g), and the gaseous lithium halides. The ground term was assumed to be similar to that of BeCl(g) and BeF(g), tabulated by G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950. A correlation of the interatomic distances for the alkali halides, BeF(g), and BeCl(g) was employed in deriving r_e .

T, °K	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	Log K _p
0					
100					
200					
298	16.500	25.400	0.000	- 88.400	61.897
300	16.542	25.502	0.031	- 88.409	61.497
400	18.100	30.506	26.072	1.774	44.605
500	18.850	34.650	27.484	3.623	34.210
600	19.350	38.114	28.889	5.535	27.315
700	19.656	41.120	30.427	7.485	22.415
800	19.900	43.782	31.932	9.484	18.759
900	20.063	46.115	33.380	11.462	15.930
1000	20.200	48.236	34.761	13.445	13.678
1100	20.311	50.167	36.075	15.501	11.846
1200	20.397	51.938	37.324	17.537	10.326
1300	20.457	53.573	38.512	19.580	9.046
1400	20.491	55.091	39.643	21.627	7.954
1500	20.500	56.505	40.720	23.677	7.012

BERYLLIUM DIBROMIDE (BeBr₂)

MOL. WT. = 168.8302

(CRYSTAL)

ΔH_f^0 = Unknown
 ΔH_f^0 298.15 = [-88.4 ± 8] kcal. mole⁻¹
 ΔH_m^0 = [4.5] kcal. mole⁻¹
 ΔH_g^0 298.15 = 29.8 ± 1.5 kcal. mole⁻¹
 $S_{298.15}^0$ = [25.4 ± 2.0] cal. mole⁻¹ deg.⁻¹
 T_m = 761°K.
Heat of Formation.
The heat of formation was estimated from the work of W. Blitz and C. Messerkecht, Z. Anorg. Chem. 148, 157 (1925) and Blitz, Klatte and Rahlfs, Z. Anorg. Chem. 166, 339 (1927) as reported in N. B. S. Circular 500, Washington, 1952. They measured the heat of solution of BeBr₂ in aq. HCl to an unknown concentration. This value was apparently adjusted and used with Be⁺⁺ and 2Br⁻ to obtain ΔH_f^0 of the crystal. However Be⁺⁺ was estimated by N. B. S. An uncertainty of 8 kcal. is thought to be realistic.

Heat Capacity and Entropy.

The heat capacity was estimated graphically by comparison with BeCl₂ and BeF₂. The entropy was also estimated by comparing with CC-BeCl₂ and BeF₂ and using additive entropy values for the halide ions.

Melting Data.

The melting point has been reported by O. Rahlfs and W. Fischer, Z. Anorg. Chem. 211, 351 (1933) and by Lebean, Ann. Chim. Phys. 16, 472 (1899) as reported in N. B. S. Circular 500, Washington, 1952. The heat of melting was estimated by comparison with the sum of the heat of transition and melting for BeF₂ and BeCl₂.

Sublimation Data.

The heat of sublimation was obtained from an analysis of the vapor pressure data of Rahlfs and Fischer, loc. cit. from 624-695°K. The 3rd law analysis gave ΔH_{sub}^0 298 = 29.78 with a drift of -2.1 ± 0.8 cal. mole⁻¹ deg.⁻¹. A 2nd law analysis gave ΔH_{sub}^0 298 = 31.1 ± 0.5 kcal. mole⁻¹. The 2nd law result was adopted in order to yield a real liquid region, no attempt was made to eliminate the drift since this would have caused the liquid region to become unreal.

Beryllium Dibromide (BeBr₂)
(Liquid) Mol. Wt. = 168.8302

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH°	ΔF°	Log K _p
0						
100						
298	16.500	28.070	28.070	0.000	- 85.880	60.634
300	16.542	28.172	28.070	0.031	- 85.889	60.245
400	18.100	33.176	28.742	1.774	- 92.825	43.812
500	27.000	37.307	30.054	3.626	- 92.360	33.692
600	27.000	42.230	31.686	6.326	- 91.090	27.008
700	27.000	46.392	33.497	9.026	- 89.855	22.299
800	27.000	48.997	35.339	11.726	- 88.646	18.815
900	27.000	51.177	37.148	14.426	- 87.461	16.142
1000	27.000	53.022	38.896	17.126	- 86.301	14.051
1100	27.000	58.596	40.572	19.826	- 85.167	12.328
1200	27.000	60.945	42.173	22.526	- 84.059	10.827
1300	27.000	63.106	43.701	25.226	- 82.976	9.757
1400	27.000	65.107	45.160	27.926	- 81.918	8.767
1500	27.000	66.970	46.552	30.626	- 80.886	7.920
1600	27.000	68.712	47.883	33.326	- 82.634	7.177
1700	27.000	70.349	49.157	36.026	- 81.537	6.517
1800	27.000	71.892	50.378	38.726	- 80.446	5.939
1900	27.000	73.352	51.549	41.426	- 79.361	5.428
2000	27.000	74.737	52.674	44.126	- 78.283	4.975

BeBr₂

MOL. WT. = 168.8302

(LIQUID)

BERYLLIUM DIBROMIDE (BeBr₂)

ΔH_f^o 298.15 = [-85.88 ± 3] kcal. mole⁻¹
 ΔH_m^o = [4.5] kcal. mole⁻¹
 ΔH_v^o = [23.9] kcal. mole⁻¹

S_{298.15} = [28.07] cal. mole⁻¹ deg.⁻¹
 T_m = 761°K.
 T_b = [794]°K.

Heat of Formation.

The heat of formation was obtained from that of BeBr₂(c) by adding ΔH_m^o and the difference between H₂₉₈ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with the measured value for BeCl₂. A glass transition was assumed at 500°K. below which the heat capacity is that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See BeBr₂(c) table for details.

Vaporization Data.

The temperature and heat of vaporization were calculated from the cross over between BeBr₂(l) and (g).

BeBr₂

Beryllium Dibromide (BeBr ₂)									
(Ideal Gas) Mol. Wt. = 168.8302									
BERYLLIUM DIBROMIDE: (BeBr ₂)									
(IDEAL GAS)									
MOL. WT. = 168.8302									
BeBr ₂									
Point Group D _{∞h}									
S _{298.15} = [66.4 ± 2] cal. mole ⁻¹ deg. ⁻¹									
Ground State Quantum Weight = 1									
ΔH _f ⁰ = [-54.2 ± 9.5] kcal. mole ⁻¹									
ΔH _f ⁰ 298.15 = [-57.3 ± 9.5] kcal. mole ⁻¹									
Vibrational Frequencies and Degeneracies									
$\frac{\omega_e}{cm^{-1}}$									
[205] (1)									
[180] (2)									
[890] (1)									
Bond Distance: Be-Br = 1.90 Å									
Bond Angle: Br-Be-Br = [180°]									
Rotational Constant: B ₀ = 0.02922 cm. ⁻¹									
Heat of Formation.									
The heat of formation was obtained from that of the crystal plus ΔH _f ⁰ 298.15, see BeBr ₂ (c) for details.									
Heat Capacity and Entropy.									
The linear structure was assumed by analogy with BeCl ₂ . The bond length was reported by F. A. Akhshin, V. P. Spirodinov and O. A. Sobolev, Dokl. Akad. Nauk. SSSR 118, 1134 (1956) from electron diffraction measurements. The vibrational frequencies were estimated by assuming a set of force constants k _i for the BeF ₂ , BeCl ₂ , BeBr ₂ , BeI ₂ series and also assuming k _i /k ₀ ^{1/2} = 50 as for BeF ₂ . The principal moment of inertia is 95.7984 x 10 ⁻³⁹ g. cm. ²									
σ = 2									
BeBr ₂									

Beryllium Monochloride (BeCl)
(Ideal Gas) GFW = 44.4652

T, °K	Cp	S° gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	-0.000	INFINITE	INFINITE	-2.118	13.947	13.947	INFINITE
100	6.959	44.250	58.426	-1.423	14.284	12.135	-26.531
200	7.138	49.057	52.662	-0.721	14.485	9.891	-10.809
298	7.563	51.984	51.984	0.000	14.500	7.625	-5.589
300	7.571	52.031	51.984	0.014	14.499	7.582	-5.524
400	7.742	54.286	52.031	0.752	14.423	5.286	-2.888
500	8.023	56.404	52.031	1.603	14.304	3.010	-1.318
600	8.437	57.595	53.533	2.437	14.162	0.771	-0.281
700	8.973	58.907	54.209	3.288	14.002	-1.449	0.452
800	9.672	60.058	54.870	4.151	13.826	-3.645	0.996
900	10.484	61.000	55.414	5.000	13.635	-5.816	1.412
1000	8.804	62.009	56.109	5.900	13.426	-7.967	1.741
1200	8.850	62.850	56.684	6.782	13.196	-10.095	2.006
1400	8.888	63.672	57.231	7.669	12.944	-12.202	2.222
1600	8.919	64.335	57.750	8.560	12.672	-14.287	2.402
1800	8.947	64.877	58.244	9.454	12.377	-16.350	2.552
2000	8.970	65.315	58.715	10.349	12.060	-18.392	2.680
2200	8.992	65.651	59.165	11.247	8.965	-20.331	2.777
2400	9.011	65.974	59.595	12.147	8.718	-22.154	2.848
2600	9.029	66.286	60.006	13.049	8.466	-23.964	2.910
2800	9.046	66.588	60.397	13.953	8.211	-25.757	2.963
3000	9.060	66.828	60.779	14.858	7.951	-27.530	3.009
3200	9.074	67.051	61.144	15.765	7.687	-29.308	3.050
3400	9.088	67.259	61.495	16.673	7.418	-31.062	3.086
3600	9.101	67.478	61.833	17.582	7.145	-32.805	3.117
3800	9.113	67.695	62.158	18.491	6.867	-34.534	3.145
4000	9.126	67.928	62.475	19.405	6.583	-36.251	3.170
4200	9.138	68.159	62.781	20.318	6.296	-37.963	3.191
4400	9.149	68.387	63.077	21.233	6.004	-39.660	3.210
4600	9.161	68.612	63.364	22.148	5.712	-41.348	3.228
4800	9.173	68.835	63.642	23.063	5.420	-43.030	3.245
5000	9.185	69.058	63.912	23.983	5.128	-44.707	3.261
5200	9.197	69.279	64.179	24.908	4.836	-46.380	3.276
5400	9.209	69.498	64.443	25.831	4.544	-48.049	3.291
5600	9.221	69.715	64.706	26.753	4.252	-49.714	3.305
5800	9.233	69.930	64.968	27.675	3.960	-51.376	3.319
6000	9.245	70.144	65.228	28.597	3.668	-53.034	3.332
6200	9.257	70.357	65.489	29.519	3.376	-54.688	3.345
6400	9.269	70.569	65.749	30.441	3.084	-56.339	3.358
6600	9.281	70.780	66.009	31.363	2.792	-57.987	3.371
6800	9.293	70.991	66.268	32.285	2.500	-59.632	3.384
7000	9.305	71.202	66.526	33.207	2.208	-61.274	3.397
7200	9.317	71.413	66.783	34.129	1.916	-62.913	3.410
7400	9.329	71.624	67.039	35.051	1.624	-64.549	3.423
7600	9.341	71.835	67.295	35.973	1.332	-66.182	3.436
7800	9.353	72.046	67.551	36.895	1.040	-67.812	3.449
8000	9.365	72.257	67.807	37.817	0.748	-69.439	3.462
8200	9.377	72.468	68.063	38.739	0.456	-71.063	3.475
8400	9.389	72.679	68.319	39.661	0.164	-72.684	3.488
8600	9.401	72.890	68.575	40.583	-0.128	-74.303	3.501
8800	9.413	73.101	68.831	41.505	-0.436	-75.919	3.514
9000	9.425	73.312	69.087	42.427	-0.744	-77.533	3.527
9200	9.437	73.523	69.343	43.349	-1.052	-79.145	3.540
9400	9.449	73.734	69.599	44.271	-1.360	-80.756	3.553
9600	9.461	73.945	69.855	45.193	-1.668	-82.366	3.566
9800	9.473	74.156	70.111	46.115	-1.976	-83.976	3.579
10000	9.485	74.367	70.367	47.037	-2.284	-85.586	3.592

Dec. 31, 1960; Sept. 30, 1961; Mar. 31, 1962; Mar. 31, 1964; Sept. 30, 1966

BERYLLIUM MONOCHLORIDE (BeCl)

(IDEAL GAS)

OPW = 44.4652

Ground State Configuration $2\Sigma^+$

$\Delta H_f^\circ = 13.9 \pm 3.0$ kcal/mol

$S_{298.15}^\circ = 51.984$ gibbs/mol

$\Delta H_f^\circ = 14.5 \pm 3.0$ kcal/mol

Electronic Levels and Quantum Weights

ϵ , cm ⁻¹	g_i
0	2
27970	4

$\omega_e = 845.29$ cm⁻¹

$\sigma = 1$

$B_e = [0.769]$ cm⁻¹

$\alpha_e = [0.0083]$

$r_e = [1.75]$ Å

Heat of Formation.

Novikov¹ measured 39 bands in the ultraviolet spectrum of BeCl(g). A linear extrapolation leads to a ground state dissociation energy of 36,555 cm⁻¹. The authors assumed that the non-crossing rule applied and that the ground and first excited states had a common dissociation limit. However, in the analogous case of BeF, treated in the same way by the above authors, it was shown by Mann² that these assumptions were not correct. If it is assumed that the excited state dissociates $A''\pi \rightarrow Be(^3P) + p(^2P)$ and the ground state $X^2\Sigma \rightarrow Be(^1S) + p(^2P)$, then $V_{00} + D'$ should equal D'' + excitation energy of Be atom. We find $V_{00} + D' = 27,960 + 30,390 = 58,350$ and $D'' + E_e = 36,555 + 21,981 = 58,536$ which is in excellent agreement. Thus the dissociation energy to ground state atoms is taken as 104.5 kcal/mol, which leads to a heat of formation of 3 kcal/mol using reaction a.

Greenbaum et al.³ report equilibrium constants for reaction b in the temperature range 1573 - 1724°K using the molecular flow effusion method. Also Hildenbrand et al.⁴ report equilibrium constants for reactions c and d which were calculated from mass spectrometric ion intensities. The $\Delta H_{298.15}^\circ$ values by second and third law analysis for these data and the corresponding $\Delta H_{298.15}^\circ$ values are listed below.

Author	Method	Reaction	$T^\circ K$	$\Delta H_{298.15}^\circ$ kcal/mol	Drift	$\Delta H_{298.15}^\circ$ kcal/mol
		(a) BeCl(g) $\rightarrow$ Be(g) + Cl(g)		Second Law	Third Law	eu

1. Novikov Spectroscopic 37-544 2.647 104.5 2.7

3. Greenbaum Kp 1573-1724 93.56 $\pm$ 7 85.87 -4.521 1.3

4. Hildenbrand Kp from Mass Spectroscopy 1382-1554 27.5 $\pm$ 2 28.25 - .779 15.3 $\pm$ 2

(d) Be(g) + BeCl₂(g) $\rightarrow$ 2 BeCl(g) 1382-1556 33.41 $\pm$ 8 36.08 2.198 14.1 $\pm$ 2.5

The equilibrium data of Greenbaum et al.³ was not weighted, since calculations indicated the possibility of reaction of BeCl(g) with the Al₂O₃ tube at the temperatures and pressures used. The data of Hildenbrand et al.⁴, which reflect the true gas phase equilibria and appear consistent with each other, were adopted, yielding $\Delta H_{298.15}^\circ = 14.5$ kcal/mol.

Heat Capacity and Entropy.

The vibrational constants used to calculate the functions were derived by Novikov¹ from a two constant equation $(\omega_e - (2v'' + 1)\omega_e x_e'' = \omega_0'' - (v'' + 1)\omega_e x_e'')$. The electronic levels were obtained from Herzberg⁵. E_e was obtained from the estimated bond length, which was taken to be slightly less than that in BeCl₂(g), and α_e was estimated from the Morse potential function.

References

1. M. M. Novikov and L. N. Tunitskii, Optics and Spectroscopy **8**, 396 (1960).
2. D. E. Mann, Natl. Bureau Standards Report 7587, July 1, 1962.
3. M. A. Greenbaum, M. L. Arin, M. Wong and M. Farber, J. Phys. Chem. **68**, 791-5 (1964).
4. D. L. Hildenbrand, E. Murad, L. P. Theard and F. J. Philco Report U-3197, Contract AF 04(611) - 10743, July 30, 1965.
5. G. Herzberg, "Molecular Spectra and Molecular Structure of Diatomic Molecules", 2nd Edition, D. Van Nostrand Company, Inc., New York, 1950.

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	Kcal/mol ΔHf°	ΔGf°	Log Kp
0						
100						
200	7.826	50.870	50.870	.000	225.970	- 165.640
300	7.834	50.919	50.871	234.009	225.920	- 164.562
400	8.211	53.228	51.183	234.056	223.154	- 121.926
500	8.454	55.068	51.764	234.856	220.283	- 98.285
600	8.613	56.468	52.468	235.231	217.332	- 79.163
700	8.722	57.991	53.162	235.583	214.320	- 66.914
800	8.802	59.151	53.839	235.918	211.259	- 57.713
900	8.863	60.192	54.488	236.236	208.159	- 50.548
1000	8.912	61.128	55.106	236.535	205.022	- 44.607
1100	8.954	61.979	55.693	236.813	201.858	- 40.105
1200	8.993	62.760	56.250	237.068	198.669	- 36.183
1300	9.031	63.482	56.779	237.303	195.458	- 32.859
1400	9.064	64.153	57.282	237.517	192.231	- 30.069
1500	9.136	64.761	57.761	237.712	188.989	- 27.536
1600	9.202	65.373	58.218	237.891	185.613	- 25.381
1700	9.263	65.933	58.656	238.047	182.124	- 23.491
1800	9.300	66.446	59.075	238.182	178.615	- 21.808
1900	9.404	66.976	59.478	238.298	175.084	- 20.302
2000	9.484	67.467	59.865	238.391	171.537	- 18.944
2100	9.771	67.940	60.238	238.547	170.204	- 17.713
2200	9.632	68.398	60.559	238.652	167.038	- 16.594
2300	10.107	68.843	60.948	238.716	163.858	- 15.570
2400	10.253	69.277	61.286	238.746	160.665	- 14.631
2500	10.488	69.701	61.614	238.730	157.435	- 13.765
2600	10.659	70.117	61.933	238.681	154.234	- 12.945
2700	10.853	70.524	62.244	238.551	150.999	- 12.223
2800	11.057	70.924	62.546	238.357	147.657	- 11.619
2900	11.300	71.317	62.842	238.076	144.166	- 11.166
3000	11.476	71.703	63.131	237.710	140.581	- 10.742
3100	11.690	72.083	63.414	237.254	136.915	- 10.343
3200	11.873	72.457	63.690	236.704	133.154	- 9.968
3300	12.046	72.825	63.962	236.154	129.394	- 9.614
3400	12.209	73.187	64.228	235.604	125.634	- 9.269
3500	12.354	73.543	64.489	235.054	121.874	- 8.933
3600	12.496	73.894	64.745	234.504	118.114	- 8.603
3700	12.650	74.238	64.997	233.954	114.354	- 8.277
3800	12.730	74.576	65.245	233.404	110.594	- 7.951
3900	12.827	74.906	65.486	232.854	106.834	- 7.625
4000	12.911	75.234	65.726	232.304	103.074	- 7.300
4100	12.983	75.553	65.964	231.754	99.314	- 6.974
4200	13.042	75.867	66.196	231.204	95.554	- 6.648
4300	13.090	76.174	66.428	230.654	91.794	- 6.322
4400	13.125	76.476	66.651	230.104	88.034	- 6.000
4500	13.155	76.771	66.871	229.554	84.274	- 5.674
4600	13.171	77.060	67.089	229.004	80.514	- 5.348
4700	13.180	77.344	67.304	228.454	76.754	- 5.022
4800	13.182	77.621	67.516	227.904	72.994	- 4.696
4900	13.176	77.893	67.721	227.354	69.234	- 4.370
5000	13.166	78.159	67.931	226.804	65.474	- 4.044
5100	13.149	78.420	68.135	226.254	61.714	- 3.718
5200	13.128	78.675	68.335	225.704	57.954	- 3.392
5300	13.103	78.926	68.532	225.154	54.194	- 3.066
5400	13.074	79.172	68.726	224.604	50.434	- 2.740
5500	13.043	79.400	68.916	224.054	46.674	- 2.414
5600	13.009	79.644	69.108	223.504	42.914	- 2.088
5700	12.974	79.873	69.295	222.954	39.154	- 1.762
5800	12.937	80.090	69.480	222.404	35.394	- 1.436
5900	12.898	80.290	69.661	221.854	31.634	- 1.110
6000	12.860	80.556	69.881	221.304	27.874	- 0.784

June 30, 1968

BERYLLIUM MONOCHLORIDE UNIPosITIVE ION (BeCl⁺) (IDEAL GAS)

Ground State Configuration [1s²]_g
S°_{298.15} = [50.9 ± 2] gibbs/mol
ΔHf° = [233 ± 20] kcal/mol
ΔHf° = [234 ± 20] kcal/mol

Electronic Levels and Quantum Weights

State	$\epsilon_i, \text{cm}^{-1}$	g_i
1s ⁺ _g	0	1
3s ⁺ _g	[10000]	6
1s ⁺ _u	[15000]	2
3s ⁺ _u	[30000]	3
1s ⁺ _g	[35000]	2
1s ⁺ _u	[40000]	1
ω _e = [700] cm ⁻¹	ω _e x _e = [4.8] cm ⁻¹	σ = 1
B _e = [0.7241] cm ⁻¹	α _e = [0.00711] cm ⁻¹	r _e = [1.8] Å

Heat of Formation

Krasnov (1) has reported calculations of the ionization potentials(IP) for the monohalides (MX, where X = F, Cl, Br, and I) of Group IIA elements (M = Mg, Ca, Sr, and Ba). Based on his data we obtain graphically the value IP(BeCl, g) = 8.9 ± 0.5 eV. The value of ΔHf°₂₉₈(BeCl⁺, g) is derived as 219 ± 15 kcal/mol, using ΔHf°₂₉₈(BeCl, g) = 13.9 kcal/mol. Beckett (2) reported the ionization potential of BeCl(g) to be approximately 9 ± 1 eV, yielding ΔHf°₂₉₈(BeCl⁺, g) = 222 ± 23 kcal/mol. Hildenbrand (3) measured the appearance potential (AP) of BeCl⁺(g) to be 9.5 ± 0.7 eV which is on the same order of the above IP values, and assumed that IP(BeCl⁺, g) = AP(BeCl⁺, g) = 9.5 ± 0.7 eV. Using this IP value, we obtain ΔHf°₂₉₈(BeCl⁺, g) = 234 ± 20 kcal/mol which is adopted.

Heat Capacity and Entropy

The six electronic states are obtained from Fougere (3). The electronic levels are estimated by comparison with those of isoelectronic molecules, BeS (4), BeO (5, 6), and MgO (5, 7). The values of ω_e, ω_ex_e are estimated by comparison with those for BeCl(g) and LiCl(g). B_e and α_e are calculated using the method suggested by Herzberg (8). The bond distance is estimated (8). The moment of inertia is 3.865 x 10⁻³⁹ cm². The enthalpy at 0°K is -2.15 kcal/mol.

References

1. K. S. Krasnov, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR, 1, 927 (1965).
2. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 6628, 1 January 1965.
3. P. F. Fougere and R. K. Nesbet, J. Chem. Phys. 44, 285 (1965).
4. G. Verhaegen and W. G. Richards, Proc. Phys. Soc. 50, 579 (1967).
5. G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950.
6. G. Verhaegen and W. G. Richards, J. Chem. Phys. 45, 1828 (1966).
7. L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).
8. K. S. Krasnov, Zh. Strukt. Khim. 1, 209 (1960).
9. D. L. Hildenbrand, E. Murad, L. P. Theard, and F. Ju, Aeronutronic, Philco Corporation, Report No. U-3197, July 30, 1965.

GFW = 44.46465

BeCl⁺

BeCl⁺

Beryllium Chloride Fluoride (BeClF)

(Ideal Gas) Mol. Wt. = 63.4636

T, °K.	C _p ^o	S ^o - (F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.000	INFINITE	-2.767	-137.177	-137.177	INFINITE
100	6.318	68.531	-2.766	-137.177	-137.177	19.957
200	10.645	54.397	-1.107	-137.044	-136.711	101.673
298	11.810	58.887	-1.000	-137.000	-136.722	101.054
300	11.827	58.860	-1.022	-137.000	-136.722	101.054
400	12.422	62.421	1.244	-137.016	-136.784	76.103
500	13.106	65.337	2.529	-137.065	-136.856	61.129
600	13.495	67.763	3.860	-137.127	-140.412	51.142
700	13.782	69.865	5.225	-137.198	-140.953	44.005
800	13.996	71.720	6.634	-137.280	-141.485	38.650
900	14.142	73.379	8.092	-137.372	-142.005	34.482
1000	14.281	74.877	9.445	-137.479	-142.514	31.145
1100	14.377	76.243	10.678	-137.605	-143.012	28.412
1200	14.454	77.497	12.319	-137.751	-143.497	26.133
1300	14.515	78.657	13.768	-137.917	-143.969	24.202
1400	14.562	79.744	15.222	-138.104	-144.428	22.545
1500	14.606	80.760	16.681	-138.314	-144.872	21.107
1600	14.640	81.684	18.143	-141.302	-145.224	19.836
1700	14.669	82.573	19.608	-141.443	-145.464	18.700
1800	14.693	83.412	21.077	-141.589	-145.698	17.689
1900	14.712	84.207	22.540	-141.740	-145.921	16.784
2000	14.732	84.962	24.019	-141.897	-146.137	15.968
2100	14.747	85.681	25.493	-142.058	-146.345	15.230
2200	14.761	86.368	26.969	-142.226	-146.547	14.557
2300	14.773	87.024	28.445	-142.400	-146.736	13.942
2400	14.783	87.653	29.923	-142.579	-146.921	13.378
2500	14.793	88.257	31.402	-142.767	-147.101	12.859
2600	14.801	88.837	32.882	-142.959	-147.267	12.378
2700	14.808	89.396	34.362	-143.157	-147.430	11.933
2800	14.815	89.934	35.843	-143.362	-147.635	11.535
2900	14.821	90.454	37.325	-143.572	-147.849	11.185
3000	14.826	90.957	38.808	-143.786	-148.069	10.885
3100	14.831	91.443	40.290	-143.999	-148.293	10.631
3200	14.836	91.914	41.774	-144.213	-148.521	10.414
3300	14.840	92.371	43.258	-144.428	-148.754	10.231
3400	14.843	92.814	44.742	-144.642	-148.991	10.081
3500	14.847	93.244	46.226	-144.856	-149.232	9.961
3600	14.850	93.662	47.711	-145.069	-149.478	9.868
3700	14.853	94.069	49.196	-145.280	-149.728	9.796
3800	14.855	94.465	50.682	-145.490	-149.981	9.745
3900	14.858	94.851	52.167	-145.699	-150.237	9.703
4000	14.860	95.227	53.653	-145.907	-150.496	9.670
4100	14.862	95.594	55.139	-146.114	-150.758	9.645
4200	14.864	95.953	56.626	-146.320	-151.022	9.628
4300	14.866	96.302	58.112	-146.525	-151.289	9.616
4400	14.868	96.644	59.599	-146.729	-151.558	9.606
4500	14.869	96.978	61.086	-146.932	-151.828	9.598
4600	14.871	97.305	62.573	-147.134	-152.098	9.591
4700	14.872	97.625	64.060	-147.338	-152.368	9.585
4800	14.874	97.938	65.547	-147.541	-152.638	9.579
4900	14.875	98.245	67.034	-147.743	-152.908	9.573
5000	14.876	98.544	68.521	-147.945	-153.178	9.567
5100	14.877	98.840	69.999	-148.146	-153.448	9.561
5200	14.878	99.129	71.468	-148.346	-153.718	9.555
5300	14.879	99.412	72.937	-148.545	-153.988	9.549
5400	14.880	99.690	74.406	-148.743	-154.258	9.543
5500	14.881	99.964	75.875	-148.940	-154.528	9.537
5600	14.882	100.231	77.344	-149.136	-154.798	9.531
5700	14.883	100.495	78.813	-149.331	-155.068	9.525
5800	14.884	100.754	80.282	-149.525	-155.338	9.519
5900	14.885	101.008	81.751	-149.718	-155.608	9.513
6000	14.885	101.258	83.220	-149.910	-155.878	9.507

Dec. 31, 1960; June 30, 1965

BeClF

MOL. WT. = 63.4636

(IDEAL GAS)

BERYLLIUM CHLORIDE FLUORIDE (BeClF)

Point Group [C_{∞v}]
 $\Delta H_f^o = [58.89] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$
 $\Delta H_f^o 298.15 = [58.89] \text{ cal. mole}^{-1}$
 $\Delta H_f^o 298.15 = [537 \pm 10] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega, \text{ cm.}^{-1}$
 [500](1)
 [270](2)
 [1300](1)

Be-F = [1.43] Å

σ = 1

Bond Distance: Be-Cl = [1.77] Å
 Bond Angle: Cl-Be-F = [180°]
 Rotational Constant: B₀ = 0.12970 cm.⁻¹

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_f^o = 0$ for the reaction $\text{BeF}_2 + \text{BeCl}_2 \rightarrow 2\text{BeClF}$

Heat Capacity and Entropy.

The structure, bond lengths and frequencies were all estimated from the properties of BeCl₂ and BeF₂.
 The principal moment of inertia is $21.579 \times 10^{-39} \text{ g. cm.}^2$

BeClF

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0	.000	.000	INFINITE	-2.863	-117.536	-117.536	INFINITE
100	6.045	6.025	31.435	-2.461	-117.845	-114.006	249.147
200	12.800	14.110	21.095	-1.397	-117.640	-110.259	120.446
298	15.500	18.760	18.760	.000	-117.535	-108.659	78.176
300	15.540	18.856	18.760	.029	-117.328	-106.592	77.649
400	17.390	24.598	20.394	1.682	-116.944	-103.070	56.312
500	18.530	28.612	21.647	3.482	-116.501	-99.651	43.555
600	19.140	32.049	23.101	5.369	-116.024	-96.324	35.085
700	19.445	35.024	24.597	7.290	-115.515	-93.000	28.559
800	19.660	37.635	26.067	9.245	-115.070	-89.694	23.073
900	19.843	39.962	27.484	11.230	-114.602	-86.786	18.296
1000	20.000	42.061	28.838	13.222	-114.144	-83.721	14.033
1100	20.131	43.973	30.129	15.220	-113.698	-80.490	10.154
1200	20.237	45.730	31.457	17.248	-113.268	-77.719	7.270
1300	20.317	47.353	32.725	19.276	-112.854	-74.773	5.000
1400	20.371	48.861	33.939	21.310	-112.460	-71.860	3.217
1500	20.400	50.267	35.101	23.349	-112.087	-68.972	1.849

$\Delta H_f^o = -117.5 \pm 0.8$ kcal. mole⁻¹
 ΔH_f^o 298.15 = -117.3 $\pm$ 0.8 kcal. mole⁻¹
 $\Delta H_m^o = 2.07 \pm 0.06$ kcal. mole⁻¹
 ΔH_g^o 298.15 = 31.3 kcal. mole⁻¹
 $S_{298.15}^o = 19.76 \pm 0.06$ cal. mole⁻¹ deg.⁻¹
 $T_m = 688^\circ\text{K}.$

Heat of Formation.

W. H. Johnson and A. A. Olliland, J. Res. Nat'l. Bur. Stand. 65A, 59 (1961) have directly reacted beryllium and chlorine and obtained $\Delta H_f^o = -118.03 \pm 0.56$ though the crystal form of the product was unknown. P. Oross, C. Hayman, P. D. Greene and J. T. Bingham, Fulmar Research Institute, Report R. 163/SR.1/Sept. 1964 under Contract AF61(052)-447 also by direct combustion of the elements obtain $\Delta H_f^o = -117.1 \pm 0.4$ kcal. mole⁻¹. The crystal form of the sample was deduced to be α' by a comparison experiment, the assumption is made here that α and α' are identical. C. J. Thompson, O. C. Sinka and D. R. Stull, J. Chem. Eng. Data 7, 380 (1962) by solution calorimetry report a $\Delta H_f^o = -118.25 \pm 0.5$ kcal. mole⁻¹. Initially this sample was reported to be of unknown crystal form. However, O. C. Sinka, private communication February 1965, reports that an x-ray of the sample used has been reinterpreted, in the light of more recent data, as being approximately 50% α' and 50% β . Using the heats of transition adopted for these tables heats of formation of -117.3 $\pm$ 0.8 kcal. mole⁻¹ for α and -118.6 $\pm$ 0.8 kcal. mole⁻¹ for β have been adopted as being the most consistent with all measurements.

Heat Capacity and Entropy.

R. A. McDonald and F. L. Oetting, J. Phys. Chem. scheduled for publication in the Nov. 1955 issue have measured the heat capacity of the α' form from 13° to 304°K. and the enthalpy (relative to the α' form) from 678° to 688°K. The assumption has been made that the α and α' forms are identical and the heat capacity curve between 304° and 678°K. has been estimated graphically. The entropy was obtained by integration of the heat capacity curve assuming $S_{13} = 0.16$ cal. mole⁻¹ deg.⁻¹. The sample was identified as α' by x-ray diffraction both before and after the experiments.

Melting Data.

The temperature and heat of melting were reported by McDonald and Oetting, loc. cit. Several investigations of the melting point are in disagreement mainly due to the uncertainty of the crystal form of the material and a solid state transition just below the pure α -liquid melting point.

Sublimation Data.

The adopted heat of sublimation was derived from that of the β form and heat of the α - β transition at 298°K.

Beryllium Dichloride, Beta (β -BeCl₂)

(Crystal) Mol. Wt. = 79.9182

BeCl₂

MOL. WT. = 79.9182

BERYLLIUM DICHLORIDE, BETA (β -BeCl₂) (CRYSTAL)

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞	INFINITE
100	7.595	5.761	30.501	2.474	-118.467	-118.467	-118.467	-118.467	INFINITE
200	12.380	12.650	19.410	1.352	-119.123	-119.123	-119.123	-119.123	251.686
298	14.920	18.120	18.120	0.000	-118.860	-118.860	-118.860	-118.860	121.460
300	14.960	18.212	18.120	0.028	-118.860	-118.860	-118.860	-118.860	78.748
400	16.420	22.728	18.728	1.000	-118.294	-118.294	-118.294	-118.294	78.212
500	17.400	26.506	19.915	3.295	-117.993	-117.993	-117.993	-117.993	54.712
600	18.120	29.744	21.290	5.073	-117.896	-117.896	-117.896	-117.896	43.730
800	18.660	32.583	22.704	8.915	-117.194	-117.194	-117.194	-117.194	35.149
900	19.450	37.437	25.191	12.795	-116.185	-116.185	-116.185	-116.185	29.041
1000	19.730	39.442	26.748	12.693	-115.938	-115.938	-115.938	-115.938	24.675
1100	19.930	41.332	27.990	14.677	-115.515	-115.515	-115.515	-115.515	19.116
1200	20.080	43.073	29.175	16.678	-115.103	-115.103	-115.103	-115.103	15.817
1300	20.200	44.685	30.315	18.685	-114.698	-114.698	-114.698	-114.698	13.907
1400	20.293	46.184	31.398	20.712	-114.303	-114.303	-114.303	-114.303	10.298
1500	20.300	47.583	32.421	22.763	-113.958	-113.958	-113.958	-113.958	9.755

$$\Delta H_f^0 = -118.7 \pm 0.8 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -118.6 \pm 0.8 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [3.65] \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{298.15} = [1.63] \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^{298.15} = 32.5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{298.15} = 18.12 \pm 0.05 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$T_m^0 = [682^\circ\text{K.}]$$

$$T_c^0 = 676^\circ\text{K. } (\beta \rightarrow \alpha)$$

Heat of Formation.

See table for α -BeCl₂ for details.

Heat Capacity and Entropy.

R. A. McDonald and P. L. Oetting, J. Phys. Chem. scheduled for publication in the November 1965 issue have measured the heat capacity of the β -form from 13 to 304°K. and the enthalpy of the β -form from 298° to 676°K. The entropy was obtained by integration of the heat capacity curve based on $S_{13} = 0.06 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$. The sample was identified as β -BeCl₂ both before and after the low temperature experiments.

Melting Data.

The temperature and heat of melting were obtained from cross over point of the tables for β -BeCl₂ and liquid BeCl₂.

Transition Data.

The temperature of the β to α transition was obtained from McDonald and Oetting, loc. cit. The heat of the transition is a function of the heat capacity curve chosen for α -BeCl₂ between 298 and 676°K. A straight line interpolation was used by McDonald and Oetting, which gives a different result (1.49 kcal. mole⁻¹) than the curve employed here. It should also be noted that the transitional heat is not included in this table, which is for β -BeCl₂ only.

Sublimation Data.

The heat of sublimation was determined by 2nd and 3rd law analysis of vapor pressure data as described fully on the table for BeCl₂ (g).

BeCl_2

MOL. WT. = 79.9182

(LIQUID)

BERYLLIUM DICHLORIDE (BeCl_2)
$$\Delta H_f^{298,15} = 19.085 \pm 1 \text{ cal. mole}^{-1} \text{ deg.}^{-1} \quad \Delta H_f^{298,15} = -117.4 \pm 1.5 \text{ kcal. mole}^{-1}$$
$$T_m = 688^\circ\text{K}.$$
$$\Delta H_b^\circ = 25.0 + 2 \text{ kcal. mole}^{-1}$$

Point of Formation:

The heat of formation was obtained from that of the α - BeCl_2 plus the difference of H_{699}^{crystal} and liquid.

Heat Capacity and Entropy.

H. A. McDonald and P. L. Oetting, *J. Phys. Chem.*, scheduled for publication in the November 1995 issue have measured the enthalpy of the liquid, relative to α -BeCl₂, from 600° to 713°K. The heat capacity was assumed constant above this point and also below the melting point to 430°K, where a glass transition was assumed. Below 430°K, the heat capacity was assumed to be that of β -BeCl₂. The entropy was calculated in a manner analogous to the heat of formation.

Melting Data.

See the table for α -BeCl₂ (c) for details.

Vaporization Date.

The boiling point and heat of vaporization were obtained from the cross over point of the BeCl_2 (1) and (2) anben. The anelyala of the liquid vapor pressure data is given on the table for BeCl_2 (7).

 BeCl_2

Sept. 30, 1961; June 30, 1965

Beryllium Dichloride (BeCl₂)

(Ideal Gas) Mol. wt. = 79.9182

T, K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	2.945	86.383	86.383	INFINITE
100	8.934	48.490	70.438	2.195	86.344	86.601	199.388
200	10.175	56.175	67.175	1.745	86.115	86.835	251.115
298	12.338	60.260	60.260	∞	86.100	87.499	304.133
300	12.353	60.337	60.260	.023	86.099	87.507	63.746
400	13.025	63.988	60.754	1.294	86.097	87.978	46.067
500	13.493	66.948	61.706	2.021	86.127	88.445	38.657
600	13.822	69.439	62.793	3.368	86.171	88.905	32.382
700	14.056	71.589	63.899	5.382	86.227	89.347	27.697
800	14.225	73.477	64.981	6.797	86.293	89.800	24.531
900	14.351	75.160	66.020	8.426	86.371	90.233	21.910
1000	14.446	76.677	67.011	9.666	86.465	90.658	19.812
1100	14.519	78.058	67.954	11.114	86.578	91.072	18.093
1200	14.576	79.324	68.849	12.569	86.712	91.476	16.659
1300	14.621	80.492	69.700	14.029	86.866	91.866	15.443
1400	14.658	81.577	70.510	15.493	87.042	92.244	14.399
1500	14.689	82.589	71.282	16.961	87.240	92.609	13.492
1600	14.714	83.538	72.019	18.431	90.217	92.881	12.686
1700	14.735	84.431	72.723	19.903	90.347	93.043	11.961
1800	14.752	85.274	73.397	21.378	90.481	93.199	11.315
1900	14.768	86.072	74.043	22.854	90.620	93.345	10.737
2000	14.781	86.826	74.662	24.331	90.766	93.484	10.215
2100	14.792	87.551	75.261	25.810	90.915	93.618	9.742
2200	14.802	88.239	75.835	27.289	91.072	93.742	9.312
2300	14.810	88.897	76.389	28.770	91.233	93.857	8.918
2400	14.818	89.528	76.923	30.251	91.401	93.969	8.557
2500	14.824	90.133	77.439	31.734	91.576	94.074	8.224
2600	14.830	90.714	77.939	33.216	91.757	94.167	7.915
2700	14.836	91.274	78.423	34.700	91.943	94.257	7.629
2800	14.840	91.814	78.891	36.183	92.134	94.342	7.362
2900	14.845	92.335	79.346	37.668	92.330	94.422	7.115
3000	14.849	92.838	79.787	39.152	92.530	94.498	6.886
3100	14.852	93.325	80.216	40.637	92.734	94.570	6.675
3200	14.855	93.797	80.633	42.123	92.942	94.638	6.482
3300	14.858	94.254	81.039	43.608	93.154	94.702	6.305
3400	14.861	94.697	81.434	45.094	93.370	94.762	6.145
3500	14.863	95.128	81.819	46.581	93.591	94.818	6.000
3600	14.865	95.547	82.195	48.067	93.816	94.870	5.869
3700	14.868	95.954	82.561	49.554	94.045	94.918	5.750
3800	14.869	96.351	82.919	51.040	94.278	94.962	5.642
3900	14.871	96.737	83.268	52.528	94.514	95.002	5.545
4000	14.873	97.114	83.610	54.015	94.752	95.038	5.458
4100	14.874	97.481	83.944	55.502	95.000	95.070	5.380
4200	14.876	97.839	84.270	56.990	95.256	95.100	5.310
4300	14.877	98.189	84.590	58.477	95.516	95.128	5.248
4400	14.878	98.531	84.903	59.965	95.780	95.154	5.194
4500	14.879	98.866	85.209	61.453	96.048	95.178	5.147
4600	14.881	99.193	85.510	62.941	96.320	95.200	5.105
4700	14.882	99.513	85.804	64.429	96.596	95.219	5.067
4800	14.883	99.826	86.093	65.917	96.876	95.235	5.033
4900	14.884	100.133	86.377	67.405	97.160	95.249	5.002
5000	14.884	100.434	86.655	68.894	97.448	95.260	4.973
5100	14.885	100.728	86.928	70.382	97.740	95.269	4.947
5200	14.886	101.017	87.196	71.871	98.034	95.275	4.924
5300	14.886	101.301	87.460	73.359	98.332	95.279	4.902
5400	14.887	101.579	87.718	74.848	98.634	95.281	4.881
5500	14.888	101.852	87.973	76.337	98.940	95.282	4.861
5600	14.888	102.121	88.223	77.826	99.249	95.282	4.842
5700	14.889	102.384	88.469	79.314	99.561	95.282	4.824
5800	14.889	102.643	88.712	80.803	99.875	95.282	4.807
5900	14.890	102.898	88.950	82.292	100.191	95.282	4.791
6000	14.890	103.148	89.184	83.781	100.508	95.282	4.776

Dec. 31, 1960; Sept. 30, 1961; Dec. 31, 1961; June 30, 1965

BERYLLIUM DICHLORIDE (BeCl₂) (IDEAL GAS) MOL. WT. = 79.9182 BeCl₂

Point Group D_{∞h}
 $\Delta H_f^0 = -86.4 \pm 2.5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = -86.1 \pm 2.5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = -86.15 \pm 2.5 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	[575] (1)	[230] (2)	1113 (1)
------------------------------	-----------	-----------	----------

Bond Distance: Be-Cl = 1.77 Å
 Bond Angle: Cl-Be-Cl = 180°
 Rotational Constant: B₀ = 0.0759 cm.⁻¹
 $\sigma = 2$

Heat of Formation

The vapor pressure data over the crystal was assumed to be for the β -form. The 2nd and 3rd law analyses of the data are summarized below after conversion to a common process. The data were also analyzed using gasous free energy functions based on a bending frequency of 170 cm.⁻¹ but no significant improvement of the results was noted.

Ref.	Temperature Range °D.	ΔH_{298}^0 sub 2nd law	β -BeCl ₂ kcal. mole ⁻¹ 3rd law	Drift in 3rd law kcal. mole ⁻¹ deg. ⁻¹
1	680 - 740*	33.5 ± 0.6	31.38	-3.4 ± 0.7
2	580 - 740	34.3	31.22	-4.7
3	613 - 663	31.6 ± 1.6	30.91	-1.3 ± 2.6
4	638 - 668	35.6	31.07	-7.0
5	441 - 518	31.4 ± 0.8	32.45	2.5 ± 1.7
6	510 - 600*	31.8 ± 0.3	32.07	0.40 ± 0.5
7	460 - 504*	32.45 ± 0.4	32.48	0.14 ± 0.8

* points rejected due to failure of a statistical test.

References

1. O. Rahlfs and W. Fischer, Z. Anorg. Allgem. Chem. **211**, 349 (1933).
2. W. Fischer, T. Petzel and S. Lauter, Z. Anorg. Allgem. Chem. **333**, 226 (1964).
3. M. A. Greenbaum et al., Rocket Power, Inc., 7th Quarterly Report March 31, 1963 under Contract AF 04(611)-7414.
4. D. L. Hildenbrand, L. P. Theard, E. Murad and F. Ju, Ford Motor Co., Aeronutronic Div., Report U-3088 April 1965 under Contract AF 04(611)-8523.

It is obvious that there is no real agreement between the data sets, and some of this is undoubtedly due to the difficulty of keeping a single crystal form throughout a series of measurements. It is also doubtful that water vapor was adequately excluded in some experiments. We have adopted the only piece of work which shows adequate 2nd and 3rd law agreement, and no third law trend, that is $\Delta H_{298}^0 = 32.5 \pm 1 \text{ kcal. mole}^{-1}$ from ref. 4. It is interesting to note that all the other data can be made much more precise and its drift removed if a constant pressure is added to all points. The addition which varied from 20-30% of the lowest pressure in each data set serves to indicate the magnitude of possible systematic errors.

Heat Capacity and Entropy

The linear structure of BeCl₂(g) has been confirmed by the electric deflection experiments of A. Buchler, A. D. Little, Inc. Progress Report No. 8, 31st Dec. 1963 under contract No. DA-19-020-ORD-5584. The bond length was obtained from the electron diffraction data of F. A. Akhain, V. P. Spiridonov and O. A. Sobolev, Dokl. Akad. Nauk SSSR **118**, 1134 (1958). A Buchler and W. Klempner, J. Chem. Phys. **29**, 121 (1958) have reported the infra-red spectrum and assigned 1113 as the asymmetric stretch ν_3 and 462 as the bending frequency ν_2 . However, A. Shellen, IIT Research Institute, Report No. ITRI-C6013-4 May 1964 under contract No. DA-31-124-AO(D)-111 using matrix isolation experiments has shown this second band to be due to beryllium chloride solid. The unobserved frequencies were estimated from a valence force field treatment by assuming that the ratio of stretching to bending force constant was 50:1 the same as for BeF₂(g). This gives 230 cm.⁻¹ for ν_2 and 375 cm.⁻¹ for the asymmetric stretch. The principal moment of inertia is 36.884 x 10⁻³⁹ g. cm.²

BeCl₂

GFW = 47.009

(CRYSTAL)

BERYLLIUM DIFLUORIDE (BeF₂)Beryllium Difluoride (BeF₂)

(Crystal)

GFW = 47.009

S_{298.15} = 12.752 ± 0.04 gibbs/mol

Tt = 500°K (low quartz + high quartz)

Tm = 825°K

 $\Delta H_f^\circ = -244.8 \pm 1.0$ kcal/mol $\Delta H_f^\circ_{298.15} = -245.4 \pm 1.0$ kcal/mol $\Delta H_t^\circ = 0.0526$ kcal/mol $\Delta H_m^\circ = 1.137$ kcal/mol $\Delta H_s^\circ_{298.15} = 55.15$ kcal/mol

Heat of Formation

ΔH_f° is the value selected by Parker (1), based on a thorough review of data for BeF₂(c, vitreous, aqueous) and BeO(c). Parker's analysis remains essentially unchanged for BeO(c) and BeF₂(c), even though the results for BeF₂(HF, aqueous) become more negative by 0.93 kcal/mol due to JANAF selections for HF(aqueous). Three values derived by Parker for BeF₂(c) from PbF₂(c) are changed due to JANAF auxiliary data; these values become -246.9, -246.0 and -247.2 for the three paths used by Parker.

The adopted ΔH_f° was derived by combination of calorimetric data for Be(c) + F₂(g) → BeF₂(vitreous) and BeF₂(c) → BeF₂(vitreous). Churney and Armstrong (2) obtained $\Delta H_f^\circ_{298.15} = -244.32 \pm 0.8$ kcal/mol for vitreous BeF₂ by combustion in fluorine of polytetrafluoroethylene and mixtures of Be(c) with polytetrafluoroethylene. $\Delta H_f^\circ_{298.15}(c \rightarrow \text{vitreous}) = 1.125 \pm 0.016$ kcal/mol was measured via solution calorimetry by Taylor and Gardner (3).

Heat Capacity and Entropy

C_p° is based on JANAF curve fits of measurements by adiabatic calorimetry (8-300°K) and by ice calorimetry (354-776°K) as reported by Taylor and Gardner (3). The sample was estimated as approximately 99.5% BeF₂. Analyses indicated that the major impurity was about 0.3% oxygen, mainly in the form of absorbed water. Petrographic examination and X-ray diffraction showed the sample to be composed almost completely of quartz-type crystals. The entropy is derived from the smoothed C_p° based on the extrapolation $S_0^\circ = 0.0065$ gibbs/mol. The adopted C_p° above 300°K agrees closely with the relative enthalpy data and shows a remarkable similarity to that of SiO₂ (low quartz, high quartz).

Transition Data

It is the value selected by Taylor and Gardner (3) from their relative enthalpy data. ΔH_t° is the corresponding difference in relative enthalpy from the JANAF curve fits for the two crystalline forms. Levina (4) studied the polymorphism of BeF₂ by observing the peaks in C_p near the transition temperatures. For low quartz → high quartz, Levina's peak began near 438°K, was complete near 503°K, and gave $\Delta H_t = 0.17$ kcal/mol. Levina found a second transition attributed to a form analogous to tridymite; this began above 670°K, was complete by 740°K, and gave $\Delta H_t = 0.24$ kcal/mol. There is no evidence for this transition in the relative enthalpy data, so we suspect that its occurrence may be due to impurities in Levina's sample. Levina also found that the cristobalite-like phase transformed in the region 380 to 420°K with $\Delta H_t = 1.27$ kcal/mol.

Melting Data

See the table for BeF₂(t).

Heat of Sublimation

See the table for BeF₂(g).

References

1. V. B. Parker, Natl. Bur. Std. Report 10004, chapter 3, p. 58, issued Jan. 1, 1969.
2. K. L. Churney and G. T. Armstrong, J. Res. Natl. Bur. Std. 73A, 281 (1969).
3. A. R. Taylor and T. Estelle Gardner, U. S. Bur. Mines RI-6668, 1965.
4. M. E. Levina, Izv. Vysch. Ucheb. Zaved., Khim. Khim. Tekhnol. 8 (2), 177 (1965).

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	.000	.000	INFINITE	-2.024	-244.846	-244.846	INFINITE
100	5.020	3.526	21.571	-1.805	-245.132	-241.602	528.070
200	9.341	6.430	13.791	-1.072	-245.437	-237.612	259.469
298	12.365	12.752	12.752	.000	-245.400	-234.078	171.564
300	12.435	12.829	12.752	.023	-245.398	-234.008	170.874
400	14.043	16.749	13.270	1.392	-245.238	-230.231	125.792
500	15.320	20.514	14.333	3.090	-244.851	-226.513	99.009
600	16.120	23.378	15.607	4.662	-244.653	-222.864	81.174
700	16.720	25.725	16.972	6.314	-244.424	-219.250	66.453
800	17.120	27.625	18.172	8.058	-244.183	-215.676	53.517
900	17.320	29.168	19.216	9.858	-243.934	-212.130	42.127
1000	17.320	30.368	19.916	11.750	-243.687	-208.627	31.595
1100	17.120	31.240	20.610	13.722	-243.451	-205.163	22.762
1200	16.720	31.731	21.265	15.764	-243.224	-201.739	15.442
1300	16.120	31.931	21.799	17.964	-242.604	-198.355	9.346

Beryllium Difluoride (BeF₂)

GFW = 47.009

(Liquid)

T, °K	Cp*	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGr°	Log Kp
0							
100							
200							
298	11.927	14.321	14.321	.000	-244.275	-233.421	171.102
300	11.977	14.395	14.321	.022	-244.274	-233.353	169.998
400	14.151	18.159	14.820	1.336	-244.169	-229.726	125.516
500	15.669	21.488	15.827	2.830	-243.986	-226.135	98.844
600	16.862	24.458	17.022	4.459	-243.731	-222.588	81.077
700	17.680	26.131	18.240	6.032	-243.506	-219.098	68.402
800	18.797	28.379	19.540	8.032	-243.042	-215.568	58.402
900	19.653	31.843	20.783	9.938	-242.613	-212.237	51.310
1000	20.469	33.956	21.996	11.961	-242.131	-208.688	45.652
1100	21.058	35.948	23.178	14.047	-241.601	-205.588	40.847
1200	22.028	39.427	25.117	18.452	-240.367	-199.140	36.671
1300	22.785	39.620	25.426	18.452	-240.367	-199.140	36.671
1400	23.532	41.336	26.502	20.768	-239.724	-195.992	30.596
1500	24.271	42.695	27.546	23.156	-239.005	-192.693	28.104
1600	25.005	46.575	28.541	25.622	-240.995	-189.764	25.821
1700	25.734	46.113	29.548	30.759	-239.079	-183.475	23.279
1800	26.460	47.604	30.510	30.759	-239.079	-183.475	23.279
1900	27.183	49.054	31.448	33.451	-238.024	-180.414	20.752
2000	27.904	50.467	32.364	36.205	-236.905	-177.410	18.386

Sept. 30, 1951; June 30, 1963; Dec. 31, 1963; June 30, 1964

Heat of Formation

ΔH_f° is obtained from that of the crystal by means of $\Delta H_r^\circ = 1.125 \pm 0.016$ kcal/mol for $\text{BeF}_2(\text{c}) \rightarrow \text{BeF}_2(\text{vitreous})$ at 298.15°K. Further details are given in the section on Melting Data. $\Delta H_f^\circ(\text{c})$ actually is based on the direct determination of $\Delta H_f^\circ(\text{vitreous})$ by Churney and Armstrong (1) as discussed on the crystal table.

Heat Capacity and Entropy

C_p° is based on a JANAF curve fit of relative enthalpies of Taylor and Gardner (2) for the liquid (828-1183°K) and vitreous (320-473°K) forms of BeF_2 . The combined data yield a normal C_p° curve and reveal no need for a glass transition. Scatter in the data is somewhat larger than for the crystal, presumably due to minor variations in the vitreous state at the conclusion of each drop. $S_{298.15}^\circ(\text{c})$ is calculated from that of the crystal by addition of ΔS_m° and the difference for crystal and liquid of $(S_{828}^\circ - S_{298.15}^\circ)$.

Melting Data

T_m is the value selected by Taylor and Gardner (2) from their relative enthalpy data. These showed premelting starting near 804°K and complete melting above 828°K. Cooling of the liquid produced the vitreous state. T_m has also been reported as 815 (3), 821 (4), 818 (5) and $816 \pm 5^\circ\text{K}$ (6).

Solution calorimetry (2) gave $\Delta H_r^\circ = 1.125 \pm 0.016$ kcal/mol for $\text{BeF}_2(\text{low quartz}) \rightarrow \text{BeF}_2(\text{vitreous})$ at 298.15°K. Confirmation of this result came from transposed temperature-drop calorimetry (1) and calorimetric conversion (3). These gave 1.1 ± 0.2 and 1.1 ± 0.5 kcal/mol, respectively. Combination of $\Delta H_r^\circ = 1.125$ with JANAF enthalpies yields $\Delta H_m^\circ = 1.137$ kcal/mol.

Vaporization Data

T_b is the calculated temperature at which $\Delta G_r^\circ = 0$ for $\text{BeF}_2(\text{l}) \rightarrow \text{BeF}_2(\text{g})$. ΔH_v° is the corresponding value of ΔH_r° . These calculations neglect the presence of dimer, which is assumed to be negligible based on extrapolation of the equations of Belousov (3). Cantor (10) obtained $T_b = 1442^\circ\text{K}$ by extrapolation of his vapor pressures (1146-1372°K).

References

1. K. L. Churney and G. T. Armstrong, J. Res. Natl. Bur. Std. **73A**, 281 (1969).
2. A. R. Taylor and T. E. Gardner, U. S. Bur. Mines RI-6664, 1965.
3. M. A. Greenbaum, J. N. Foster, M. L. Arin and M. Farber, J. Phys. Chem. **67**, 36 (1963).
4. R. E. Thoma, H. Insley, H. A. Friedman and C. F. Weaver, J. Phys. Chem. **64**, 865 (1960).
5. K. A. Sense and R. W. Stone, J. Phys. Chem. **62**, 453 (1958).
6. D. M. Roy, R. Roy and E. F. Osborn, J. Amer. Ceram. Soc. **36**, 185 (1953).
7. M. E. Melnichak, unpublished result quoted by J. L. Holm and O. J. Kleppa, Inorg. Chem. **8**, 207 (1969).
8. P. Gross, Pulver Res. Inst. Report R.163/19/April 1965, Stokes Porges, England.
9. V. I. Belousov, L. N. Sidorov, S. A. Komarov and P. A. Akishin, Zh. Fiz. Khim. **41**, 2969 (1967); Russ. J. Phys. Chem. **41**, 1598 (1967).
10. S. Cantor, J. Chem. Eng. Data **10**, 237 (1965).

Beryllium Difluoride (BeF₂)

GFW = 47.009

(Ideal Gas)

Point Group D_{∞h}S_{298.15} = 54.36 ± 0.3 gibbs/mol

Ground State Quantum Weight = 1

ΔH_f⁰ = -190.3 ± 1.0 kcal/molΔH_f⁰298.15 = -190.25 ± 1.0 kcal/mol

T, °K	C _p gibbs/mol	S ⁰ -(G ⁰ -H ⁰ ₂₉₈)/T	H ⁰ -H ⁰ ₂₉₈	ΔH ⁰ kcal/mol	Log Kp
0	-0.00	INFINITE	2.415	-190.287	INFINITE
100	44.198	53.257	-1.920	-190.283	1.000
200	9.774	50.192	-1.029	-190.284	206.604
298	11.091	54.360	-0.000	-190.250	146.251
300	11.100	54.459	1.021	-190.250	139.391
400	11.955	57.787	1.176	-190.304	104.738
500	12.573	60.484	2.404	-190.387	83.938
600	13.038	62.819	3.685	-192.355	70.065
700	13.392	64.857	5.008	-190.580	60.151
800	13.663	66.664	6.361	-192.561	52.712
900	13.873	68.256	7.738	-190.804	46.972
1000	14.036	69.676	9.134	-190.733	42.261
1100	14.166	71.100	10.544	-191.079	38.492
1200	14.269	72.337	12.365	-191.243	35.327
1300	14.353	73.483	14.177	-191.226	32.647
1400	14.422	74.552	15.982	-191.030	30.347
1500	14.479	75.546	17.782	-191.056	28.351
1600	14.527	76.482	19.580	-194.060	26.592
1700	14.567	77.364	21.387	-195.016	25.026
1800	14.602	78.198	23.198	-195.178	23.633
1900	14.631	78.986	25.017	-195.343	22.385
2000	14.656	79.739	26.854	-195.514	21.261
2100	14.678	80.455	28.702	-195.690	20.243
2200	14.698	81.138	30.559	-195.872	19.317
2300	14.715	81.792	32.428	-196.059	18.471
2400	14.729	82.419	34.306	-196.253	17.694
2500	14.743	83.020	36.193	-196.455	16.979
2600	14.755	83.599	38.088	-196.661	16.318
2700	14.765	84.156	40.000	-196.872	15.705
2800	14.775	84.693	41.928	-197.089	15.139
2900	14.783	85.211	43.872	-197.311	14.628
3000	14.791	85.713	45.830	-197.538	14.164
3100	14.798	86.198	47.797	-197.767	13.742
3200	14.804	86.668	49.772	-197.996	13.359
3300	14.810	87.123	51.754	-198.225	13.012
3400	14.815	87.566	53.741	-198.454	12.699
3500	14.820	87.995	55.733	-198.683	12.420
3600	14.825	88.413	57.730	-198.911	12.174
3700	14.829	88.819	59.732	-199.139	11.950
3800	14.833	89.214	61.739	-199.366	11.746
3900	14.836	89.600	63.750	-199.593	11.561
4000	14.840	89.975	65.764	-199.819	11.394
4100	14.843	90.342	67.782	-200.044	11.244
4200	14.846	90.700	69.804	-200.268	11.109
4300	14.848	91.049	71.829	-200.491	10.988
4400	14.851	91.390	73.857	-200.713	10.877
4500	14.853	91.724	75.886	-200.935	10.774
4600	14.855	92.051	77.915	-201.156	10.678
4700	14.857	92.370	79.944	-201.376	10.586
4800	14.859	92.683	81.972	-201.595	10.498
4900	14.861	92.989	84.000	-201.813	10.414
5000	14.863	93.290	86.028	-202.030	10.333
5100	14.864	93.584	88.056	-202.246	10.254
5200	14.866	93.873	90.084	-202.461	10.178
5300	14.867	94.156	92.112	-202.675	10.104
5400	14.868	94.434	94.140	-202.888	10.032
5500	14.869	94.706	96.168	-203.100	9.961
5600	14.871	94.974	98.196	-203.311	9.891
5700	14.872	95.238	100.224	-203.521	9.822
5800	14.873	95.496	102.252	-203.730	9.754
5900	14.874	95.751	104.280	-203.938	9.687
6000	14.875	96.001	106.308	-204.145	9.621

Dec 31, 1960; Sept. 30, 1961; June 30, 1963; Dec. 31, 1963; June 30, 1964; June 30, 1970

Vibrational Frequencies and Degeneracies

ω, cm⁻¹

σ = 2

Bond Distance: Be-F = 1.40 ± 0.03 Å

Bond Angle: F-Be-F = 180°

Rotational Constant: B₀ = 0.22635 cm⁻¹

Heat of Formation

ΔH_f⁰ is calculated from that of the crystal by means of ΔH_{298.15} = 55.15 ± 0.1 kcal/mol. The selected value of ΔH_f⁰ is an average of those obtained by third-law analysis of vapor pressures measured by manometry (3), torsion effusion (4) and entrainment (8-10). Mass-spectrometric data (1, 2) are in reasonable agreement and so is the average of two Knudsen-effusion studies (6, 7). Several techniques (1, 2, 5) were used to show that the amount of dimer in the vapor is negligible up to at least 1000°K. JANAF analyses of the vaporization data are summarized as follows:

Source	Method	T, °K	ΔH _f ⁰ /mol	ΔS ⁰
(1) Efimenko (1968)	Mass Spectrometry	705-819	---	---
(2) Belousov (1967)	Mass Spectrometry	815-977	---	---
(3) Cantor (1965)	Manometry	1146-1372	0.65±0.08	---
(4) Hildenbrand (1965)	Torsion Effusion	Cell 13 Cell 27 Cell 12 Cell 14	891-942 872-907 821-921 840-921	4.2 ± 0.4 0.9 ± 0.3 0.8 ± 0.3 3.4 ± 0.3
(5) Blauer (1965)	Torsion Effusion	Cells A & B	713-795	6.2 ± 0.9
(6) Greenbaum (1963)	Effusion	823-1053	2.4 ± 0.6	---
(7) Khandamirova (1959)	Entrainment	846-950	3.4 ± 0.4	---
(8) Greenbaum (1963)	Entrainment	1123-1223	1.5 ± 0.0	---
(9) Ozhigov (1961)	Entrainment	1019-1241	1.4 ± 0.8	---
(10) Sense (1958)	Entrainment	1075-1298	-0.06±0.43	---
(11) Novoselova (1958)	Entrainment	1095-1376	-2.1 ± 0.5	---
*ΔS = ΔS ⁰ (2nd law) - ΔS ⁰ (3rd law)				

Heat Capacity and Entropy

The bond length and angle are those derived by Aikshin et al. (11) from electron-diffraction data for the vapor. Linearity of BeF₂ was confirmed by electric-deflection studies (12) of the vapor and by infrared studies (13) of matrix-isolated BeF₂. Infrared absorptions were found near 330 and 1540 cm⁻¹ in neon matrices, leading to gas-phase estimates of 345 and 1555 cm⁻¹ (13). The latter absorption was observed (14) at 1520 cm⁻¹ in the infrared spectra of the vapor at 1000°C. We adopt a compromise of 1530 cm⁻¹ and use this value in the valence-force-field approximation to estimate 670 cm⁻¹ for the symmetric stretching mode.

References

1. J. Efimenko, J. Res. Natl. Bur. Std. 72A, 75 (1968).
2. V. I. Belousov, L. N. Sidorov, S. A. Komarov and P. A. Aikshin, Zh. Fiz. Khim. 41, 2969 (1967); Russ. J. Phys. Chem. 41, 1598 (1967).
3. S. Cantor, J. Chem. Eng. Data 10, 237 (1965).
4. D. L. Hildenbrand and L. P. Theard, J. Chem. Phys. 42, 3230 (1965).
5. J. A. Blauer, M. A. Greenbaum and H. Farber, J. Phys. Chem. 69, 1069 (1965).
6. M. A. Greenbaum, J. N. Foster, M. L. Asin and H. Farber, J. Phys. Chem. 67, 36 (1963).
7. N. E. Khandamirova, A. M. Evseev, G. V. Pozharovskaya, E. A. Borisov, An. N. Nesmeyanov and Ya. I. Garasimov, Zh. Neorg. Khim. 8, 2192 (1959).
8. E. P. Ozhigov and A. I. Zatearin, Tr. Dal'nevost. Filiala, Akad. Nauk SSSR, Ser. Khim. 1961, No. 5, 24.
9. K. A. Sense and R. Stone, J. Phys. Chem. 62, 453 (1958).
10. A. V. Novoselova, F. Sh. Muratov, L. P. Soboleva and I. V. Gordaev, Vestn. Mosk. Univ., Ser. Mat., Mekh., Astron., Fiz., Khim. 13, No. 6, 181 (1958).
11. P. A. Aikshin, V. P. Spiridonov and G. A. Sobolev, Dokl. Akad. Nauk SSSR 118, 1114 (1958); Proc. Acad. Sci. USSR (English trans.), Phys. Chem. Sec. 118, 111 (1958).
12. L. Wharton, R. A. Berg and W. Klemperer, J. Chem. Phys. 39, 2023 (1963); J. A. Buehler, J. L. Stauffer and W. Klemperer, J. Amer. Chem. Soc. 86, 1544 (1964).
13. A. Snellson, J. Phys. Chem. 72, 250 (1968); 70, 3708 (1966).
14. A. Buehler and W. Klemperer, J. Chem. Phys. 29, 121 (1958).

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0						
100						
200						
298	22.140	21.300	21.300	0.000	- 372.171	272.808
300	22.200	21.437	21.300	0.041	- 372.059	271.045
400	25.200	28.244	22.208	2.414	- 366.019	199.083
500	27.800	34.154	24.019	5.068	- 359.958	157.337
600	30.000	39.426	26.155	7.862	- 353.871	128.827
700	32.500	44.176	28.332	10.682	- 347.863	108.868
800	34.770	48.489	30.642	14.271	- 341.940	93.414
900	35.620	52.392	32.845	17.592	- 336.099	81.616
1000	34.330	55.971	34.981	20.960	- 330.339	72.196
1100	35.000	59.275	37.041	24.457	- 324.654	64.503
1200	35.070	62.344	39.029	27.986	- 319.042	58.106
1300	36.100	65.214	40.929	31.570	- 313.498	52.704
1400	36.550	67.906	42.761	35.203	- 308.020	48.084
1500	37.000	70.443	44.523	38.860	- 302.602	44.089

LITHIUM TRIFLUOROBERYLLATE (LiBeF₃) (CRYSTAL) GFW = 72.9464

ΔHf° = Unknown
ΔHf°_{298.15} = -390.2 ± 0.7 kcal/mol
ΔHm° = Unknown

S°_{298.15} = [21.3 ± 2] gibbs/mol
Tm = 633°K

Heat of Formation.

The ΔHf°_{298.15} = -390.2 ± 0.7 kcal/mol was calculated from the ΔHr°_{298.15} = -2.24 ± 0.08 kcal/mol of the reaction $\text{LiF}(c) + \text{LiBeF}_3(c) = \text{Li}_2\text{BeF}_4(c)$ measured (calorimetrically) by P. Gross, Fulmer Research Institute, Administrative Report No. 4, January 1966.

Heat Capacity and Entropy.

The heat capacity (298 - 1100°K) was estimated from the difference of the Cp° values for $\text{Li}_2\text{BeF}_4(c)$ and $\text{LiF}(c)$. Above 1100°K the values were extrapolated graphically. The entropy was estimated by addition of S°₂₉₈ for $\text{BeF}_2(c)$ and $\text{LiF}(c)$.

Melting Data.

Tm was obtained from the phase diagram of a mixture of $\text{LiF}(c)$ and $\text{BeF}_2(c)$ reported by A. L. Mathews and C. F. Bass, Jr., ORNL-TM 1129, May 1955.

Lithium Trifluoroberyllate (LiBeF₃)
(Ideal Gas) Mol. Wt. = 72.953 INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0	0.000	0.000	INFINITE	-2.978	-210.240	-	-	INFINITE
100	6.150	52.222	7.124	-2.180	-210.614	-	-	457.999
200	10.450	65.103	12.633	-1.623	-211.214	-	-	227.575
298	14.601	69.889	16.699	-1.066	-211.800	-	-	131.436
300	14.665	69.979	63.889	-1.027	-212.012	-	-	150.498
400	17.636	68.629	64.503	-1.551	-212.603	-	-	111.836
500	19.704	72.891	65.753	-3.524	-213.862	-	-	58.545
600	21.137	75.528	67.244	5.570	-214.319	-	-	72.950
700	22.148	76.667	68.813	7.737	-214.701	-	-	61.789
800	22.879	82.874	70.395	9.691	-215.033	-	-	53.404
900	23.420	85.602	71.927	12.337	-215.339	-	-	46.873
1000	23.830	88.591	73.421	14.570	-215.533	-	-	41.540
1100	24.146	90.378	74.850	17.070	-215.924	-	-	37.353
1200	24.395	92.480	76.243	19.497	-215.219	-	-	33.776
1300	24.593	94.451	77.569	21.947	-214.522	-	-	30.745
1400	24.754	95.280	78.841	24.415	-213.835	-	-	28.143
1500	24.885	97.992	80.561	26.897	-213.153	-	-	25.885
1600	24.996	99.602	81.232	29.391	-220.261	-	-	23.895
1700	25.088	101.120	82.358	31.895	-225.554	-	-	21.954
1800	25.155	102.556	83.441	34.408	-255.519	-	-	20.129
1900	25.232	103.919	84.483	35.928	-255.685	-	-	18.495
2000	25.289	105.214	85.487	36.454	-255.755	-	-	17.024
2100	25.338	106.449	86.456	41.986	-255.931	-	-	15.494
2200	25.381	107.629	87.792	44.522	-255.912	-	-	14.580
2300	25.419	108.758	88.297	47.062	-255.698	-	-	13.763
2400	25.452	109.841	89.172	49.605	-256.092	-	-	12.354
2500	25.481	110.880	90.020	52.152	-255.195	-	-	11.431
2600	25.507	111.880	90.841	54.701	-256.324	-	-	10.470
2700	25.531	112.843	91.638	57.253	-256.421	-	-	9.571
2800	25.552	113.772	92.412	59.807	-327.575	-	-	8.947
2900	25.571	114.669	93.165	62.353	-327.460	-	-	8.052
3000	25.588	115.536	93.995	64.921	-327.352	-	-	7.240
3100	25.603	116.374	94.698	67.481	-327.250	-	-	6.471
3200	25.617	117.189	95.301	70.031	-327.156	-	-	5.750
3300	25.630	117.977	95.975	72.562	-327.072	-	-	5.073
3400	25.642	118.743	96.534	75.168	-326.998	-	-	4.436
3500	25.652	119.486	97.277	77.733	-326.934	-	-	3.835
3600	25.662	120.209	97.904	80.298	-326.882	-	-	3.268
3700	25.671	120.912	98.516	82.665	-326.843	-	-	2.732
3800	25.680	121.597	99.114	84.933	-326.818	-	-	2.224
3900	25.688	122.254	99.700	88.001	-326.818	-	-	1.742
4000	25.695	122.914	100.272	90.570	-326.813	-	-	1.284
4100	25.701	123.569	100.832	93.140	-326.836	-	-	0.849
4200	25.708	124.168	101.380	95.710	-326.876	-	-	0.439
4300	25.713	124.773	101.917	98.282	-326.932	-	-	0.038
4400	25.719	125.365	102.443	100.853	-327.010	-	-	0.340
4500	25.724	125.943	102.959	103.425	-327.109	-	-	0.700
4600	25.729	126.508	103.465	105.998	-327.229	-	-	1.044
4700	25.733	127.061	103.961	108.571	-327.370	-	-	1.366
4800	25.737	127.603	104.448	111.145	-327.537	-	-	1.694
4900	25.741	128.134	104.926	113.718	-327.730	-	-	2.024
5000	25.745	128.654	105.395	116.293	-327.946	-	-	2.291
5100	25.748	129.164	105.856	118.867	-328.182	-	-	2.572
5200	25.752	129.664	106.310	121.442	-328.445	-	-	2.872
5300	25.755	130.154	106.755	124.018	-328.768	-	-	3.103
5400	25.758	130.636	107.193	126.593	-329.102	-	-	3.354
5500	25.760	131.108	107.523	129.169	-329.468	-	-	3.596
5600	25.763	131.573	108.047	131.745	-329.868	-	-	3.836
5700	25.765	132.029	108.463	134.322	-330.301	-	-	4.080
5800	25.768	132.477	108.874	136.898	-330.769	-	-	4.275
5900	25.770	132.917	109.277	139.475	-331.275	-	-	4.486
6000	25.772	133.350	109.675	142.052	-331.818	-	-	4.691

December 31, 1962

BeF₃Li

BeF₃Li

LITHIUM TRIFLUORBERYLLATE (LiBeF₃) (Ideal Gas)

Mol. Wt. = 72.953
ΔH°_f 298.15 = -212 kcal. mole⁻¹
S°_{298.15} = (64) cal. deg⁻¹ mole⁻¹
Point Group (C_{3v})

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[1530] (1)	(485) (2)
[820] (2)	(800) (5)
[700] (1)	

Bond distance: Be-F = [1.40] Å Li-Be = [1.205] Å
Li-F = [1.85] Å
Bond angle: F-Be-F = [120]° Li-Be-F = [90]°
Moment of inertia: I_{ABIC} = 2.1604 X 10⁻¹¹⁴ g. cm² σ = (5)
72, 1075 (1960).

Heat of Formation. ΔH°_f 298.15 was calculated from ΔH°_f 900 = 53 kcal. mole for the reaction: LiF(g) + BeF₂(g) = LiBeF₃(g) reported by J. Berkowitz and N. A. Chupka, Ann. N. Y. Acad. Sci., 72, 1075 (1960).

Heat Capacity and Entropy. The molecular structure was assumed to be pyramidal with Li atom at the top and BeF₃ located at the bottom. Beryllium atom was taken at the center of the equilateral triangle formed by the three F atoms. The Be-F distance was estimated from that of BeF₂(g). The bond distance of Li-F was taken from R. P. Porter and E. Zeller, J. Chem. Phys., 33, 888 (1960). Vibrational frequencies were estimated by comparison with related fluorides.

Dilithium Tetrafluoroberyllate (Li_2BeF_4)
(Crystal) GFW = 98.8838



T, °K	Cp°	$\frac{\text{gibbs/mol}}{S}$	$\frac{-(G^\circ - H^\circ_{298})}{T}$	$\frac{\text{kcal/mol}}{H^\circ - H^\circ_{298}}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	32.290	29.800	29.800	+0.00	- 539.000	- 514.169	376.896
300	32.300	30.000	29.801	+0.60	- 538.997	- 514.016	374.460
400	35.960	38.794	31.111	3.473	- 538.805	- 505.713	276.309
500	39.590	48.210	33.707	7.251	- 539.981	- 497.324	217.380
600	43.140	55.742	36.762	11.388	- 539.476	- 488.823	178.057
700	46.680	62.661	39.074	15.881	- 538.657	- 480.434	139.005
800	49.760	68.105	40.217	20.711	- 537.538	- 472.214	112.705
900	52.235	73.113	40.431	25.813	- 536.187	- 464.127	99.703
1000	54.360	80.729	40.583	31.146	- 534.644	- 456.202	80.097
1100	56.053	85.992	42.456	36.460	- 532.945	- 448.430	80.287
1200	57.560	90.935	42.932	42.392	- 531.121	- 440.836	72.859
1300	58.800	95.592	48.170	58.193	- 529.193	- 433.389	66.516
1400	59.840	99.992	61.343	54.108	- 527.175	- 426.095	61.041
1500	60.965	104.163	64.060	60.154	- 525.077	- 418.947	56.258
1600	61.620	108.128	66.402	66.209	- 525.663	- 411.863	51.702
1700	62.810	111.409	69.241	72.536	- 523.409	- 402.166	47.474
1800	63.620	115.523	71.713	78.858	- 520.623	- 390.997	43.708
1900	64.350	118.983	74.110	85.257	- 517.769	- 379.983	40.336
2000	65.000	122.300	76.437	91.726	- 514.858	- 369.120	

June 30, 1966

DILITHIUM TETRAFLUOROBERYLLATE (Li_2BeF_4) (CRYSTAL)

$\Delta H^\circ_{\text{f}} = \text{Unknown}$

$\Delta H^\circ_{\text{f}} 298.15 = -539.0 \pm 1.3 \text{ kcal/mol}$

$\Delta H^\circ_{\text{f}} = 10.606 \text{ kcal/mol}$

$S^\circ_{298.15} = [29.8 \pm 2] \text{ gibbs/mol}$

$T_m = 745^\circ\text{K}$

Heat of Formation.

The $\Delta H^\circ_{\text{f}} 298.15 = -539.0 \pm 1.3 \text{ kcal/mol}$ was calculated from the $\Delta H^\circ_{\text{f}} 298.15 = -5.05 \pm 0.06 \text{ kcal/mol}$ of the reaction $2\text{LiF}(c) + \text{BeF}_2(c) = \text{Li}_2\text{BeF}_4(c)$ measured (calorimetrically) by F. Gross, Fulmer Research Institute, R.163/23/May 1966. A value of $\Delta H^\circ_{\text{f}} 298 = 1.17 \text{ kcal/mol}$ was used for $\text{BeF}_2(c) \rightarrow \text{BeF}_2(g)$.

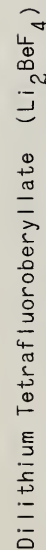
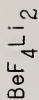
Heat Capacity and Entropy.

The heat capacity is based on the enthalpy data ($323\text{--}723^\circ\text{K}$) of T. B. Douglas and W. H. Payne, Natl. Bur. Std. Report 8186, January, 1964. The entropy was estimated by addition of values for the component fluorides.

Melting Data.

T_m and ΔH_m° were obtained from Douglas et al., loc. cit., who measured the high temperature enthalpies.





(Liquid) GFW = 98.8838

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	32.290	39.304	39.404	0.000	- 531.217	- 509.220	373.268
300	32.300	39.504	39.305	0.060	- 531.214	- 509.084	370.868
400	35.960	49.298	40.615	3.473	- 531.022	- 501.732	274.134
500	55.500	57.713	43.211	7.251	- 532.198	- 494.293	216.055
600	55.500	67.832	46.497	12.801	- 530.280	- 486.801	177.350
700	55.500	76.387	53.171	18.561	- 526.200	- 465.810	149.350
800	55.500	83.758	57.622	23.501	- 520.565	- 443.944	126.216
900	55.500	90.335	57.612	29.451	- 524.766	- 465.407	113.259
1000	55.500	96.182	61.182	35.001	- 523.006	- 460.017	100.537
1100	55.500	101.472	64.468	40.551	- 521.280	- 453.802	90.162
1200	55.500	106.301	67.894	46.101	- 518.280	- 443.794	81.277
1300	55.500	110.744	71.012	51.651	- 517.929	- 441.823	74.277
1400	55.500	114.857	73.999	57.601	- 516.599	- 436.030	68.057
1500	55.500	118.686	76.852	62.751	- 514.697	- 430.352	62.702
1600	55.500	122.268	79.480	68.301	- 511.878	- 424.702	58.012
1700	55.500	125.652	82.191	73.851	- 508.311	- 419.092	53.242
1800	55.500	128.864	84.693	79.401	- 504.297	- 413.578	48.365
1900	55.500	131.805	87.094	84.951	- 500.292	- 408.568	43.650
2000	55.500	134.652	89.402	90.501	- 496.300	- 387.266	42.318

DILITHIUM TETRAFLUOROBERYLLATE (Li_2BeF_4)

(LIQUID)

GFW = 98.8838

$$\Delta H^\circ_{298.15} = -531.2 \pm 1.3 \text{ kcal/mol}$$

$$\Delta H^\circ = -10.506 \text{ kcal/mol}$$

$$S^\circ_{298.15} = [39.3 \pm 2] \text{ gibbs/mol}$$

$$T_m = 745^\circ\text{K}$$

Heat of Formation.

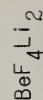
The $\Delta H^\circ_{298.15}$ was obtained from $\Delta H^\circ_{298.15}(c)$ by adding ΔH°_f and the difference between $H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 500°K . The heat capacity below 500°K was obtained from the heat capacity of the crystal. Above 500°K the heat capacity was assumed constant at 55.5 gibbs/mol calculated from the liquid enthalpy equation given by T. B. Douglas and W. H. Payne, Natl. Bur. Std. Report No. 8186, Washington, 1964. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $\text{Li}_2\text{BeF}_4(c)$ table.



T, °K.	C _p	S° -(R°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	INFINITE	-2.066	76.181	76.181	INFINITE
100	6.962	34.625	48.434	76.478	76.478	-162.260
200	6.967	39.452	42.874	76.735	76.735	-78.563
298	6.985	42.236	40.884	76.788	76.788	-50.948
300	6.986	42.279	42.236	76.767	69.462	-50.901
400	7.050	44.298	42.511	76.683	67.038	-36.626
500	7.205	45.887	43.033	76.542	64.642	-28.254
600	7.393	47.217	43.522	76.380	62.277	-22.683
700	7.593	48.372	43.966	76.206	60.042	-18.443
800	7.785	49.338	44.804	76.027	57.628	-15.743
900	7.958	50.326	45.367	75.843	55.340	-13.438
1000	8.111	51.172	45.906	75.646	53.072	-11.598
1100	8.245	51.952	46.421	75.437	50.825	-10.098
1200	8.361	52.674	46.912	75.212	48.597	-8.850
1300	8.462	53.347	47.381	74.969	46.389	-7.768
1400	8.550	53.978	47.830	74.707	44.200	-6.900
1500	8.628	54.570	48.260	74.423	42.031	-6.124
1600	8.697	55.130	48.672	74.121	39.894	-5.458
1700	8.758	55.659	49.068	73.805	37.800	-4.885
1800	8.813	56.161	49.448	73.478	35.746	-4.378
1900	8.862	56.639	49.814	73.137	33.729	-3.926
2000	8.908	57.094	50.167	72.786	31.749	-3.520
2100	8.949	57.530	50.507	72.428	29.802	-3.153
2200	8.988	57.947	50.836	72.061	27.885	-2.822
2300	9.023	58.348	51.154	71.686	25.921	-2.520
2400	9.057	58.732	51.461	71.305	23.967	-2.244
2500	9.088	59.103	51.760	70.917	22.079	-1.991
2600	9.118	59.460	52.049	70.521	20.267	-1.759
2700	9.146	59.804	52.330	70.118	18.533	-1.545
2800	9.172	60.137	52.603	69.707	16.878	-1.343
2900	9.198	60.460	52.868	69.289	15.300	-1.140
3000	9.222	60.772	53.127	68.864	13.800	-0.946
3100	9.246	61.075	53.378	68.433	12.375	-0.762
3200	9.269	61.369	53.623	67.997	11.025	-0.588
3300	9.291	61.654	53.862	67.556	9.750	-0.424
3400	9.312	61.932	54.096	67.110	8.550	-0.270
3500	9.333	62.202	54.323	66.659	7.425	-0.126
3600	9.354	62.465	54.546	66.203	6.375	0.010
3700	9.374	62.722	54.763	65.742	5.400	0.130
3800	9.393	62.972	54.976	65.276	4.500	0.240
3900	9.412	63.216	55.184	64.805	3.675	0.340
4000	9.431	63.455	55.388	64.329	2.925	0.430
4100	9.450	63.688	55.588	63.848	2.250	0.510
4200	9.468	63.916	55.783	63.362	1.650	0.580
4300	9.486	64.139	55.975	62.871	1.125	0.640
4400	9.504	64.357	56.163	62.375	0.675	0.690
4500	9.521	64.571	56.348	61.874	0.300	0.730
4600	9.539	64.780	56.529	61.368	0.000	0.760
4700	9.556	64.986	56.706	60.857	-0.300	0.780
4800	9.573	65.187	56.881	60.341	-0.600	0.790
4900	9.590	65.385	57.052	59.819	-0.900	0.790
5000	9.606	65.579	57.221	59.292	-1.200	0.780
5100	9.623	65.769	57.387	58.759	-1.500	0.760
5200	9.639	65.956	57.550	58.221	-1.800	0.730
5300	9.656	66.140	57.710	57.678	-2.100	0.690
5400	9.672	66.320	57.868	57.130	-2.400	0.640
5500	9.688	66.498	58.023	56.577	-2.700	0.580
5600	9.704	66.673	58.176	56.019	-3.000	0.510
5700	9.720	66.845	58.327	55.456	-3.300	0.430
5800	9.736	67.014	58.475	54.888	-3.600	0.340
5900	9.752	67.180	58.621	54.315	-3.900	0.240
6000	9.767	67.344	58.765	53.738	-4.200	0.130

Dec. 31, 1960 Mar. 31, 1963

BERYLLIUM MONOHYDRIDE (BeH)

(IDEAL GAS)

MOL. WT. = 10.021

Ground State Configuration $2s^+$
 $\Delta H_f^0 = 42.236 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = 76 \pm 7 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = 77 \pm 7 \text{ kcal. mole}^{-1}$

Electronic Level and Multiplicity

$$\epsilon, \text{ cm.}^{-1} = \frac{g_1}{2}$$

$$\omega_e x_e = 35.5 \text{ cm.}^{-1}$$

$$\sigma^- = 1$$

$$\omega_e = 10.308 \text{ cm.}^{-1}$$

$$r_e = 1.3431 \text{ \AA}$$

Heat of Formation.

Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., London, 1953, selected a value of $2.3 \pm 0.3 \text{ e.v. (53} \pm 7 \text{ kcal. mole}^{-1})$ for D_0 . Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950, estimated D_0 as being $2.2 \text{ e.v. (50.7 kcal. mole}^{-1})$. Gaydon's value was used in this table.

Heat Capacity and Entropy.

Molecular constants were found in Herzberg, op. cit.

BeH

BeH⁺

OPW = 10.01962

BERYLLIUM MONOHYDRIDE UNIPosITIVE ION (BeH⁺) (IDEAL GAS)

Ground State Configuration 1 Σ
 $\Delta H_f^\circ = 274.3 \pm 10$ kcal/mol
 $\Delta H_f^\circ = 276.4 \pm 10$ kcal/mol
 $S_{298.15}^\circ = 40.75$ gibbs/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	1
[20000]	[3]
$\omega_e x_e = 39.79$ cm ⁻¹	
$\sigma = 1$	
$r_e = 1.31216$ Å	
$\omega_e = 2221.7$ cm ⁻¹	
$B_e = 10.7998$ cm ⁻¹	
$\omega_e^2 = 0.2935$ cm ⁻¹	

Heat of Formation.

The heat of formation was calculated from the equation $\text{BeH}(g) \rightarrow \text{BeH}^+(g) + e^-$ with the JANAP auxiliary data for $\text{BeH}(g)$, using an ionization potential = 8.6 ± 0.4 eV (198.34 ± 9.23 kcal/mol) obtained from C. W. Beckett, NBS Report 8828, Jan. 1, 1985.

The dissociation energy, D_0 ($\text{Be}^+ - \text{H}$) = 3.2 ± 0.2 eV (73.8 kcal/mol), has been reported by A. G. Gaydon, "Dissociation Energies," 2nd Ed., Chapman and Hall Ltd., London, 1953. This yields $\Delta H_f^\circ(\text{BeH}^+, g) = 270.0$ kcal/mol, which is in agreement with the value adopted.

Heat Capacity and Entropy.

The molecular constants were obtained from the ultraviolet spectroscopic studies by W. W. Watson and R. P. Humphreys, Phys. Rev. 52, 318 (1937).

The ground state configuration was given by O. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, New York, 1950. The estimated electronic level and quantum weight were obtained by assuming that a 3Σ level lies below the first observed excited state ($1\Sigma^-$) at 40,000 cm⁻¹.

BeH⁺

Beryllium Monohydride Unipositive Ion (BeH⁺)

(Ideal Gas) GFW = 10.01962

T, K	Cp ^a	gibbs/mol S ^b - (G° - H° ₂₉₈)/T	kcal/mol ΔH ^c	H° - H° ₂₉₈	ΔG ^d	Log Kp
0						
100						
200						
298	6.977	40.760	276.400	.000	268.092	- 196.517
300	6.978	40.803	276.408	.013	268.041	- 195.267
400	7.050	42.816	276.819	.713	265.187	- 184.892
500	7.144	44.396	277.171	1.421	262.238	- 174.624
600	7.307	45.713	277.498	2.143	259.220	- 164.421
700	7.490	46.853	277.811	2.883	256.148	- 154.273
800	7.673	47.855	278.118	3.641	253.032	- 144.179
900	7.856	48.727	278.418	4.417	249.879	- 134.129
1000	8.000	49.463	278.709	5.210	246.693	- 124.115
1100	8.137	50.382	278.986	6.017	243.479	- 114.146
1200	8.258	51.096	279.246	6.836	240.239	- 104.219
1300	8.364	51.761	279.490	7.668	236.977	- 94.373
1400	8.459	52.384	279.715	8.508	233.699	- 84.602
1500	8.539	52.971	279.919	9.359	230.404	- 74.910
1600	8.612	53.524	277.345	10.216	227.175	- 65.301
1700	8.677	54.048	277.620	11.081	224.032	- 55.773
1800	8.735	54.546	277.890	11.951	220.870	- 46.317
1900	8.785	55.017	278.158	12.828	217.698	- 36.933
2000	8.836	55.471	278.420	13.709	214.508	- 27.620
2100	8.880	55.904	278.678	14.595	211.304	- 18.381
2200	8.921	56.318	278.931	15.485	208.090	- 9.212
2300	8.950	56.715	279.179	16.379	204.866	- 0.017
2400	8.978	57.097	279.422	17.277	201.632	9.183
2500	9.031	57.465	279.659	18.178	198.383	17.343
2600	9.065	57.820	279.893	19.083	195.129	25.402
2700	9.099	58.163	280.123	19.991	191.865	33.450
2800	9.131	58.494	280.348	20.903	188.600	41.497
2900	9.162	58.816	280.569	21.818	185.334	49.544
3000	9.198	59.127	210.261	22.736	182.069	57.591
3100	9.232	59.429	210.732	23.657	178.819	65.638
3200	9.267	59.722	211.203	24.582	175.571	73.685
3300	9.303	60.008	211.672	25.511	172.324	81.732
3400	9.338	60.286	212.139	26.443	169.076	89.779
3500	9.379	60.556	212.605	27.379	165.828	97.826
3600	9.419	60.822	213.070	28.319	162.580	105.873
3700	9.461	61.081	213.531	29.263	159.332	113.920
3800	9.505	61.334	213.990	30.211	156.084	121.967
3900	9.547	61.581	214.447	31.164	152.836	130.014
4000	9.597	61.824	214.899	32.121	149.588	138.061
4100	9.646	62.061	215.349	33.083	146.340	146.108
4200	9.696	62.294	215.796	34.050	143.092	154.155
4300	9.748	62.523	216.239	35.022	139.844	162.202
4400	9.799	62.748	216.677	36.000	136.596	170.249
4500	9.856	62.969	217.108	36.982	133.348	178.296
4600	9.912	63.186	217.531	37.971	130.100	186.343
4700	9.969	63.400	217.959	38.965	126.852	194.390
4800	10.027	63.610	218.377	39.965	123.604	202.437
4900	10.084	63.816	218.789	40.970	120.356	210.484
5000	10.147	64.022	219.194	41.982	117.108	218.531
5100	10.208	64.224	219.593	42.999	113.860	226.578
5200	10.269	64.422	219.987	44.024	110.612	234.625
5300	10.331	64.619	220.373	45.054	107.364	242.672
5400	10.392	64.813	220.753	46.090	104.116	250.719
5500	10.455	65.004	221.126	47.132	100.868	258.766
5600	10.517	65.192	221.491	48.181	97.620	266.813
5700	10.579	65.379	221.851	49.236	94.372	274.860
5800	10.641	65.564	222.203	50.297	91.124	282.907
5900	10.703	65.748	222.548	51.364	87.876	290.954
6000	10.763	65.926	222.886	52.437	84.628	299.001

Sept. 30, 1986

Beryllium Monohydroxide Unipositive Ion (BeOH⁺)

(Ideal Gas) GFW = 26.01902

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o)/T	H ^o - H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	Log K _p
100						
200						
298	7.663	47.983	.000	194.000	190.844	-139.893
300	7.679	48.030	.014	194.003	190.824	-139.915
400	6.605	50.364	.526	184.162	183.669	-130.649
500	6.468	52.382	1.733	194.356	188.611	-92.482
600	10.217	54.178	2.720	194.570	187.442	-68.276
700	10.604	55.799	50.410	194.806	186.235	-58.185
800	11.283	57.274	51.177	195.061	184.993	-56.538
900	11.682	58.626	51.931	195.327	183.719	-44.613
1000	12.023	59.875	52.684	195.597	182.415	-39.667
1100	12.317	61.035	53.373	195.865	181.085	-35.978
1200	12.572	62.118	54.057	196.127	179.730	-32.733
1300	12.766	63.134	54.716	196.379	178.352	-29.984
1400	12.933	64.089	55.352	196.621	176.956	-27.624
1500	13.166	64.982	55.965	196.847	175.543	-25.577
1600	13.320	65.846	56.556	194.302	174.194	-23.794
1700	13.455	66.658	57.127	194.611	172.929	-22.231
1800	13.576	67.431	57.678	194.917	171.643	-20.840
1900	13.683	68.168	58.211	195.224	170.343	-19.594
2000	13.779	68.872	58.726	195.528	169.025	-18.470
2100	13.864	69.546	59.225	195.830	167.692	-17.452
2200	13.941	70.193	59.709	196.127	166.345	-16.525
2300	14.010	70.814	60.179	196.421	164.985	-15.677
2400	14.072	71.412	60.634	196.709	163.615	-14.899
2500	14.129	71.986	61.077	196.991	162.228	-14.162
2600	14.180	72.543	61.507	197.269	160.833	-13.519
2700	14.226	73.079	61.926	197.542	159.427	-12.905
2800	14.268	73.597	62.334	126.779	159.117	-12.420
2900	14.307	74.096	62.731	127.291	160.266	-12.078
3000	14.342	74.584	63.116	127.600	161.391	-11.757
3100	14.374	75.055	63.495	128.307	162.500	-11.456
3200	14.404	75.512	63.864	128.811	163.600	-11.173
3300	14.432	75.955	64.224	129.310	164.679	-10.906
3400	14.457	76.386	64.575	129.804	165.742	-10.654
3500	14.480	76.806	64.916	130.294	166.791	-10.415
3600	14.502	77.214	65.254	130.779	167.830	-10.189
3700	14.522	77.612	65.583	131.256	168.848	-9.973
3800	14.540	77.999	65.905	131.728	169.861	-9.769
3900	14.557	78.377	66.220	132.193	170.859	-9.575
4000	14.574	78.746	66.526	132.640	171.841	-9.389
4100	14.589	79.106	66.831	133.097	172.812	-9.212
4200	14.603	79.456	67.127	133.538	173.760	-9.043
4300	14.616	79.801	67.418	133.969	174.736	-8.881
4400	14.628	80.141	67.703	134.391	175.693	-8.726
4500	14.640	80.466	67.983	134.800	176.608	-8.577
4600	14.651	80.788	68.258	135.201	177.536	-8.435
4700	14.661	81.103	68.528	135.590	178.450	-8.298
4800	14.670	81.412	68.793	135.969	179.358	-8.166
4900	14.679	81.715	69.054	136.336	180.259	-8.040
5000	14.688	82.011	69.310	136.691	181.154	-7.918
5100	14.696	82.302	69.562	137.033	182.039	-7.801
5200	14.704	82.588	69.810	137.364	182.914	-7.688
5300	14.711	82.868	70.053	137.681	183.792	-7.579
5400	14.718	83.143	70.293	137.996	184.653	-7.473
5500	14.724	83.413	70.529	138.278	185.517	-7.372
5600	14.730	83.678	70.762	138.555	186.368	-7.273
5700	14.736	83.939	70.991	138.822	187.228	-7.179
5800	14.742	84.196	71.216	139.074	188.075	-7.087
5900	14.747	84.449	71.437	139.316	188.914	-6.998
6000	14.752	84.696	71.657	139.539	189.754	-6.912

June 30, 1968

BERYLLIUM MONOHYDROXIDE UNIPOSITIVE ION (BeOH⁺)

(IDEAL GAS)

GFW = 26.01902

ΔH_f^o = [194 ± 30] kcal/mol

ΔH_f^o_{298.15} = [194 ± 30] kcal/mol

Point Group [C_{∞v}]

S_{298.15}^o = [48.0] gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
[1300] (1)
[1100] (2)
[3500] (1)

O-H = [0.96] Å

Bond Distance: Be-O = [1.4] Å
Bond Angle: Be-O-H = [180°]
Rotational Constant: B₀ = [1.2602] cm⁻¹
σ = 1

Heat of Formation

The ionization potential (IP) of BeOH(g) is estimated as 9.5 ± 1 eV by comparison with the values IP(BeI, g) = 9.1 ± 0.5, IP(NgF, g) = 7.8 ± 0.3 (1) and IP(MgOH, g) = 8.5 eV. (JANAF values). Based on IP(BeOH, g) = 9.5 eV or 219 kcal/mol and ΔH_f^o(BeOH, g) = -25 ± 10 kcal/mol, we derive the heat of formation at 298°K for BeOH(g) as 194 ± 30 kcal/mol, which is tentatively adopted.

Heat Capacity and Entropy

The BeOH⁺(g) molecule has eight valence electrons. Based on the criterion given by Walsh (2) that ABH molecules (H = hydrogen atom) containing ten or less valence electrons will be linear in their ground state, we assume that the structure of BeOH⁺(g) is linear. The vibrational frequencies are estimated by comparison with those for BeOH(g) and LiOH(g). The Be-O and O-H bond distances are assumed to be the same as those in BeOH and H₂O molecules, respectively. The ground state quantum weight of BeOH⁺(g) is assumed to be the same as that of the isoelectronic molecule LiOH(g). The moment of inertia is 2.221 × 10⁻⁴⁰ g cm². The enthalpy at 0°K is -2.11 kcal/mol.

References

1. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 6628, 1 January 1965.
2. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

BeHO⁺

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔF ₂₉₈ kcal. mole ⁻¹	Log K _p
0	6.900	INFINITE	0.000	INFINITE	INFINITE
100	33.700	47.616	30.331	29.413	-64.276
200	6.980	38.524	42.002	30.286	-31.128
298	7.259	41.350	46.966	30.000	-27.656
300	7.268	41.395	47.013	29.993	-27.641
400	7.593	43.571	41.452	29.618	-20.136
500	8.005	45.435	42.218	29.253	-14.704
600	9.667	47.117	42.897	28.934	-9.366
700	10.439	48.657	43.612	28.668	-5.201
800	11.068	50.085	44.361	28.444	-3.688
900	11.468	51.415	45.131	28.254	-2.863
1000	12.102	52.656	45.754	28.083	-2.509
1100	12.477	53.868	46.439	27.921	-2.348
1200	12.699	54.957	47.106	27.769	-2.241
1300	12.865	55.952	47.758	27.625	-2.166
1400	13.264	56.977	48.374	27.425	-2.113
1500	13.447	57.858	48.978	27.236	-2.086
1600	13.603	58.771	49.563	27.044	-2.052
1700	13.745	59.618	50.127	26.850	-2.018
1800	13.875	60.398	50.678	26.654	-1.987
1900	13.946	61.150	51.209	26.456	-1.955
2000	14.034	61.888	51.723	26.254	-1.929
2100	14.109	62.544	52.222	26.046	-1.903
2200	14.181	63.213	52.700	25.832	-1.876
2300	14.233	63.853	53.177	25.610	-1.848
2400	14.285	64.440	53.634	25.396	-1.820
2500	14.331	65.024	54.078	25.176	-1.792
2600	14.372	65.597	54.509	24.951	-1.764
2700	14.402	66.155	54.939	24.721	-1.736
2800	14.422	66.655	55.359	24.486	-1.708
2900	14.472	67.162	55.738	24.243	-1.680
3000	14.500	67.653	56.127	24.000	-1.652
3100	14.524	68.129	56.507	23.751	-1.624
3200	14.545	68.599	56.879	23.500	-1.596
3300	14.568	69.059	57.239	23.246	-1.568
3400	14.587	69.474	57.593	23.000	-1.540
3500	14.604	69.897	57.938	22.746	-1.512
3600	14.620	70.309	58.274	22.491	-1.484
3700	14.635	70.709	58.607	22.236	-1.456
3800	14.649	71.100	58.930	21.980	-1.428
3900	14.661	71.481	59.247	21.721	-1.400
4000	14.673	71.852	59.556	21.461	-1.372
4100	14.684	72.218	59.862	21.200	-1.344
4200	14.694	72.576	60.164	20.936	-1.316
4300	14.704	72.914	60.453	20.670	-1.288
4400	14.713	73.252	60.740	20.400	-1.260
4500	14.721	73.583	61.022	20.126	-1.232
4600	14.729	73.907	61.298	19.850	-1.204
4700	14.736	74.224	61.570	19.570	-1.176
4800	14.743	74.534	61.837	19.286	-1.148
4900	14.749	74.838	62.099	19.000	-1.120
5000	14.755	75.136	62.357	18.710	-1.092
5100	14.761	75.428	62.610	18.416	-1.064
5200	14.766	75.715	62.860	18.120	-1.036
5300	14.771	75.996	63.105	17.824	-1.008
5400	14.776	76.272	63.346	17.526	-0.980
5500	14.781	76.544	63.584	17.228	-0.952
5600	14.785	76.810	63.817	16.928	-0.924
5700	14.789	77.072	64.046	16.626	-0.896
5800	14.793	77.329	64.274	16.320	-0.868
5900	14.797	77.582	64.498	16.016	-0.840
6000	14.800	77.830	64.718	15.710	-0.812

December 31, 1960.

Beryllium Dihydride (BeH₂)

(Ideal Gas)

Mol. Wt. = 11.029

ΔH_f⁰ 298.15 = [30] kcal. mole⁻¹

S_{298.15}⁰ = 41.4 cal. deg.⁻¹ mole⁻¹

Point Group [D_{∞h}]

Ground State Multiplicity = 1

Vibrational Levels and Multiplicities

Q, cm. ⁻¹
[2200] (1)
[1500] (2)
[1300] (1)

Moment of Inertia: I = [6.01 X 10⁻⁴⁰] g. cm.² σ = 2.

Heat of Formation. Estimated by C. J. O'Brien and J. R. Perrin, Marquardt Corp., Van Nuys, Calif., and J. Perrine, Olin Mathieson Chemical Corp., New York 22, N. Y., "Estimation of the Heats of Formation of Gaseous Combustion Product Molecules", October, 1959.

Heat Capacities and Entropies. Molecular and spectroscopic parameters estimated.

Beryllium Dihydroxide, Alpha (α -Be(OH)₂)
(Crystal)

GFW = 43.02694

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^c	Log K _p
0							
100							
200							
298	15.630	11.800	11.800	.000	-215.750	-194.673	142.699
300	15.704	11.897	11.800	.029	-215.754	-194.583	141.724
400	19.330	16.931	17.462	1.789	-215.639	-197.452	105.419
500	22.136	21.358	13.825	3.867	-215.694	-180.367	76.839
600	24.253	25.784	15.472	6.188	-215.370	-173.330	63.135
700	26.174	29.669	17.226	8.710	-214.900	-166.359	51.939
800	27.976	33.283	19.010	11.418	-214.291	-159.466	43.564



BERYLLIUM DIHYDROXIDE, ALPHA (α -Be(OH)₂)
(CRYSTAL)

OPW = 43.02694

ΔH_f^o = Unknown

ΔH_f^o_{298.15} = -215.75 ± 0.5 kcal/mol

S^o_{298.15} = [11.8 ± 2] gibbs/mol

Td = [407]°K

Heat of Formation.

The heat of formation is based on ΔH_f^o_{298.15} = -79.16 ± 0.5 kcal/mol for the reaction Be(c) + 2H₂O(l) = Be(OH)₂(_{a,c}) + H₂(g). The heat of this reaction is obtained by combination of the calorimetric heats of solution for pure beryllium metal and α-Be(OH)₂ in aqueous HP, measured by I. J. Bear and A. G. Turnbull, J. Phys. Chem. **69**, 2828-33 (1965).

Heat Capacity and Entropy.

The heat capacity was assumed the same as that of the beta phase. The entropy is calculated from the value of ΔG^o_{298.15} = -0.50 kcal/mol for the change α-Be(OH)₂ → β-Be(OH)₂ which is obtained from the solubilities in concentrated alkali measured by R. Fricke and H. Humme, Z. Anorg. Allgem. Chem. **178**, 400 (1929). This is combined with the ΔH_f^o_{298.15} difference and gives a change in entropy, ΔS^o_{298.15} = -0.8 eu and an entropy of α-Be(OH)₂, S^o_{298.15} = 11.8 ± 2 eu.

Decomposition Data.

Td is calculated as the temperature at which ΔG_f^o equals zero for Be(OH)₂(_{a,c}) = BeO(c) + H₂O(g).



T, °K	C _p	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log K _p
0							
100							
200							
298	15.430	11.000	11.000	.000	- 216.500	- 195.185	143.074
300	15.704	11.097	11.000	.029	- 216.504	- 195.053	142.096
400	19.330	16.131	11.662	1.788	- 216.589	- 187.882	102.654
500	22.130	20.758	13.025	3.867	- 216.444	- 180.717	78.992
600	24.253	24.984	14.672	6.188	- 216.120	- 173.600	61.284
700	25.774	28.836	16.516	8.716	- 215.636	- 166.488	48.599
800	27.274	32.483	18.210	11.418	- 215.041	- 159.376	43.594
900	29.568	35.877	19.986	14.302	- 214.300	- 152.684	37.077
1000	31.298	39.089	21.737	17.352	- 213.435	- 145.683	31.883

BERYLLIUM DIHYDROXIDE, BETA (β -Be(OH)₂) (CRYSTAL)
OFW = 43.02694
 $\Delta H_f^\circ =$ Unknown
 $\Delta H_f^\circ_{298.15} = -216.50 \pm 0.5$ kcal/mol
 $S^\circ_{298.15} = [11.0 \pm 2]$ gibbs/mol
Td = [417] °K

Heat of Formation.

The heat of formation is based on $\Delta H_f^\circ_{298.15} = -79.89 \pm 0.5$ kcal/mol for the reaction $\text{Be}(c) + 2\text{H}_2\text{O}(l) = \text{Be}(\text{OH})_2(\beta, c) + \text{H}_2(g)$. The heat of this reaction is obtained by combination of the calorimetric heats of solution measured by Bear and Turnbull for pure beryllium metal and β -Be(OH)₂ in aqueous HF. Third law analyses of two studies of the decomposition pressure of water vapor over the β -phase are in good agreement with the selected heat of formation, as summarized below. Fricke and Severin observed a decomposition temperature of 105°C at a pressure of 100 mm, while Bear and Lecocq found 223°C for equilibrium with saturated water vapor at 24.2 atm. We have reduced the latter data to a standard state value of $\Delta G^\circ_{196.15} = -3028$ cal/mol for the decomposition reaction given below.

Source	Method	Reaction	T, °K	$\Delta H^\circ_{298.15}$ kcal/mol	$\Delta H^\circ_{298.15}$ kcal/mol
1 Bear & Turnbull	Calorimetric	$\text{Be}(c) + 2\text{H}_2\text{O}(l) \rightarrow \text{Be}(\text{OH})_2(\beta, c) + \text{H}_2(g)$	294	-79.89	-216.50 ± 0.5
2 Fricke & Severin	Kp	$\text{Be}(\text{OH})_2(\beta, c) \rightarrow \text{BeO}(c) + \text{H}_2\text{O}(g)$	378	15.68	-216.58
3 Bear & Lecocq	Kp	"	496	15.44	-216.34

Sources.

1. I. J. Bear and A. G. Turnbull, J. Phys. Chem. **69**, 2828-33 (1965).
2. R. Fricke and H. Severin, Z. Anorg. Allgem. Chem. **205**, 287 (1932).
3. A. Bear and A. Lecocq, Comm. Energie At. (France), Rappt. CEA-R2611, 17 pp. (1964).

Heat Capacity and Entropy.

The heat capacity is estimated from that for $\text{Mg}(\text{OH})_2$ by subtracting the values for MgO and adding those for BeO.

The entropy is estimated by extrapolation to beryllium of the differences in S°_{298} between the chlorides and hydroxides of magnesium and calcium. Entropies of $\text{Mg}(\text{OH})_2$, MgCl_2 and BeCl_2 are taken from the JANAP tables, while those of $\text{Ca}(\text{OH})_2$ and CaCl_2 are taken to be 19.9 ± 0.1 and 25.0 ± 1.0 eu, respectively. [Recent low temperature data for SrCl_2 and BaCl_2 suggest that the CaCl_2 extrapolation should be $S^\circ_{50} = 2.4 \pm 1.0$ eu rather than the original value of $S^\circ_{50} = 4.59$ eu used by K. K. Kelley and G. E. Moore, J. Am. Chem. Soc. **65**, 782 (1943)]. Confirmation of the adopted entropy is obtained from the good agreement between the calorimetric heat of formation and the third law values derived from the equilibrium data.

Decomposition Data.

Td is calculated as the temperature at which ΔG_r° equals zero for $\text{Be}(\text{OH})_2(\beta, c) = \text{BeO}(c) + \text{H}_2\text{O}(g)$.

Beryllium Dihydroxide (Be(OH)₂)

GFW = 43.02694

(IDEAL GAS)

BEYLLIUM DIHYDROXIDE (Be(OH)₂)

OPW = 43.02694

BeH₂O₂

T, °K	Cp ^a	gibbs/mol S ^b - (G ^c - H ^c)/T	H ^c - H ^c ₂₉₈	ΔH ^c kcal/mol	ΔG ^c	Log Kp
0	0.000	INFINITE	-	-	-	INFINITE
100	6.576	47.684	2.989	-154.822	-154.822	335.014
200	11.072	54.378	2.182	-155.478	-155.478	165.727
298	13.359	59.238	1.802	-155.935	-156.461	107.562
300	13.398	59.320	1.825	-156.408	-156.408	108.655
400	15.284	64.444	1.463	-156.814	-157.032	80.335
500	16.751	67.019	1.068	-157.143	-157.447	61.181
600	17.899	68.178	8.802	-157.426	-157.426	51.728
700	18.665	68.813	8.563	-157.796	-157.796	43.374
800	19.095	69.256	10.557	-157.945	-157.945	32.581
900	20.212	77.925	12.614	-158.073	-158.073	28.744
1000	20.852	80.091	18.725	-158.101	-158.101	25.603
1100	21.360	82.103	19.085	-158.315	-158.315	20.774
1200	21.907	83.752	21.322	-158.532	-158.532	18.641
1300	22.512	87.400	23.592	-158.659	-158.659	17.211
1400	22.846	89.666	25.890	-161.555	-161.555	15.755
1500	23.114	90.489	28.900	-161.632	-161.632	13.302
1600	23.521	91.198	30.559	-161.670	-161.670	12.266
1700	23.748	92.477	32.225	-161.710	-161.710	11.339
1800	23.914	94.700	37.707	-161.753	-161.753	10.497
1900	24.063	96.800	40.883	-161.808	-161.808	9.727
2000	24.114	98.071	44.983	-161.858	-161.858	9.033
2100	24.134	100.108	47.430	-162.058	-162.058	8.338
2200	24.159	101.107	49.886	-232.108	-232.108	7.703
2300	24.179	102.070	52.321	-232.160	-232.160	7.257
2400	24.198	102.900	54.821	-232.209	-232.209	6.198
2500	24.214	103.612	57.302	-232.243	-232.243	5.570
2600	24.228	104.270	59.788	-232.266	-232.266	4.984
2700	24.240	104.889	62.279	-232.281	-232.281	4.437
2800	24.250	105.467	64.771	-232.292	-232.292	3.942
2900	24.258	106.004	67.264	-232.300	-232.300	3.490
3000	24.264	106.497	69.761	-232.306	-232.306	3.083
3100	24.269	106.949	72.259	-232.311	-232.311	2.724
3200	24.273	107.366	74.766	-232.315	-232.315	2.406
3300	24.276	107.748	77.284	-232.318	-232.318	2.120
3400	24.278	108.097	79.811	-232.320	-232.320	1.869
3500	24.279	108.415	82.346	-232.321	-232.321	1.649
3600	24.280	108.699	84.889	-232.322	-232.322	1.457
3700	24.281	108.950	87.430	-232.322	-232.322	1.292
3800	24.281	109.175	89.969	-232.322	-232.322	1.151
3900	24.281	109.377	92.509	-232.322	-232.322	1.032
4000	24.281	109.552	95.052	-232.322	-232.322	0.932
4100	24.281	109.701	97.599	-232.322	-232.322	0.848
4200	24.281	109.828	100.142	-232.322	-232.322	0.778
4300	24.281	109.936	102.681	-232.322	-232.322	0.720
4400	24.281	110.027	105.216	-232.322	-232.322	0.672
4500	24.281	110.102	107.748	-232.322	-232.322	0.633
4600	24.281	110.163	110.279	-232.322	-232.322	0.602
4700	24.281	110.211	112.806	-232.322	-232.322	0.577
4800	24.281	110.248	115.333	-232.322	-232.322	0.556
4900	24.281	110.275	117.859	-232.322	-232.322	0.538
5000	24.281	110.294	120.386	-232.322	-232.322	0.522
5100	24.281	110.306	122.913	-232.322	-232.322	0.508
5200	24.281	110.313	125.440	-232.322	-232.322	0.495
5300	24.281	110.317	127.967	-232.322	-232.322	0.483
5400	24.281	110.319	130.494	-232.322	-232.322	0.472
5500	24.281	110.320	133.021	-232.322	-232.322	0.462
5600	24.281	110.320	135.548	-232.322	-232.322	0.453
5700	24.281	110.320	138.075	-232.322	-232.322	0.445
5800	24.281	110.320	140.602	-232.322	-232.322	0.438
5900	24.281	110.320	143.129	-232.322	-232.322	0.432
6000	24.281	110.320	145.656	-232.322	-232.322	0.427

Dec. 31, 1960; Sept. 30, 1965; Dec. 31, 1966; Mar. 31, 1967

Point Group [C₂]

S^o 298.15 = [59.2] gibbs/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω _e , cm ⁻¹	ω _e , cm ⁻¹	ω _e , cm ⁻¹
[3200] (1)	[649] (1)	[1200] (1)
[1000] (1)	[750] (1)	[1600] (1)
[360] (1)	[360] (1)	[3300] (1)

Bond Distances: Be-O = [1.35] Å

Bond Angles: Be-O-H = [100°]

Angle between Be-O-H planes = [95°]

Product of the Moments of Inertia: I_AI_BI_C = [32.26] x 10⁻¹¹⁷ g³cm⁶

Heat of Formation.

The equilibrium reaction (A) BeO(c) + H₂O(g) → Be(OH)₂(g) has been studied by several investigators; all of them inferred that Be(OH)₂(g) was the major product, but there has been no direct proof of this. D. P. Hildenbrand, L. P. Theard and F. Ju, Aeronautics, 3rd Quarterly Technical Report No. U-2231, Contract AF 04(611)-8523, 31 July 1963, have examined the BeO-H₂O system at 2300°C mass-spectroscopically and report only BeOH and Be(OH)₂. They report a maximum value of the equilibrium constant for reaction (B) BeO(g) + H₂O(g) → Be(OH)₂(g) of 3.5 x 10⁻¹ atm⁻¹ at 2327°K; this yields ΔH^o 298.15 (Be(OH)₂, g) ≥ -157.7 ± 10 kcal/mol using JANAF functions.

L. I. Grossweiner and R. L. Seifert, J. Am. Chem. Soc. 74, 2701 (1952); W. A. Young, J. Phys. Chem. 54, 1003 (1950); and W. I. Stuart and O. H. Price, J. Nucl. Mater. 14, 417 (1964), have all studied reaction (A) under similar conditions. Each of these investigators varied and H₂O(g) flow rate without detectable change of K_p values. However, Grossweiner and Seifert used a considerably larger flow rate than the other investigators, and the reaction that they studied may not have been quite at equilibrium. The residence times in all cases were quite comparable. A second and third law analysis of the above data are shown below.

J. Blauer, M. A. Greenbaum and M. Farber, J. Phys. Chem. 70, 973 (1966), have also studied reaction (A) using the molecular flow effusion technique. They obtained a large variation of K_p with surface area, although the sample area and size were comparable to that in the earlier investigations. They operated at 300μ pressure, which is at the upper limits of the molecular flow regime. Also encountered was an unexpected variation of the blank experiments with sample size. All the samples investigated were relatively coarse with surface areas <60 cm²/g; it seems likely that surface area effects would have been found in the three earlier investigations with up to threefold variation in sample weights. We conclude that the variation observed by Blauer et al. is not wholly caused by sample size. A second and third law analysis of the data are shown below.

O.R.B. Elliott, UCRL 1831 (1952), has also investigated reaction (A), but details of the sample are not available and the results show considerable scatter.

A. Baur and A. Lecoq, Comm. Energie At. (France), Rappt. CEA-R2611, Direction des Matériaux et Combustibles Nucleaires, Nov. 1964, cite the results of Morize, Roudier and Elison, DM/948, in equation form.

Reference	No. of Points	Range, °K	ΔH ^o 298 Kcal/mole	3rd law	ΔH ^o 298.15 ^o Kcal/mole	drift eu
Stuart	15	1338-1653	40.6 ± 0.9	44.53	-156.4	2.6 ± 0.6
Young	7	1576-1839	43.9 ± 1.5	44.51	-156.4	0.25 ± 0.9
Grossweiner	24	1472-1873	43.7 ± 1.1	45.22	-155.7	0.7 ± 0.7
Blauer	11	1673	39.6 ± 4.4	44.62	-156.3	-182.7
Elliott	6	1567-1808	47.0	40.6	-153.9	-19 ± 44
Morize	Equation	?	50.8	40.6	-160.3	-6.2

*calculated using the 3rd law ΔH^o 298^o

ΔH^o 298 (Be(OH)₂, g) = -156.4 ± 5 kcal/mol is adopted, with a large uncertainty to cover errors due to the functions as well as the experimental uncertainty.

Heat Capacity and Entropy.

The structure is that assumed by R. L. Altman, J. Chem. Eng. Data 8, 534 (1965). One vibrational frequency was reported by M. Farber, M. A. Greenbaum, M. A. Frisch et al., Rocket Power, Inc., Final Report AFRL-TR-66-220, Contract AF 04(611)-10929, September 1966. The remaining frequencies were estimated and adjusted to give reasonable agreement between the second and third law heats of reaction. The three principal moments of inertia are I_A = 2.865 x 10⁻⁴⁰, I_B = 10.60 x 10⁻³⁹, and I_C = 10.62 x 10⁻³⁹ g cm².

BeH₂O₂

Ground State Configuration $2\sum^+$
 $\Delta H_f^0 = [56.70] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = [24.6 \pm 5.0] \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = [24.7 \pm 5.0] \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$$\frac{E_i \text{ cm.}^{-1}}{0} \quad g_i \quad [2]$$

$$\omega_e = [657] \text{ cm.}^{-1} \quad \omega_e x_e = [3.90] \text{ cm.}^{-1} \quad \sigma^- = 1$$

$$E_e = [0.41894] \text{ cm.}^{-1} \quad \alpha_e = [0.00249] \text{ cm.}^{-1}$$

$$r_e = [2.19] \text{ \AA}$$

Heat of Formation.

The dissociation energy was estimated from the experimental energies for BeF(g) , BeCl(g) , and the gaseous lithium halides. The resulting value, $79.1 \text{ kcal. mole}^{-1}$, was combined with JANAF heats of formation for Be(g) and I(g) in arriving at ΔH_f^0 298.15.

Heat Capacity and Entropy.

The vibrational frequency was estimated from those of BeF(g) , BeCl(g) , and the gaseous lithium halides. The ground term was assumed to be similar to that of BaCl(g) and BeF(g) , tabulated by G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950. A correlation of the interatomic distances for the alkali halides, BeF(g) , and BeCl(g) was employed in deriving r_e .

BeI₂Beryllium Diiodide (BeI₂)
(Crystal) Mol. Wt. = 262.821

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0							
100	17.000	28.800	28.800	0.000	-50.600	-50.231	36.816
200	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
300	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
400	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
500	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
600	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
700	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
800	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
900	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
1000	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
1100	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
1200	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
1300	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800
1400	17.041	28.905	28.800	0.031	-50.600	-50.228	36.800

BERYLLIUM DIIODIDE (BeI₂) (CRYSTAL)

MOL. WT. = 262.821

$$\Delta H_f^0 = 0 = \text{Unknown}$$

$$\Delta H_f^0 298.15 = [-50.6 \pm 8] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [5] \text{ kcal. mole}^{-1}$$

$$\Delta H_g^0 298.15 = 30.3 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = [28.8 \pm 2] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$T_m = 753^\circ \text{K.}$$

Heat of Formation.

The heat of formation was estimated from the work of W. Biltz and C. Messerknecht, Z. anorg. Chem. 148, 157 (1925) and Biltz, Klatte and Rahlfs, Z. anorg. Chem. 166, 339 (1927) as reported in N.B.S. Circular 500, Washington 1952. They measured the heat of solution of BeI₂ in aq. HCl to an unknown concentration. This value was apparently adjusted and used with Be⁺⁺ and 2I⁻ to obtain ΔH_f⁰ of the crystal. However Be⁺⁺ was estimated by the Bureau and a total uncertainty of 8 kcal. is thought to be realistic.

Heat Capacity and Entropy.

The heat capacity was estimated graphically by comparison with BeCl₂ and BeF₂. The entropy was also estimated by comparing with α-BeCl₂ and BeF₂ and using additive entropy values for the halide ions. K. N. Semenov and T. N. Naumova, Zhur. Strukt. Khim. 4, 67 (1963) have reported that between 563 and 643°C BeI₂ exists in a β form and above 643°C a β form and an unknown form also exist. No allowance has been made for these modifications in the present table.

Melting Data.

The melting point was reported by O. Rahlfs and W. Fischer, Z. anorg. Chem. 211, 351 (1933). The heat of melting was estimated by comparison with the heats of transition and melting for BeCl₂ and BeF₂.

Sublimation Data.

The heat of sublimation was obtained from a third law analysis of the vapor pressure data of Rahlfs and Fischer, loc. cit. from 578-703°K. This gave ΔH_g⁰ 298 = 30.34 kcal. mole⁻¹ with a drift of 3.2 ± 1.1 cal. mole⁻¹ deg.⁻¹. A second law analysis gave ΔH_g⁰ 298 = 28.1 ± 0.7 kcal. mole⁻¹. No attempt was made to change the functions to eliminate the drift, since a correlation with BeCl₂, BeBr₂ and BeI₂ indicated that the drift was probably due to the data rather than the functions.

BeI₂

T, °K.	C _p	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0							
100							
200							
298	17.000	32.397	32.397	0.000	- 47.446	- 48.149	35.293
300	17.041	32.502	32.397	0.031	- 47.446	- 48.153	35.078
400	18.500	37.636	33.087	1.820	- 51.268	- 48.258	26.365
500	21.000	41.850	34.432	3.709	- 61.406	- 48.550	20.346
600	27.000	46.772	36.091	6.409	- 60.145	- 43.699	15.917
700	27.000	50.935	37.921	9.109	- 58.916	- 41.056	12.618
800	27.000	54.540	39.778	11.809	- 57.712	- 38.586	10.541
900	27.000	57.720	41.599	14.509	- 56.533	- 36.267	8.806
1000	27.000	60.585	43.356	17.209	- 55.378	- 34.077	7.447
1100	27.000	63.138	45.039	19.909	- 54.240	- 32.001	6.358
1200	27.000	65.487	46.646	22.609	- 53.147	- 30.028	5.469
1300	27.000	67.649	48.180	25.309	- 52.068	- 28.145	4.731
1400	27.000	69.649	49.643	28.009	- 51.016	- 26.344	4.112
1500	27.000	71.512	51.040	30.709	- 49.989	- 24.619	3.587
1600	27.000	73.255	52.374	33.409	- 51.742	- 22.881	3.125
1700	27.000	74.892	53.651	36.109	- 50.651	- 21.112	2.714
1800	27.000	76.435	54.874	38.809	- 49.566	- 19.405	2.356
1900	27.000	77.895	56.048	41.509	- 48.488	- 17.759	2.053
2000	27.000	79.280	57.175	44.209	- 47.416	- 16.172	1.767

MOL. WT. = 262.821

(LIQUID)

BERYLLIUM DIODIDE (BeI₂)

$$\Delta H_f^\circ 298.15 = [-47.45 \pm 3] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = [5] \text{ kcal. mole}^{-1}$$

$$\Delta F_v^\circ = [23] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = [32.4] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$T_m^\circ = 753^\circ \text{K.}$$

$$T_b^\circ = [755]^\circ \text{K.}$$

Heat of Formation.

The heat of formation was obtained from that of the crystal by adding ΔH_m° and the difference between $H_{755}^\circ - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with the measured value for BeCl₂. A glass transition was assumed at 500°K. below which the heat capacity was that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See BeI₂(c) table for details.

Vaporization Data.

The temperature and heat of vaporization were calculated from the cross over point BeI₂(l) and (g).

Beryllium Diodide (BeI₂)
(Ideal Gas) Mol. Wt. = 262.821

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0	-0.000	INFINITE	-3.340	-20.018	-20.018	INFINITE
100	11.050	57.007	81.746	-20.776	-20.776	12.453
200	12.611	65.254	71.641	-20.776	-20.776	23.945
298	13.364	70.441	70.441	-20.010	-32.346	23.709
300	13.376	70.524	70.441	-20.306	-32.421	23.617
400	14.116	77.572	71.990	-20.776	-36.266	19.814
500	14.690	82.397	74.110	-20.776	-38.183	16.689
600	14.990	85.338	75.445	-20.776	-38.785	14.127
700	15.150	87.000	76.550	-20.776	-39.382	12.295
800	15.275	88.469	77.462	-20.776	-39.973	10.920
900	15.375	89.765	78.199	-20.776	-40.559	9.849
1000	15.450	90.937	78.800	-20.776	-41.137	8.990
1100	15.500	91.990	79.269	-20.776	-41.707	8.286
1200	15.530	92.940	79.606	-20.776	-42.266	7.697
1300	15.550	93.790	79.815	-20.776	-42.813	7.197
1400	15.560	94.560	80.000	-20.776	-43.348	6.767
1500	15.560	95.260	80.166	-20.776	-43.873	6.392
1600	15.550	95.900	80.315	-20.776	-44.391	6.051
1700	15.530	96.480	80.450	-20.776	-44.900	5.737
1800	15.500	97.010	80.570	-20.776	-45.400	5.456
1900	15.460	97.490	80.680	-20.776	-45.890	5.204
2000	15.410	97.930	80.780	-20.776	-46.370	4.977
2100	15.350	98.340	80.870	-20.776	-46.840	4.770
2200	15.280	98.720	80.950	-20.776	-47.300	4.581
2300	15.200	99.070	81.020	-20.776	-47.750	4.408
2400	15.110	99.390	81.080	-20.776	-48.190	4.249
2500	15.010	99.690	81.130	-20.776	-48.620	4.102
2600	14.900	99.970	81.170	-20.776	-49.040	3.966
2700	14.780	100.230	81.200	-20.776	-49.450	3.839
2800	14.650	100.480	81.220	-20.776	-49.850	3.719
2900	14.510	100.710	81.240	-20.776	-50.240	3.604
3000	14.360	100.930	81.250	-20.776	-50.620	3.493
3100	14.200	101.140	81.260	-20.776	-50.990	3.386
3200	14.030	101.340	81.270	-20.776	-51.350	3.283
3300	13.850	101.530	81.280	-20.776	-51.700	3.184
3400	13.660	101.710	81.290	-20.776	-52.040	3.089
3500	13.460	101.880	81.300	-20.776	-52.370	2.998
3600	13.250	102.040	81.310	-20.776	-52.690	2.911
3700	13.030	102.190	81.320	-20.776	-53.000	2.828
3800	12.800	102.330	81.330	-20.776	-53.300	2.748
3900	12.560	102.460	81.340	-20.776	-53.590	2.671
4000	12.310	102.580	81.350	-20.776	-53.870	2.597
4100	12.050	102.690	81.360	-20.776	-54.140	2.526
4200	11.790	102.790	81.370	-20.776	-54.400	2.458
4300	11.520	102.880	81.380	-20.776	-54.650	2.393
4400	11.240	102.960	81.390	-20.776	-54.890	2.331
4500	10.960	103.030	81.400	-20.776	-55.120	2.272
4600	10.670	103.090	81.410	-20.776	-55.340	2.216
4700	10.370	103.140	81.420	-20.776	-55.550	2.163
4800	10.060	103.190	81.430	-20.776	-55.750	2.112
4900	9.740	103.230	81.440	-20.776	-55.940	2.063
5000	9.410	103.270	81.450	-20.776	-56.120	2.016
5100	9.070	103.300	81.460	-20.776	-56.290	1.972
5200	8.720	103.330	81.470	-20.776	-56.450	1.930
5300	8.360	103.360	81.480	-20.776	-56.600	1.889
5400	8.000	103.390	81.490	-20.776	-56.740	1.850
5500	7.630	103.420	81.500	-20.776	-56.870	1.812
5600	7.250	103.450	81.510	-20.776	-56.990	1.776
5700	6.870	103.480	81.520	-20.776	-57.100	1.741
5800	6.480	103.510	81.530	-20.776	-57.200	1.707
5900	6.090	103.540	81.540	-20.776	-57.290	1.674
6000	5.690	103.570	81.550	-20.776	-57.370	1.642

Dec. 31, 1961 June 30, 1965

BeI₂

MOL. WT. = 262.821

BERYLLIUM DIODIDE (BeI₂) (IDEAL GAS)

Point Group D_{∞h}
S°_{298.15} = [70.44 ± 2] cal. mole⁻¹ deg.⁻¹
ΔH°_f 0 = -20 ± 4 kcal. mole⁻¹
ΔH°_f 298.15 = [-20.3 ± 10] kcal. mole⁻¹
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹
[140](1)
[155](2)
[770](1)

Bond Distance: Be-I = 2.12 Å
Bond Angle: I-Be-I = [180°]
Rotational Constant: B₀ = 0.01478 cm.⁻¹
σ = 2

Heat of Formation.

The heat of formation was obtained from that of the crystal plus ΔH_g 298; see BeI₂ (c) table for details.

Heat Capacity and Entropy.

The linear structure was assumed by analogy with BeCl₂. The bond length was reported by P. A. Akishin, V. P. Spirodinov and G. A. Sobolev, Dokl. Akad. Nauk SSSR, 116, 1134 (1958) from electron diffraction measurements. The vibrational frequencies were estimated by assuming a set of force constants k₁ for the BeF₂, BeCl₂, BeBr₂ and BeI₂ series and also assuming k₁/k₁ = 50 as for BeF₂. The principal moment of inertia is 189.402 x 10⁻⁵⁹ g. cm.²

Beryllium Nitride (BeN)

(Ideal Gas) Mol. Wt. = 23.021

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	0.000	INFINITE	- 2.085	101.400	101.400	INFINITE
100	6.958	42.221	1.391	101.431	99.438	- 217.311
200	6.958	42.221	1.391	101.431	99.438	- 217.311
298	7.192	49.872	0.000	101.981	94.615	- 69.931
300	7.197	49.916	0.013	101.981	94.569	- 68.890
400	7.514	50.158	0.749	101.929	92.105	- 50.321
500	7.820	53.740	1.516	101.840	86.659	- 39.188
600	8.069	55.188	2.311	101.737	87.232	- 31.773
700	8.264	56.447	3.128	101.618	84.823	- 26.482
800	8.414	57.561	3.962	101.486	82.433	- 22.519
900	8.531	58.559	4.809	101.337	80.061	- 19.440
1000	8.624	59.463	5.667	101.168	77.705	- 16.992
1100	8.699	60.289	6.534	100.976	75.368	- 14.974
1200	8.760	61.048	7.407	100.760	73.050	- 13.303
1300	8.812	61.752	8.285	100.521	70.750	- 11.894
1400	8.856	62.406	9.169	100.258	68.469	- 10.688
1500	8.894	63.019	10.056	99.971	66.208	- 9.646
1600	8.927	63.594	10.947	99.605	64.046	- 8.748
1700	8.957	64.136	11.842	99.150	61.999	- 7.970
1800	8.984	64.649	12.739	98.605	59.965	- 7.280
1900	9.008	65.135	13.638	97.979	57.944	- 6.665
2000	9.031	65.598	14.540	97.266	55.935	- 6.112
2100	9.051	66.039	15.444	96.474	53.938	- 5.613
2200	9.071	66.460	16.351	95.510	51.952	- 5.161
2300	9.089	66.864	17.259	94.463	49.979	- 4.749
2400	9.106	67.251	18.168	93.330	48.017	- 4.372
2500	9.123	67.623	19.080	92.100	46.062	- 4.027
2600	9.139	67.981	19.993	90.763	44.122	- 3.709
2700	9.154	68.326	20.908	89.320	42.190	- 3.415
2800	9.169	68.660	21.825	87.775	40.263	- 3.141
2900	9.183	68.982	22.741	86.120	38.347	- 2.884
3000	9.197	69.293	23.660	84.355	36.435	- 2.646
3100	9.211	69.595	24.581	82.480	34.525	- 2.424
3200	9.224	69.888	25.502	80.500	32.615	- 2.215
3300	9.237	70.172	26.425	78.415	30.705	- 2.015
3400	9.250	70.448	27.350	76.225	28.795	- 1.825
3500	9.262	70.716	28.275	73.930	26.885	- 1.645
3600	9.275	70.977	29.202	71.530	24.975	- 1.475
3700	9.287	71.231	30.130	69.025	23.065	- 1.315
3800	9.299	71.479	31.060	66.415	21.155	- 1.165
3900	9.311	71.721	31.990	63.700	19.245	- 1.025
4000	9.323	71.957	32.922	60.880	17.335	- 0.895
4100	9.334	72.187	33.855	57.955	15.425	- 0.775
4200	9.346	72.412	34.789	54.925	13.515	- 0.665
4300	9.358	72.632	35.724	51.890	11.605	- 0.565
4400	9.369	72.847	36.660	48.845	9.695	- 0.475
4500	9.380	73.056	37.596	45.790	7.785	- 0.395
4600	9.392	73.264	38.536	42.725	5.875	- 0.325
4700	9.403	73.466	39.476	39.660	3.965	- 0.265
4800	9.414	73.665	40.417	36.595	2.055	- 0.215
4900	9.425	73.859	41.359	33.530	0.145	- 0.175
5000	9.436	74.049	42.302	30.465	- 1.775	- 0.145
5100	9.447	74.236	43.246	27.400	- 3.715	- 0.125
5200	9.458	74.420	44.191	24.335	- 5.655	- 0.115
5300	9.469	74.600	45.138	21.270	- 7.595	- 0.115
5400	9.480	74.777	46.085	18.205	- 9.535	- 0.125
5500	9.491	74.951	47.034	15.140	- 11.475	- 0.145
5600	9.501	75.122	47.983	12.075	- 13.415	- 0.175
5700	9.512	75.291	48.934	9.010	- 15.355	- 0.215
5800	9.523	75.456	49.886	5.945	- 17.295	- 0.265
5900	9.534	75.623	50.838	2.880	- 19.235	- 0.325
6000	9.545	75.789	51.792	18.774	- 21.174	- 0.395

June 30, 1963

$$\Delta H_f^0 = [101] \text{ kcal mole}^{-1}$$

$$\Delta H_f^0 = [102] \text{ kcal mole}^{-1}$$

Electronic Levels and Multiplicities

$$\frac{E_i, \text{ cm}^{-1}}{0}$$

$$\omega_e = [1194] \text{ cm}^{-1}$$

$$\sigma = 1$$

$$B_e = [1.655] \text{ cm}^{-1}$$

$$r_e = [1.406] \text{ \AA}$$

Heat of Formation

The heat of formation was estimated by J. S. Gordon, Astronomical International, Livingston, New Jersey, private communication, April 26, 1963.

Molecular Constants

The molecular constants were taken from J. S. Gordon, loc. cit.

Beryllium Oxide (BeO)

(Crystal) Mol. Wt. = 25.013

BeO

MOL. WT. = 25.013

BERYLLIUM OXIDE (BeO)

(CRYSTAL)

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	∞	INFINITE	-	-142.282	-	INFINITE
100	0.675	24.3	6.933	-142.282	-142.282	307.190
200	3.415	1.486	3.856	-142.630	-142.630	151.213
298	6.100	3.378	4.774	-142.913	-136.385	99.775
300	6.144	3.416	4.805	-143.102	-136.079	99.128
400	8.022	5.463	3.644	-143.181	-133.723	73.059
500	9.244	7.391	4.204	-143.184	-131.357	57.413
600	10.138	8.163	4.885	-143.130	-128.996	46.984
700	10.778	10.778	6.352	-142.916	-126.312	33.939
800	11.237	13.588	7.082	-142.621	-121.990	29.622
900	11.527	14.814	7.795	-142.711	-119.682	26.155
1000	11.730	15.940	8.485	-142.613	-117.384	23.321
1100	11.900	16.983	9.150	-142.452	-112.811	18.964
1200	12.070	17.955	9.791	-142.387	-110.534	17.254
1300	12.242	18.869	10.407	-142.332	-108.261	15.773
1400	12.418	19.732	11.000	-142.332	-105.912	14.466
1500	12.595	20.550	11.571	-144.190	-103.471	13.301
1600	12.770	21.326	12.125	-144.490	-101.405	12.242
1700	12.940	22.074	12.655	-144.791	-99.617	11.263
1800	13.117	22.788	13.170	-144.559	-98.043	10.351
1900	13.291	23.474	13.668	-144.379	-96.204	9.485
2000	13.465	24.136	14.151	-144.190	-93.799	8.686
2100	13.640	24.786	14.617	-142.936	-91.405	7.961
2200	13.815	25.422	15.074	-142.658	-89.043	7.308
2300	13.988	26.042	15.518	-142.384	-86.643	6.734
2400	14.159	26.659	15.950	-142.122	-84.283	6.237
2500	14.327	27.266	16.372	-141.865	-81.930	5.806
2600	14.491	27.864	16.786	-141.611	-79.586	5.442
2700	14.651	28.454	17.186	-141.361	-77.254	5.137
2800	14.810	29.037	17.576	-141.113	-74.932	4.885
2900	14.968	29.613	17.956	-140.868	-72.622	4.683
3000	15.125	30.183	18.327	-140.627	-70.331	4.437
3100	15.280	30.747	18.690	-140.390	-68.060	4.243
3200	15.434	31.306	19.044	-140.157	-65.810	4.094
3300	15.586	31.860	19.391	-139.928	-63.579	3.937
3400	15.736	32.410	19.731	-139.701	-61.366	3.771
3500	15.884	32.955	20.066	-139.478	-59.171	3.602
3600	16.030	33.500	20.400	-139.257	-56.992	3.428
3700	16.174	34.041	20.732	-139.038	-54.831	3.250
3800	16.316	34.578	21.062	-138.821	-52.686	3.068
3900	16.456	35.112	21.391	-138.606	-50.556	2.882
4000	16.594	35.642	21.718	-138.392	-48.440	2.692

$\Delta H_f^0 = -142.3 \pm 0.1 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = -143.1 \pm 0.1 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = 0.06 \pm 1.0 \text{ kcal. mole}^{-1}$
 $T_m = 2325^\circ\text{K.}$
 $\Delta H_m^0 = 15.1 \pm 0.4 \text{ kcal. mole}^{-1}$
 $\Delta H_m^{298.15} = 174.1 \pm 3.0 \text{ kcal. mole}^{-1}$

Heat of Formation.

L. A. Cosgrove and P. E. Snyder, J. Am. Chem. Soc. 75, 3102 (1953) have reviewed earlier determinations of the heat of formation and have made a very careful oxygen bomb calorimeter determination, their value is adopted here.

Heat Capacity and Entropy.

The high temperature enthalpy of BeO(c) has been reported by A. Magnua and H. Denz, Ann. Physik. [4] 81, 407 (1926) up to 1172°K; E. N. Rodigina and K. Z. Gornel'skii, Zhur. Fiz. Khim. 35, 1828 (1961) up to 1128°K; V. V. Kandyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Ponomarev, Doklady. Akad. Nauk. S.S.S.R. 131, 566 (1960) up to 2840°K; B. E. Walker, C. T. Ewing, and R. R. Miller, private communication, U. S. Naval Research Laboratory 18th April 1963 up to 1100°K; A. C. Victor and T. B. Douglas, J. Res. Natl. Bureau Standards 67A, 325 (1963) up to 1173°K. A high temperature phase transition has been reported by S. B. Austerman, Bull. Am. Physical Soc. 117 (1), 28 (1962) and has been confirmed using high temperature X-rays by T. W. Baker and P. J. Baldock, Nature 193, 1172 (1962). K. K. Kelley, J. Am. Chem. Soc. 81, 1217 (1959) has reported the low temperature heat capacities from 55.5 to 292.4°K. The heat capacity was assumed to follow the T^3 law below 55.5°K. and this gave $S_{55.5} = 0.045 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. The high temperature enthalpy data was smoothed using both 18 and 27 point groupings and was assumed to be discontinuous at 2325°K. The heat capacity obtained from the smoothed enthalpy was itself smoothed graphically so as to fit with the low temperature heat capacity. The data of Kandyba, et al., show no effect of the transition at 2325° and a value of 0.06 kcal. mole⁻¹ was adopted simply to provide a somewhat improved fit of the data above 2700°K. The data above 2700°K. were not included because of apparent premelting effects and the heat capacity curve from 2700 to 2820°K. is extrapolated.

Transition Data.

See heat capacity and entropy.

Melting Data.

Obtained from the enthalpy measurements of Kandyba, et al., loc. cit.

Heat of Sublimation.

The gas above BeO(c) is complex and the value given is for the reaction BeO(c) → BeO(g) and simply read from the respective tables.

$$\Delta H_f^{298.15} = 8.04 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{298.15} = -129.562 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 15.1 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$T_m = 2820^\circ\text{K.}$$

$$T_b = [4060]^\circ\text{K.}$$

Heat of Formation.

The heat of formation was obtained from that of the crystal by adding ΔH_m^0 and the difference between H_{298}^0 and H_{298}^0 for crystal and liquid.

Heat Capacity and Entropy.

The enthalpy of three points in the liquid phase was determined by V. V. Kandyba, P. B. Kantor, R. M. Krasovitskiy and E. N. Pomichov, Dokl. Akad. Nauk S.S.S.R. 131, 566 (1960). These values were used to obtain a heat capacity for the liquid which was assumed constant. At 1900°K. a glass transition was assumed below which the heat capacity was that of the solid. The entropy at 298°K. was obtained in a manner analogous to the heat of formation.

Melting Data.

See the table for BeO(c).

Vaporization Data.

The vapor composition over BeO(c) at 2300°K. is composed of Be(g), O(g), BeO(g), (BeO)₂(g), (BeO)₃(g), (BeO)₄(g), (BeO)₅(g), (BeO)₆(g) and other species and thus a boiling point becomes almost meaningless and the value given here is the point at which the total pressure reaches 1 atm.

Beryllium Oxide (BeO)

(Ideal Gas) Mol. Wt. = 25.013

BeO

BERYLLIUM OXIDE (BeO) (IDEAL GAS) MOL. WT. = 25.013

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞	INFINITE	-2.076	30.429	30.429	INFINITE
100	6.957	36.593	5.418	-1.781	28.886	-63.128
200	9.965	44.416	4.784	-0.687	26.916	-29.412
298	7.046	47.208	4.000	0.000	24.910	-18.259
300	7.049	47.252	4.013	0.013	31.000	-18.119
400	7.254	48.306	4.687	0.727	22.840	-12.678
500	7.510	50.952	4.821	1.465	20.835	-9.106
600	7.757	52.363	4.828	2.229	18.858	-6.969
700	7.969	53.555	4.945	3.022	16.859	-5.270
800	8.145	54.631	4.954	3.832	14.986	-4.094
900	8.287	55.599	5.040	4.643	13.068	-3.178
1000	8.402	56.478	5.100	5.478	11.213	-2.651
1100	8.497	57.284	5.135	6.323	9.361	-1.860
1200	8.575	58.021	5.157	7.177	7.511	-1.262
1300	8.640	58.715	5.169	8.038	5.725	-0.815
1400	8.695	59.358	5.197	8.905	3.939	-0.317
1500	8.741	59.959	5.244	9.776	2.176	-0.070
1600	8.782	60.525	5.267	10.653	0.435	-0.172
1700	8.817	61.063	5.281	11.536	-1.258	-0.312
1800	8.848	61.563	5.285	12.424	-2.958	-0.468
1900	8.876	62.042	5.281	13.302	-4.673	-0.609
2000	8.901	62.498	5.263	14.181	-6.403	-0.735
2100	8.924	62.933	5.231	15.062	-8.144	-0.850
2200	8.944	63.349	5.189	15.947	-9.897	-0.950
2300	8.963	63.747	5.141	16.837	-11.661	-1.042
2400	8.981	64.129	5.075	17.768	-13.436	-1.126
2500	8.997	64.496	5.002	18.667	-15.221	-1.202
2600	9.013	64.849	4.923	19.568	-17.016	-1.273
2700	9.027	65.189	4.839	20.500	-18.821	-1.340
2800	9.041	65.518	4.753	21.473	-20.636	-1.403
2900	9.054	65.835	4.658	22.478	-22.461	-1.461
3000	9.066	66.142	4.544	23.514	-24.306	-1.515
3100	9.078	66.440	4.420	24.591	-26.171	-1.565
3200	9.089	66.729	4.289	25.709	-28.056	-1.612
3300	9.100	67.008	4.157	26.869	-30.000	-1.656
3400	9.111	67.280	4.025	28.069	-32.000	-1.697
3500	9.122	67.544	3.892	29.311	-34.056	-1.735
3600	9.132	67.801	3.759	30.594	-36.169	-1.770
3700	9.141	68.052	3.627	31.919	-38.339	-1.802
3800	9.151	68.298	3.495	33.286	-40.566	-1.831
3900	9.161	68.533	3.364	34.694	-42.850	-1.857
4000	9.170	68.765	3.233	36.142	-45.191	-1.880
4100	9.179	68.992	3.102	37.639	-47.589	-1.900
4200	9.188	69.213	2.972	39.186	-50.044	-1.918
4300	9.197	69.430	2.842	40.783	-52.556	-1.934
4400	9.205	69.641	2.712	42.430	-55.125	-1.948
4500	9.214	69.848	2.582	44.127	-57.752	-1.960
4600	9.222	70.051	2.452	45.874	-60.437	-1.970
4700	9.231	70.250	2.322	47.671	-63.172	-1.979
4800	9.239	70.443	2.192	49.518	-65.957	-1.987
4900	9.247	70.634	2.062	51.415	-68.792	-1.994
5000	9.255	70.821	1.932	53.362	-71.677	-1.999
5100	9.263	71.004	1.802	55.359	-74.612	-2.003
5200	9.271	71.184	1.672	57.406	-77.597	-2.006
5300	9.279	71.361	1.542	59.503	-80.632	-2.008
5400	9.287	71.534	1.412	61.650	-83.717	-2.010
5500	9.295	71.705	1.282	63.847	-86.852	-2.012
5600	9.302	71.872	1.152	66.094	-90.037	-2.014
5700	9.309	72.039	1.022	68.391	-93.272	-2.016
5800	9.318	72.209	0.892	70.738	-96.557	-2.017
5900	9.325	72.356	0.762	73.135	-100.000	-2.018
6000	9.333	72.515	0.647	75.582	-103.600	-2.019

Ground State Configuration $1s^2 + s^2$
 $S^{\circ}_{298.15} = 47.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^{\circ}_f 0 = 30 \pm 3 \text{ kcal. mole}^{-1}$
 $\Delta H^{\circ}_f 298.15 = 31 \pm 3 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$\frac{\epsilon_i}{\epsilon_0} \text{ cm.}^{-1} \frac{g_i}{1}$

$\omega_e x_e = 11.8297 \text{ cm.}^{-1}$
 $\omega_e = 0.0190 \text{ cm.}^{-1}$
 $r_e = 1.3308 \text{ \AA}$

$\sigma = 1$

Heat of Formation.

W. A. Chupko, J. Berkowitz, and C. F. Giese, J. Chem. Phys. 30, 827 (1959) obtained a value of 106 ± 3 kcal. mole⁻¹ for D_0 from the reactions $\text{BeO}(g) \rightarrow \text{Be}(g) + \text{O}(g)$ and $\text{BeO}(g) + \text{O}(g) \rightarrow \text{Be}(g) + \text{O}_2(g)$. The reactions were followed mass spectrometrically at low electron energies in order to eliminate fragmentation of higher polymers. A Lagerqvist, Arkiv. Fysik 1, 473 (1954) had previously reported a value for $D_0 = 110 \pm 10$ kcal. mole⁻¹ based on the dissociation limit of the lowest $1\bar{1}\bar{1}$ state which was assumed to dissociate to $\text{Be}(\bar{1}s)$ and $\text{O}(\bar{1}D)$. The $\Delta H^{\circ}_{f 298} \text{ BeO}(g) = 31 \pm 3 \text{ kcal. mole}^{-1}$ from $D_0 = 106 \pm 3 \text{ kcal. mole}^{-1}$ was adopted.

Heat Capacity and Entropy.

The spectroscopic constants are from O. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York 1950. The ground state configuration has been confirmed by B. A. Thrush, Proc. Chem. Soc. (London), 339 (1960) using absorption spectroscopy.

BERYLLIUM SULFATE (α - BeSO₄) (CRYSTAL) $\Delta H_f^\circ = -284.4 \pm 0.8$ kcal/mol

OPW = 105.0738

$\Delta H_f^\circ = -284.4 \pm 0.8$ kcal/mol
 $\Delta H_f^\circ_{298.15} = -287.0 \pm 0.8$ kcal/mol
 $\Delta H^\circ_1 = [0.266]$ kcal/mol
 $\Delta H^\circ_2 = [4.673]$ kcal/mol

$S^\circ_{298.15} = 18.635$ gibbs/mol

$T^\circ_1 = 863^\circ\text{K}$

$T^\circ_2 = 908^\circ\text{K}$

Heat of Formation.

Bear et al. measured the heats of solution of Be(c) and BeSO₄(α) in concentrated HF and the heat of reaction of H₂SO₄ (aq) with BeSO₄ (aq HF). Combination of these yield reaction (a) below. Taylor et al. measured heats of solution of Be(c) and BeSO₄(α) in H₂SO₄ (aq) which yields reaction (b). Marchal measured the total vapor pressure of BeSO₄(c) in the temperature range 863-1103°K. Partial pressures of SO₃(g) were calculated from Marchal's data using JANAF values for the SO₃ - SO₂ equilibrium. Third law analysis of these data yields ΔH_f° for reaction (c) as given below. This was converted to ΔH_f° for α -BeSO₄ using JANAF heats of transition.

Author	Method	Reaction	T°K	ΔH_f° kcal/mol	ΔH_f° kcal/mol
1. Bear (1966)	Calorimetric	(a) Be(c) + H ₂ SO ₄ (109 H ₂ O) = H ₂ (g) + α -BeSO ₄	294	-74.47	-286.65 $\pm$ 0.5
2. Taylor (1966)	Calorimetric	(b) Be(c) + H ₂ SO ₄ (47.849 H ₂ O) = H ₂ (g) + α -BeSO ₄	298	-76.38	-287.55 $\pm$ 0.13
3. Marchal (1925)	Kp (973-1083°K)	(c) BeSO ₄ (γ)-BeO(c) + SO ₃ (g) = H ₂ (g) + α -BeSO ₄	298	+43.92	-286.55 $\pm$ 0.5

References: 1. I. J. Bear and A. G. Turnbull, J. Phys. Chem. **70**, 711-17 (1966).

2. A. R. Taylor, Jr., B. E. Lefson and D. P. Smith, U. S. Bureau of Mines, Report No. 6724, 1966.

3. G. Marchal, J. Chim. Phys. **22**, 502 (1925).

The adopted $\Delta H_f^\circ_{298.15} = -287.0 \pm 0.8$ is an average value of reactions (a) and (b). This value is for relatively finely divided crystals of BeSO₄ as was indicated by Bear et al.

Heat Capacity and Entropy.

Low temperature heat capacities (12-301°K) and high temperature enthalpies (366-864°K) were measured by A. R. Taylor, Jr., T. E. Gardner and D. P. Smith, U. S. Bureau of Mines, Report No. 6240, 1963. These data were joined smoothly at 298°K and extrapolated graphically above 864°K. The entropy was obtained from the heat capacities using $S^\circ_{12.56} = 0.034$ eu.

Transition Data.

I. I. Bosik, A. V. Novoselova and Yu. P. Simanov, Russ. J. Inorg. Chem. **5**, 1295 (1961), observed two endothermic effects at 863-863°K and 908-913°K on the heating and cooling curves of BeSO₄(c); thus we have adopted T₁($\alpha \rightarrow \beta$) = 863°K and T₂($\beta \rightarrow \gamma$) = 908°K. ΔH° ($\alpha \rightarrow \beta$) = 0.266 kcal/mol was obtained from the single enthalpy point at 863.9°K observed by Taylor, Gardner and Smith. ΔH° ($\beta \rightarrow \gamma$) = 4.673 kcal/mol was chosen in order to give good agreement with the equilibrium data of Marchal, loc. cit.



Beryllium Sulfate, Beta (β -BeSO₄)
(Crystal) GFW = 105.0738

OPW = 105.0738

(CRYSTAL)

BERYLLIUM SULFATE, BETA (β -BeSO₄)

$\Delta H_f^0 = \text{Unknown}$
 $\Delta H_{298.15}^0 = [-286.734] \text{ kcal/mol}$
 $\Delta H_1^0 = [0.266] \text{ kcal/mol}$
 $\Delta H_2^0 = [4.673] \text{ kcal/mol}$

$S_{298.15}^0 = [18.943] \text{ gibbs/mol}$
 $T_1 = 863^\circ\text{K}$
 $T_2 = 908^\circ\text{K}$

Heat of Formation.

The heat of formation was calculated from that of the alpha phase by adding ΔH_1^0 , since the heat capacities of both phases are assumed the same.

Heat Capacity and Entropy.

The heat capacity was assumed to be the same as that of alpha phase. The entropy was obtained in a manner analogous to that of the heat of formation.

Transition Data.

See alpha phase.

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	20.482	18.943	0.000	-286.734	-260.206	190.736
300	20.581	18.943	+038	-286.739	-260.041	189.440
400	24.828	25.611	2.322	-287.415	-251.093	137.191
500	27.810	31.487	4.961	-287.680	-241.976	105.767
600	30.310	36.778	7.866	-287.684	-232.831	84.808
700	32.980	41.668	11.099	-287.669	-223.680	69.596
800	35.800	46.235	14.467	-287.669	-215.470	58.973
900	38.730	50.620	18.193	-287.692	-207.409	49.880
1000	41.630	54.859	22.220	-287.692	-199.507	42.634
1100	43.759	58.935	26.497	-286.200	-184.889	36.734
1200	45.258	62.858	30.901	-282.871	-164.928	31.573
1300	46.258	66.478	35.526	-282.871	-144.928	27.227
1400	46.984	69.927	40.190	-281.118	-125.154	24.221
1500	47.480	73.186	44.915	-289.343	-185.505	21.200
1600	47.892	76.262	49.680	-280.319	-135.895	18.562
1700	47.972	79.162	54.484	-286.532	-116.290	16.237
1800	48.000	81.908	59.269	-286.532	-116.290	14.163
1900	48.000	84.504	64.069	-284.705	-107.437	12.358
2000	48.000	86.966	68.869	-282.864	-98.158	10.726
2100	48.000	89.308	73.669	-281.039	-88.947	9.250
2200	48.000	91.540	78.469	-279.233	-79.860	7.933
2300	48.000	93.674	83.269	-277.441	-70.839	6.731



T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ-H^\circ_{298})/T$	$H^\circ-H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
100							
200							
298	20.482	24.088	24.088	+000	- 282.061	- 257.067	188.435
300	20.481	24.215	24.088	+038	- 282.066	- 256.912	187.160
400	24.878	30.476	24.951	+222	- 282.072	- 256.762	185.262
500	27.810	36.632	28.711	+4.961	- 282.097	- 256.675	184.649
600	30.310	41.923	28.812	7.866	- 283.011	- 251.245	84.231
700	32.980	46.793	31.037	11.029	- 282.776	- 222.608	68.501
800	35.900	51.380	33.296	14.757	- 282.531	- 215.317	48.821
900	38.950	55.733	35.583	18.151	- 282.276	- 207.987	28.821
1000	41.690	60.004	37.785	22.220	- 282.019	- 195.528	4.737
1100	43.759	64.080	39.991	26.497	- 281.527	- 185.875	36.830
1200	45.222	67.953	42.162	30.950	- 280.903	- 176.340	32.116
1300	46.588	71.679	44.282	35.584	- 280.158	- 167.884	28.036
1400	47.802	75.272	46.358	40.150	- 280.195	- 159.584	24.091
1500	47.480	78.331	48.398	44.515	- 284.670	- 148.569	21.644
1600	47.802	81.407	50.356	49.680	- 285.646	- 139.454	18.048
1700	47.970	84.310	52.269	54.470	- 283.762	- 130.372	16.761
1800	48.000	87.049	54.128	58.889	- 281.849	- 121.311	15.411
1900	48.000	89.649	55.928	64.069	- 280.032	- 113.559	14.045
2000	48.000	92.111	57.676	68.869	- 278.191	- 103.775	11.340
2100	48.000	94.453	59.372	73.669	- 276.366	- 95.088	9.897
2200	48.000	96.685	61.018	78.469	- 274.560	- 86.506	8.594
2300	48.000	98.819	62.615	83.269	- 272.768	- 77.995	7.412

$\Delta H^\circ_f = \text{Unknown}$

$S^\circ_{298.15} = [24.088] \text{ gibbs/mol}$

$\Delta H^\circ_{298.15} = [282.06] \text{ kcal/mol}$

$\Delta H^\circ_1 = [0.286] \text{ kcal/mol}$

$\Delta H^\circ_2 = [4.673] \text{ kcal/mol}$

$T^*_1 = 863^\circ\text{K}$

$T^*_2 = 908^\circ\text{K}$

Heat of Formation.

The heat of formation was calculated from that of the beta phase by adding ΔH°_2 , since the heat capacities of both phases are assumed the same.

Heat Capacity and Entropy.

The heat capacity was assumed to be the same as that of alpha phase. The entropy was obtained in a manner analogous to that of the heat of formation.

Transition Data.

See alpha phase.

Beryllium Tungstate (BeWO₄)
(Crystal) GFW = 256.8598

T, K	Cp	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100	20.250	21.120	21.120	.000	-361.700	-335.769	246.125
200	21.250	21.120	21.120	.000	-361.701	-335.769	246.125
298	21.250	21.120	21.120	.000	-361.701	-335.769	246.125
300	21.350	21.268	21.268	.003	-361.424	-335.498	246.490
400	21.550	21.568	21.568	.003	-361.424	-335.498	246.490
500	21.750	21.868	21.868	.003	-361.424	-335.498	246.490
600	21.950	22.168	22.168	.003	-361.424	-335.498	246.490
700	31.390	40.370	26.286	8.451	-360.973	-309.682	112.801
800	32.820	45.318	28.658	11.662	-360.511	-301.169	94.029
900	34.150	49.788	31.928	15.085	-359.995	-286.155	79.051
1000	35.370	53.678	35.586	22.088	-358.744	-276.050	60.331
1100	37.700	61.213	37.756	25.802	-358.036	-267.816	53.210
1200	38.780	64.539	39.051	29.624	-357.272	-259.445	47.288
1300	39.830	67.685	41.672	33.527	-356.478	-251.308	41.603
1400	40.850	70.668	44.400	37.500	-355.646	-243.408	36.137
1500	41.930	73.533	47.110	41.735	-354.646	-235.534	31.081
1600	43.000	76.273	49.535	45.981	-353.412	-227.566	26.222
1700	44.050	78.911	51.903	50.334	-352.247	-219.526	21.631
1800	45.100	81.450	54.210	54.787	-351.291	-211.407	17.240
1900	46.150	83.898	56.469	59.354	-350.491	-203.703	13.047
2000	47.200	86.319	58.609	64.021	-351.297	-195.497	9.047

BERYLLIUM TUNGSTATE (BeWO₄)

(CRYSTAL)

OPW = 256.8598

ΔH° = Unknown

ΔH°_{298.15} = [-361.7 ± 15] kcal/mol

ΔH° = Unknown

S°_{298.15} = [21.12 ± 2] gibbs/molT_m = Unknown

Heat of Formation.

The heat of formation, ΔH°₂₉₈(BeWO₄, c) = -361.7 kcal/mol, is calculated from ΔH°₂₉₈ = -17.1 kcal/mol for BeO(c) + WO₃(c) → BeWO₄(c). The value of ΔH°₂₉₈ is assumed to be the same as that for MgO(c) + WO₃(c) → MgWO₄(c), using -143.7, -143.1, -201.5 and -362.3 kcal/mol for the heats of formation of MgO(c), BeO(c), WO₃(c) and MgWO₄(c), respectively.

Heat Capacity and Entropy.

Heat capacities are estimated by comparison with those of CaWO₄(c)¹, BeO(c)², and CaO(c)³.

The entropy, S°₂₉₈ = 21.12 eu, is calculated from ΔS°₂₉₈ = -0.4 eu for BeO(c) + WO₃(c) → BeWO₄(c). The value of ΔS°₂₉₈ is assumed to be the same as that for MgO(c) + WO₃(c) → MgWO₄(c), using 6.44, 3.38, 18.14 and 24.18 eu for MgO(c), BeO(c), WO₃(c) and MgWO₄(c), respectively.

References.

1. R. A. Yakovleva and T. N. Resnikina, Russ. J. Phys. Chem. (English transl.) **34**, 390 (1960).
2. JANAF BeO table (Sept. 30, 1965).
3. K. K. Kelley, U. S. Bur. Mines Bull. 594 (1960).

BERYLLIUM DICHLORIDE, DIMERIC (Be₂Cl₄) (IDEAL GAS)

MOL. WT. = 159.8364

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	∞.000	∞.000	- 6.048	- 179.724	- 179.724	INFINITE
100	18.636	65.446	113.638	- 4.810	- 179.017	- 177.598	387.064
200	24.953	90.550	116.286	- 4.000	- 178.000	- 176.286	126.836
280	27.574	91.150	116.500	- 3.851	- 177.993	- 176.003	126.027
300	27.610	91.321	91.151	- 3.851	- 178.993	- 171.055	93.456
400	29.054	99.481	92.764	- 3.851	- 178.993	- 169.173	73.942
500	29.890	106.062	94.379	- 3.851	- 178.993	- 167.350	60.949
600	30.406	111.561	94.707	- 3.851	- 178.993	- 165.729	51.678
700	30.793	116.275	95.251	- 3.851	- 178.993	- 164.344	44.731
800	30.973	120.366	96.042	- 3.851	- 178.993	- 163.249	39.329
900	31.136	124.054	103.933	- 3.851	- 178.993	- 162.403	35.011
1000	31.286	127.342	106.112	- 3.851	- 178.993	- 161.800	31.478
1100	31.446	130.325	108.180	- 3.851	- 178.993	- 161.448	28.534
1200	31.616	133.056	110.150	- 3.851	- 178.993	- 161.316	26.042
1300	31.771	135.572	112.001	- 3.851	- 178.993	- 161.353	23.904
1400	31.914	137.906	113.769	- 3.851	- 178.993	- 161.557	22.051
1500	31.550	140.082	115.452	- 3.851	- 178.993	- 161.994	20.405
1600	31.570	142.119	117.055	- 3.851	- 178.993	- 162.681	18.926
1700	31.604	144.034	118.587	- 3.851	- 178.993	- 163.559	17.612
1800	31.654	145.841	120.051	- 3.851	- 178.993	- 164.627	16.435
1900	31.664	147.552	121.454	- 3.851	- 178.993	- 165.887	15.376
2000	31.656	149.175	122.800	- 3.851	- 178.993	- 167.342	14.417
2100	31.649	150.720	124.093	- 3.851	- 178.993	- 168.982	13.545
2200	31.680	152.193	125.337	- 3.851	- 178.993	- 170.795	12.748
2300	31.690	153.602	126.535	- 3.851	- 178.993	- 172.768	12.017
2400	31.699	154.951	127.691	- 3.851	- 178.993	- 174.892	11.344
2500	31.706	156.245	128.808	- 3.851	- 178.993	- 177.169	10.722
2600	31.713	157.488	129.887	- 3.851	- 178.993	- 179.595	10.146
2700	31.719	158.685	130.932	- 3.851	- 178.993	- 182.171	9.617
2800	31.724	159.839	131.944	- 3.851	- 178.993	- 184.892	9.137
2900	31.729	160.952	132.925	- 3.851	- 178.993	- 187.661	8.705
3000	31.734	162.028	133.877	- 3.851	- 178.993	- 190.481	8.322
3100	31.738	163.069	134.802	- 3.851	- 178.993	- 193.356	7.986
3200	31.741	164.076	135.701	- 3.851	- 178.993	- 196.281	7.696
3300	31.744	165.053	136.576	- 3.851	- 178.993	- 199.251	7.451
3400	31.747	166.001	137.427	- 3.851	- 178.993	- 202.261	7.246
3500	31.750	166.921	138.257	- 3.851	- 178.993	- 205.306	7.076
3600	31.753	167.816	139.066	- 3.851	- 178.993	- 208.381	6.936
3700	31.755	168.686	139.855	- 3.851	- 178.993	- 211.481	6.821
3800	31.757	169.533	140.625	- 3.851	- 178.993	- 214.601	6.726
3900	31.759	170.358	141.376	- 3.851	- 178.993	- 217.736	6.646
4000	31.761	171.162	142.111	- 3.851	- 178.993	- 220.881	6.576
4100	31.763	171.946	142.829	- 3.851	- 178.993	- 224.031	6.516
4200	31.764	172.711	143.532	- 3.851	- 178.993	- 227.181	6.461
4300	31.766	173.450	144.219	- 3.851	- 178.993	- 230.331	6.411
4400	31.767	174.169	144.892	- 3.851	- 178.993	- 233.481	6.366
4500	31.768	174.865	145.551	- 3.851	- 178.993	- 236.631	6.326
4600	31.769	175.541	146.197	- 3.851	- 178.993	- 239.781	6.291
4700	31.771	176.285	146.829	- 3.851	- 178.993	- 242.931	6.261
4800	31.772	176.993	147.450	- 3.851	- 178.993	- 246.081	6.236
4900	31.773	177.669	148.059	- 3.851	- 178.993	- 249.231	6.216
5000	31.774	178.290	148.656	- 3.851	- 178.993	- 252.381	6.196
5100	31.774	178.880	149.243	- 3.851	- 178.993	- 255.531	6.181
5200	31.775	179.437	149.819	- 3.851	- 178.993	- 258.681	6.171
5300	31.776	180.102	150.384	- 3.851	- 178.993	- 261.831	6.166
5400	31.776	180.776	150.940	- 3.851	- 178.993	- 264.981	6.166
5500	31.777	181.457	151.487	- 3.851	- 178.993	- 268.131	6.166
5600	31.778	182.142	152.024	- 3.851	- 178.993	- 271.281	6.166
5700	31.779	182.834	152.552	- 3.851	- 178.993	- 274.431	6.166
5800	31.780	183.536	153.073	- 3.851	- 178.993	- 277.581	6.166
5900	31.780	184.250	153.586	- 3.851	- 178.993	- 280.731	6.166
6000	31.780	184.944	154.086	- 3.851	- 178.993	- 283.881	6.166

Dec. 31, 1960; June 30, 1965

Point Group [D_{2h}]
S°_{298.15} = [91.15] cal. mole⁻¹ deg.⁻¹
Ground State Quantum Weight = 1
ΔH_f⁰ = [-180] kcal. mole⁻¹
ΔH_f⁰ 298.15 = [-179] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies	
ω, cm. ⁻¹	ω, cm. ⁻¹
[220](1)	[185](1)
[110](1)	[100](1)
[180](1)	[800](1)
[105](1)	[300](1)

Bond Length: Be-Cl = [1.71] Å
Bond Angle: Cl'-Be-Cl' (in ring) = [89°]
Product of the Moments of Inertia: I_AI_BI_C = 2.62616 x 10⁻¹¹² g.³ cm.⁶
Be-Cl' (in ring) = [1.8] Å
Cl'-Be-Cl = [136°]
σ = 4

Heat of Formation.

The heat of formation was estimated by assuming that the concentration of dimer in equilibrium with the monomer was ~5% at 500°K. as reported by D. L. Hildenbrand, L. P. Theard, E. Murel and P. Ju, Aeronutronic Div. of Philco Corp., Report U-3068, April 1965 under contract AF 04(611)-8523, giving an effective K_p = 5.5 x 10⁻⁴ for 2BeCl₂(g) → Be₂Cl₄ at 500°K.

Heat Capacity and Entropy.

The structure was assumed planar with a D_{2h} symmetry, the bond lengths were estimated from the values for BeCl₂ (g), a lengthening being assumed in the ring. The frequencies were estimated using K₂Cl₂ as a basis for the ring vibrations. Two polymeric frequencies had been observed by A. Shelson, IIT Research Institute, Report No. IITRI-C6013-4, May 1964, under Contract No. DA-31-124-AHQ(D)-111. These were observed in matrix isolated BeCl₂ gas and were ascribed to polymeric species on account of their warm up behavior. They are here assigned to the B_{2u} asymmetric stretching mode and the B_{1u} asymmetric out of plane wag of the non ring chlorines. The order of the frequencies listed above is arbitrary and not related to their specie types. The individual moments of inertia are: I_A = 18.396 x 10⁻³⁵ g. cm.², I_B = 110.638 x 10⁻³⁵ g. cm.² and I_C = 129.034 g. cm.²



(Ideal Gas) GFW = 72.0206

OPF = 72.0206

DIBERYLLIUM OXIDE DIFLUORIDE (Be₂O₂F₂)

(IDEAL GAS)

Point Group [C_{2v}]
 $S^{\circ}_{298.15} = [71.4]$ gibbs/mol
 $\Delta H^{\circ}_{f,298.15} = -287.9 \pm 5$ kcal/mol
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹
[1200](1)	[1500](1)
[800](1)	[900](1)
[400](1)	[300](1)
[100](1)	[300](1)
[300](1)	

Bond Distance: Be-O = [1.33] Å Be-F = [1.43] Å

Bond Angle: O-Be-F = [180]° Be-O-Be = [150]°

Product of the Moments of Inertia: $I_A I_B I_C = [2.554374] \times 10^{-114}$ g³ cm⁶

$\sigma = [2]$

Heat of Formation

J. Sfilenko, NBS Report 8186, Jan. 1984, has studied mass spectrometrically the reaction $\text{BeO}(c) + \text{BeF}_2(g) \rightarrow \text{Be}_2\text{O}_2\text{F}_2(g)$ and also reported two sets of equilibrium constants. Using JANAF thermodynamic functions, the heat of reaction has been calculated from those reported equilibrium constants by the second law and the third law methods.

Number of Measurements	Temperature Range (°K)	$\Delta H^{\circ}_{f,298}$ kcal/mol	2nd law value	3rd law value	3rd law drift (kcal)
1st Set	13	1570-1891	41.448 ± 3.04	41.981	0.408 ± 1.726
2nd Set	21*	1872-2195	42.553 ± 0.70	42.714	0.015 ± 0.359

*Four points are rejected due to failure of statistical test.

A weighted average value, $\Delta H^{\circ}_{f,298} = 42.70$ kcal/mol, was chosen for the heat of reaction. The heat of formation, $\Delta H^{\circ}_{f,298}(\text{Be}_2\text{O}_2\text{F}_2, g) = -287.9 \pm 5$ kcal/mol, was calculated from the selected heat of reaction, using $\Delta H^{\circ}_{f,298}(\text{BeO}, c) = 143.1$ kcal/mol and $\Delta H^{\circ}_{f,298}(\text{BeF}_2, g) = -187.5$ kcal/mol.

Heat Capacity and Entropy

The adopted "v" shape molecular structure with nine fundamental vibrational frequencies was obtained from an estimation by D. E. Mann, NBS Report 8186, Jan. 1, 1984. The bond distances Be-O and Be-F were estimated to be the same as those in BeO(g) and BeF₂(g), respectively. The three principal moments of inertia are $I_A = 1.0103 \times 10^{-39}$, $I_B = 49.7805 \times 10^{-39}$ and $I_C = 50.7908 \times 10^{-39}$ g cm².

T, °K	Cp*	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-3.964	-287.780	-287.780	INFINITE
100	11.661	58.459	1.070	-1.070	-287.780	-287.780	31.1257
200	18.239	62.454	73.005	-1.070	-287.780	-287.780	31.1257
298	18.239	71.415	71.415	0.000	-287.900	-286.083	209.704
300	18.239	71.415	71.415	1.034	-287.901	-286.072	208.403
400	20.032	77.634	72.154	1.952	-287.986	-285.450	155.962
500	21.344	81.653	73.404	4.024	-288.094	-284.804	124.488
600	22.307	85.634	75.285	6.209	-288.203	-284.135	103.496
700	23.019	89.129	77.018	8.477	-288.319	-283.448	88.697
800	23.550	92.230	78.740	10.807	-288.444	-282.766	77.243
900	23.952	95.037	80.389	13.183	-288.585	-282.024	68.485
1000	24.261	97.577	81.983	15.594	-288.752	-281.286	61.475
1100	24.503	99.911	83.408	18.033	-288.953	-280.530	55.736
1200	24.695	102.042	84.664	20.493	-289.192	-279.754	50.950
1300	24.849	104.025	85.785	22.971	-289.470	-278.956	46.897
1400	24.971	105.811	87.684	25.462	-289.789	-278.137	43.419
1500	25.078	107.398	89.354	27.965	-290.153	-277.292	40.401
1600	25.164	108.719	90.171	30.477	-290.560	-276.424	37.736
1700	25.237	110.747	91.337	32.997	-291.000	-275.519	35.356
1800	25.298	112.191	92.456	35.524	-291.474	-274.583	33.239
1900	25.351	113.860	93.531	38.057	-291.978	-273.622	31.343
2000	25.396	115.662	94.565	40.594	-292.503	-272.649	29.636
2100	25.435	116.102	95.561	43.136	-293.050	-271.656	28.090
2200	25.469	117.286	96.522	45.681	-293.620	-270.643	26.683
2300	25.500	118.419	97.450	48.229	-294.214	-269.610	25.396
2400	25.526	119.505	98.346	50.781	-294.824	-268.558	24.216
2500	25.550	120.547	99.213	53.334	-295.444	-267.486	23.130
2600	25.570	121.550	100.053	55.890	-296.084	-266.403	22.126
2700	25.589	122.515	100.867	58.448	-296.744	-265.300	21.195
2800	25.606	123.446	101.657	61.008	-297.424	-264.183	20.357
2900	25.621	124.345	102.424	63.570	-298.124	-263.053	19.608
3000	25.635	125.214	103.169	66.132	-298.844	-261.900	18.960
3100	25.647	126.054	103.894	68.696	-299.584	-260.724	18.423
3200	25.658	126.869	104.599	71.262	-300.344	-259.533	17.985
3300	25.669	127.658	105.286	73.828	-301.124	-258.324	17.643
3400	25.678	128.425	105.956	76.395	-301.924	-257.093	17.370
3500	25.687	129.169	106.608	78.964	-302.744	-255.843	17.157
3600	25.695	129.893	107.245	81.533	-303.584	-254.583	16.992
3700	25.702	130.597	107.867	84.103	-304.444	-253.324	16.865
3800	25.709	131.283	108.474	86.673	-305.324	-252.063	16.770
3900	25.715	131.944	109.067	89.244	-306.224	-250.803	16.700
4000	25.721	132.602	109.648	91.816	-307.144	-249.543	16.643
4100	25.726	133.237	110.215	94.388	-308.084	-248.283	16.592
4200	25.731	133.857	110.771	96.961	-309.044	-247.023	16.546
4300	25.736	134.462	111.315	99.535	-310.024	-245.763	16.501
4400	25.740	135.054	111.848	102.108	-311.024	-244.503	16.457
4500	25.744	135.633	112.370	104.683	-312.044	-243.243	16.413
4600	25.748	136.199	112.882	107.257	-313.084	-241.983	16.369
4700	25.751	136.752	113.384	109.832	-314.144	-240.723	16.324
4800	25.755	137.294	113.876	112.408	-315.224	-239.463	16.279
4900	25.758	137.824	114.354	114.984	-316.324	-238.203	16.234
5000	25.761	138.346	114.834	117.559	-317.444	-236.943	16.189
5100	25.764	138.856	115.300	120.135	-318.584	-235.683	16.143
5200	25.766	139.356	115.758	122.712	-319.744	-234.423	16.097
5300	25.769	139.847	116.208	125.289	-320.924	-233.163	16.051
5400	25.771	140.329	116.654	127.866	-322.124	-231.903	16.005
5500	25.773	140.802	117.095	130.443	-323.344	-230.643	15.959
5600	25.776	141.266	117.513	133.020	-324.584	-229.383	15.913
5700	25.777	141.723	117.933	135.598	-325.844	-228.123	15.867
5800	25.779	142.171	118.347	138.176	-327.124	-226.863	15.821
5900	25.781	142.610	118.756	140.754	-328.424	-225.603	15.775
6000	25.783	143.045	119.156	143.332	-329.744	-224.343	15.729

June 30, 1986



T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	7.000	∞	INFINITE	2.372	-15.399	-15.399	INFINITE
100	7.433	49.114	50.546	1.600	-15.399	-15.399	2.928
200	8.433	49.114	50.546	1.600	-15.399	-15.399	2.928
298	9.788	52.754	52.754	0.000	-15.000	-22.000	16.172
300	9.809	52.815	52.754	0.018	-15.002	-22.017	16.104
400	10.860	55.783	53.152	1.053	-15.201	-24.448	11.357
500	11.656	58.294	53.636	2.119	-15.448	-26.731	11.683
600	12.292	60.477	54.848	3.378	-15.711	-28.963	10.549
700	12.763	62.411	55.793	4.633	-15.989	-31.150	9.725
800	13.161	64.153	56.730	5.931	-16.280	-33.297	9.096
900	13.454	65.711	57.662	7.262	-16.590	-35.405	8.597
1000	13.683	67.141	58.592	8.619	-16.926	-37.477	8.190
1100	13.865	68.454	59.366	9.997	-17.296	-39.514	7.850
1200	14.011	69.667	60.174	11.391	-17.704	-41.517	7.561
1300	14.129	70.793	60.948	12.798	-18.149	-43.483	7.310
1400	14.224	71.844	61.685	14.215	-18.625	-45.415	7.089
1500	14.306	72.828	62.400	15.643	-19.134	-47.311	6.893
1600	14.374	73.754	63.081	17.077	-19.677	-49.011	6.694
1700	14.430	74.627	63.734	18.517	-20.253	-50.485	6.490
1800	14.479	75.453	64.363	19.963	-20.868	-51.935	6.305
1900	14.520	76.234	64.967	21.413	-21.513	-53.354	6.138
2000	14.556	76.963	65.550	22.867	-22.184	-54.772	5.985
2100	14.587	77.654	66.111	24.324	-22.885	-56.151	5.844
2200	14.614	78.373	66.653	25.784	-23.617	-57.523	5.714
2300	14.638	79.023	67.177	27.247	-24.381	-58.866	5.593
2400	14.659	79.698	67.684	28.711	-25.177	-60.181	5.481
2500	14.677	80.245	68.174	30.178	-25.996	-61.481	5.376
2600	14.694	80.821	68.650	31.647	-26.829	-62.787	5.277
2700	14.709	81.376	69.111	33.117	-27.685	-64.057	5.185
2800	14.722	81.911	69.558	34.589	-28.566	-65.294	5.094
2900	14.733	82.428	69.971	36.061	-29.471	-66.504	4.996
3000	14.745	82.928	70.416	37.535	-30.399	-67.687	4.896
3100	14.755	83.412	70.828	39.010	-31.350	-68.844	4.796
3200	14.764	83.880	71.228	40.486	-32.323	-70.000	4.696
3300	14.772	84.375	71.619	41.963	-33.318	-71.163	4.596
3400	14.779	84.847	71.999	43.441	-34.334	-72.332	4.496
3500	14.787	85.204	72.370	44.919	-35.371	-73.504	4.396
3600	14.793	85.621	72.733	46.398	-36.428	-74.681	4.296
3700	14.799	86.026	73.086	47.878	-37.504	-75.861	4.196
3800	14.804	86.414	73.432	49.359	-38.599	-77.044	4.096
3900	14.809	86.801	73.772	50.839	-39.713	-78.231	3.996
4000	14.814	87.181	74.101	52.320	-40.844	-79.421	3.896
4100	14.818	87.547	74.424	53.801	-41.989	-80.614	3.796
4200	14.822	87.904	74.741	55.283	-43.150	-81.811	3.696
4300	14.825	88.253	75.055	56.759	-44.323	-83.011	3.596
4400	14.830	88.593	75.355	58.239	-45.504	-84.214	3.496
4500	14.833	88.927	75.653	59.732	-46.699	-85.421	3.396
4600	14.836	89.253	75.945	61.215	-47.904	-86.631	3.296
4700	14.839	89.572	76.232	62.699	-49.123	-87.844	3.196
4800	14.843	89.884	76.514	64.184	-50.354	-89.059	3.096
4900	14.846	90.190	76.789	65.667	-51.599	-90.274	2.996
5000	14.846	90.490	77.060	67.152	-52.854	-91.494	2.896
5100	14.849	90.784	77.326	68.637	-54.119	-92.719	2.796
5200	14.851	91.073	77.588	69.912	-55.394	-93.944	2.696
5300	14.853	91.357	77.844	71.184	-56.679	-95.169	2.596
5400	14.855	91.633	78.098	72.451	-57.964	-96.394	2.496
5500	14.856	91.906	78.346	73.702	-59.254	-97.619	2.396
5600	14.858	92.174	78.591	74.957	-60.549	-98.844	2.296
5700	14.860	92.437	78.831	76.203	-61.844	-100.069	2.196
5800	14.861	92.694	79.064	77.446	-63.139	-101.289	2.096
5900	14.863	92.949	79.301	78.684	-64.434	-102.509	1.996
6000	14.864	93.199	79.531	80.008	-65.729	-103.729	1.896

Sept. 30, 1963.

Point Group [D_{∞h}]
 $\Delta H_f^\circ 0 = -15.4 \pm 10$ kcal. mole⁻¹
 $\Delta H_f^\circ 298.15 = [52.7]$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^\circ 298.15 = -15 \pm 10$ kcal. mole⁻¹
 Ground State Quantum Weight = [3]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	g_i
[1100]	(1)
[500]	(2)
[1600]	(1)

Bond distance: Be-O = [1.4] Å

Bond Angle: Be-O-Be = [180°]

 $\sigma = 2$ Moment of Inertia: $I_A = 5.8656 \times 10^{-39}$ g. cm.²

Heat of Formation.

D. L. Hildenbrand, L. P. Theard, and P. Ju, Ford Motor Co., Aeronautics Division, Third Quarterly Technical Report U-2231, April-June 1963, have reported the heat of formation. Equilibrium constants were determined in a mass spectrometer for the reactions $2BeO(c) \rightarrow Be_2O(g) + O(g) - (1)$ $2BeO(g) \rightarrow Be_2O(g) + O(g) - (2)$ and $Be_2O(g) \rightarrow Be_2O(g) + O(g) - (3)$. Using our own free energy functions we obtain $\Delta H_f^\circ 298$ Be₂O(g) = -13.1, -14.5, and -16.7 kcal. mole⁻¹, all ± 10 ; the 2nd law treatment of reaction 1 gives -18.3 ± 10 kcal. mole⁻¹. We adopt a median value -15 ± 10 kcal. mole⁻¹.

Heat Capacity and Entropy.

A. Buchler, J. L. Stauffer, W. Klemperer and C. Wharton, A. D. Little, Inc., Interim Technical Report No. 5, 1963, have shown Li₂O to be linear. Also A. D. Walsh, J. Chem. Soc. London 2269 (1953) predicted that AP₂ molecules with less than 16 bonding electrons would be linear. Thus Be₂O was taken to be linear and symmetrical, with a Be-O bond length of 1.4 Å, which is a little longer than in BeO(g). The vibrational frequencies were estimated by taking ω_3 to be larger than the stretch in BeO(g) and then calculating ω_4 from the valence force field assumption. The bending force constant was estimated as 1/20th of the stretching force constant. The two outermost electrons were considered unpaired and so gave a $\sum$ ground state.

Vibrotional Frequencies and Degeneracies

Bond Distance: Be-O = [1.63] Å $\sigma = 4$

Bond Angle: Be-O-Be = $[90^\circ]$ O-Be-O = $[90^\circ]$

Product of the Moments of Inertia: $I_{L_1 L_2} = \{3.0957\} \times 10^{-115} \text{ g. cm.}^6$

Heat of Formation.

W. A. Chupke, J. Berkowitz, and C. P. Glase, *J. Chem. Phys.* **30**, 827 (1959) studied the temperature dependence of the $(\text{BeO})_2$ ion in a mass spectrometer and obtained a second law heat of vaporization of 172 ± 8 kcal. per mole $^{-1}$ at 2150°K. No correction was made for fragmentation of higher polymers and this is reflected in the uncertainty. We adopted a heat of sublimation of 178 kcal. mole $^{-1}$ in order to match more closely the equilibrium constant found by Chupke, et al. However, it was not possible to alter either the heat or entropy sufficiently to obtain exact agreement, the predicted pressure being too high by a factor of 20.

Heat Capacity and Entropy.

A planer ring configuration was assumed which has six vibrational frequencies of the type $2\nu_{2a}$, ν_{2b} , ν_{2c} , ν_{2d} , ν_{2e} , and ν_{2f} . These were estimated by comparison with $(110)_2$ for which values have been calculated by D. White, ν_{2a} , ν_{2b} , D. F. Dever, D. E. Mann, and M. J. Linevsky, prepublication communication, July, 1963. It seems unlikely that any other structure than that of a ring is possible, so, in order to approach the observed equilibrium constant even lower entropy is needed. A non-linear chain would have a higher entropy due to the change in symmetry number and the two odd electrons. A linear chain would have approximately the same entropy due to the change in symmetry number and the two odd electrons. The vibrational frequencies were also made as high as possible by normalizing them using B_{20} equal to the BeO stretch in BeO(g) . The bond length was taken as the sum of the covalent radii of O and Be, which is in general agreement with other polymeric structures which generally increase in bond length by 10–20% in going from monomer to polymer. The bond angle was chosen arbitrarily, however, changes in the angle would change the entropy less than 1 eu.

The individual moments of inertia were $I_A = 7.057$, $I_B = 3.976$, and $I_C = 11.033 \times 10^{-39}$ g. cm.²

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ktal. mole ⁻¹	ΔF _f ^o	Log K _p
0	∞.000	∞.000	INFINITE	-2.726	-97.716	-97.716	97.716	INFINITE	
100	8.089	48.886	68.186	-1.930	-97.652	-97.362	98.362	214.961	
200	9.670	54.897	60.156	-1.054	-97.732	-99.061	99.061	108.243	
298	11.772	59.916	61.936	-0.000	-98.000	-99.667	99.667	73.054	
300	11.831	59.229	59.156	-0.022	-98.034	-99.677	99.677	72.611	
400	13.689	62.487	59.663	1.302	-98.315	-100.188	54.738	54.738	
500	15.105	66.112	60.622	2.745	-98.610	-100.621	43.979	43.979	
600	16.146	68.963	61.779	4.310	-98.884	-100.908	36.787	36.787	
700	17.011	71.512	62.901	5.965	-99.181	-101.329	31.635	31.635	
800	17.747	73.859	64.202	7.686	-99.418	-101.623	27.761	27.761	
900	17.904	75.893	65.587	9.456	-99.696	-101.881	22.314	22.314	
1000	18.221	77.797	67.043	11.263	-99.996	-102.107	16.972	16.972	
1100	18.486	79.467	67.639	13.099	-100.327	-102.343	12.035	12.035	
1200	18.697	81.125	68.659	14.958	-100.694	-102.467	8.661	8.661	
1300	18.849	82.667	69.717	16.816	-101.097	-102.598	17.241	17.241	
1400	18.980	84.069	70.802	18.727	-101.542	-102.698	16.331	16.331	
1500	19.098	85.382	71.628	20.661	-102.029	-102.765	15.972	15.972	
1600	19.178	86.641	72.527	22.564	-102.471	-102.639	14.039	14.039	
1700	19.224	87.782	73.390	24.466	-102.847	-102.299	13.149	13.149	
1800	19.318	88.685	74.221	26.365	-103.148	-101.918	12.374	12.374	
1900	19.372	89.430	75.020	28.329	-103.416	-101.517	11.678	11.678	
2000	19.419	90.025	75.791	30.269	-103.650	-101.151	11.049	11.049	
2100	19.460	91.874	76.536	32.213	-103.903	-100.688	10.478	10.478	
2200	19.496	92.780	77.282	34.161	-104.103	-100.226	9.910	9.910	
2300	19.527	93.647	77.947	36.112	-104.714	-99.771	9.480	9.480	
2400	19.555	94.479	78.618	38.066	-105.118	-99.284	9.041	9.041	
2500	19.579	95.278	79.269	40.023	-111.577	-98.787	8.636	8.636	
2600	19.601	96.046	79.899	41.984	-112.026	-98.262	8.259	8.259	
2700	19.620	97.786	80.511	43.963	-112.489	-97.724	7.810	7.810	
2800	19.637	97.500	81.105	45.906	-255.021	-94.954	7.411	7.411	
2900	19.653	98.189	81.762	47.870	-255.005	-89.253	6.724	6.724	
3000	19.667	98.856	82.244	49.836	-255.996	-83.539	6.084	6.084	
3100	19.680	99.501	82.700	51.804	-256.991	-77.898	5.485	5.485	
3200	19.692	100.126	83.122	53.772	-256.993	-72.087	4.923	4.923	
3300	19.702	100.732	83.641	55.742	-255.003	-66.372	4.395	4.395	
3400	19.712	101.320	84.346	57.713	-255.023	-60.657	3.899	3.899	
3500	19.721	101.892	84.839	59.684	-255.050	-54.944	3.341	3.341	
3600	19.729	102.468	85.321	61.657	-255.087	-49.220	2.988	2.988	
3700	19.737	102.988	85.791	63.630	-255.136	-43.504	2.570	2.570	
3800	19.744	103.515	86.251	65.604	-255.197	-37.793	2.173	2.173	
3900	19.750	104.028	86.700	67.579	-255.268	-32.058	1.796	1.796	
4000	19.756	104.528	87.139	69.554	-255.355	-26.338	1.439	1.439	
4100	19.762	105.016	87.569	71.530	-255.456	-20.615	1.099	1.099	
4200	19.767	105.492	87.990	73.507	-255.560	-14.889	0.775	0.775	
4300	19.772	105.957	88.403	75.483	-255.702	-9.145	0.465	0.465	
4400	19.776	106.412	88.807	77.461	-255.851	-3.413	0.170	0.170	
4500	19.781	106.856	89.203	79.439	-256.000	-2.326	-	-	
4600	19.784	107.291	89.592	81.417	-256.205	8.069	-	-	
4700	19.788	107.717	89.973	83.396	-256.410	13.813	-	-	
4800	19.792	108.133	90.347	85.375	-256.636	19.569	-	-	
4900	19.795	108.541	90.714	87.354	-256.882	25.322	-	-	
5000	19.798	108.951	91.075	89.334	-257.149	31.089	-	-	
5100	19.801	109.333	91.429	91.316	-257.440	36.899	-	-	
5200	19.804	109.718	91.777	93.294	-257.752	42.621	-	-	
5300	19.806	110.095	92.119	95.274	-258.089	48.410	-	-	
5400	19.809	110.465	92.455	97.255	-258.447	54.189	-	-	
5500	19.811	110.829	92.786	99.236	-258.820	59.985	-	-	
5600	19.813	111.186	93.111	101.217	-259.246	65.783	-	-	
5700	19.815	111.537	93.432	103.199	-259.664	71.594	-	-	
5800	19.817	111.881	93.747	105.180	-260.118	77.448	-	-	
5900	19.819	112.220	94.057	107.162	-260.596	83.263	-	-	
6000	19.821	112.553	94.362	109.144	-261.099	89.062	-	-	

Dec. 31, 1960; Sept. 30, 1963

Beryllium Orthosilicate (Be_2SiO_4)
(Crystal) Mol. Wt. = 110.108

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	0.000	INFINITE	2.922	-503.096	-503.096	INFINITE	
100	4.492	1.798	2.765	-503.096	-503.096	1.147	
200	14.444	7.046	2.765	-503.096	-503.096	532.778	
298	22.840	15.342	2.765	-503.096	-503.096	350.666	
300	22.968	15.483	2.765	-503.096	-503.096	348.579	
400	28.960	22.946	2.765	-503.096	-503.096	250.401	
500	35.730	29.619	2.765	-503.096	-503.096	201.085	
600	35.650	36.054	2.765	-503.096	-503.096	164.221	
700	37.970	41.732	23.377	-503.096	-503.096	137.906	
800	39.680	46.920	26.000	-503.096	-503.096	118.188	
900	40.810	51.602	28.582	-503.096	-503.096	102.867	
1000	41.600	55.693	31.119	-503.096	-503.096	90.624	
1100	42.150	59.996	33.566	-503.096	-503.096	80.618	
1200	42.590	63.681	35.924	-503.096	-503.096	72.289	
1300	42.934	67.106	38.102	-503.096	-503.096	65.248	
1400	43.200	70.320	40.150	-503.096	-503.096	59.249	
1500	43.472	73.291	42.069	-503.096	-503.096	53.794	
1600	43.702	76.104	44.484	-503.096	-503.096	49.413	
1700	43.930	78.760	46.423	-503.096	-503.096	45.331	
1800	44.156	81.277	48.290	-503.096	-503.096	41.633	
1900	44.376	83.661	50.096	-503.096	-503.096	38.359	
2000	44.600	85.953	51.826	-503.096	-503.096	35.458	
2100	44.812	88.134	53.504	-503.096	-503.096	32.673	
2200	45.024	90.224	55.125	-503.096	-503.096	30.236	
2300	45.236	92.230	56.692	-503.096	-503.096	28.013	
2400	45.448	94.159	58.206	-503.096	-503.096	26.013	
2500	45.660	96.019	59.692	-503.096	-503.096	24.108	
2600	45.872	97.814	61.123	-503.096	-503.096	22.383	
2700	46.084	99.549	62.515	-503.096	-503.096	20.789	
2800	46.296	101.230	63.867	-503.096	-503.096	19.314	
2900	46.508	102.857	65.184	-503.096	-503.096	17.940	
3000	46.720	104.437	66.466	-503.096	-503.096	15.743	

Sept. 30, 1961; June 30, 1965

BERYLLIUM ORTHOSILICATE (Be_2SiO_4) (CRYSTAL)

MOL. WT. = 110.108

$\Delta H^\circ_f = -503.1 \pm 7$ kcal. mole⁻¹
 $\Delta F^\circ_f = -506.0 \pm 7$ kcal. mole⁻¹
 $S^\circ_{298.15} = 15.342 \pm 0.1$ cal. deg.⁻¹ mole⁻¹
 $T_m = 1833^\circ\text{K}.$

Heat of Formation.

The ΔH°_f 298.15 was estimated from the ΔH°_f 298.15 of Mg, Ca and Be oxides with SiO_2 given by K. K. Kelley in the report of investigations 5801, U. S. Department of the Interior, Bureau of Mines 1962, and from the ΔH°_f 298.15 of $\text{BeO}(c)$ (Sept. 30, 1963) and $\text{SiO}_2(c)$ (Dec. 31, 1962) in JANAP tables. The ΔH°_f 298.15 = 0 ± 7 kcal. mole⁻¹ was estimated for the reaction $2\text{BeO}(c) + \text{SiO}_2(c) \rightarrow \text{Be}_2\text{SiO}_4(c)$.

Heat Capacity and Entropy.

At low temperatures C_p was used from K. K. Kelley, J. Am. Chem. Soc., 61, 1217 (1939). Above 298.15°K. C_p values were estimated by summation of the component oxides using JANAP tables, BaO (Sept. 30, 1963) and SiO_2 (Dec. 31, 1962). The entropy was calculated at 54.7°K. using the Debye and Planck-Einstein Functions $D(\frac{422}{T}) + 25(\frac{227}{T})$ given by K. K. Kelley, J. Am. Chem. Soc., 61, 1217 (1939). The value of $S^\circ_{54.7} = 13.59$ cal. deg.⁻¹ mole⁻¹.

Melting Data.

The incongruent melting point was taken from Kubaschewski and Evans, "Metallurgical Thermochemistry" 3rd edition, Pergamon Press., New York 1958.





Beryllium Nitride, Alpha (α -Be₃N₂)

(Crystal) GFW = 55.050

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	-0.000	-0.000	INFINITE	-1.691	-136.415	-136.415	INFINITE
100	1.460	4.41	17.011	-1.657	-139.504	-135.492	296.555
200	6.462	3.421	9.351	-1.186	-140.143	-131.623	143.631
298	15.362	8.157	8.157	0.000	-140.400	-127.346	93.347
300	15.454	8.252	8.157	0.029	-140.405	-127.246	92.711
400	25.480	18.253	10.232	1.027	-140.821	-125.778	67.043
500	23.306	18.254	10.232	4.011	-140.852	-119.260	51.691
600	25.458	22.704	11.946	6.455	-140.746	-113.749	41.433
700	26.989	26.750	13.776	9.082	-140.563	-109.265	34.114
800	28.105	30.731	15.632	11.839	-140.300	-105.810	28.572
900	28.970	34.672	17.504	14.716	-140.000	-103.340	24.000
1000	29.544	36.672	19.254	17.618	-139.559	-95.983	20.977
1100	30.000	39.710	20.986	20.596	-139.661	-91.604	18.200
1200	30.335	42.336	22.658	23.614	-139.511	-87.244	15.669
1300	30.570	44.604	24.269	26.720	-139.172	-82.982	13.242
1400	30.710	46.546	25.820	29.872	-138.702	-78.806	10.911
1500	30.843	49.171	27.300	32.406	-139.404	-74.208	8.509
1600	30.966	51.163	28.730	35.893	-147.770	-69.416	6.323
1700	30.908	53.037	30.105	38.883	-147.602	-64.739	4.019
1800	30.810	54.695	31.423	41.055	-147.323	-59.807	2.581
1900	30.690	56.062	32.693	42.665	-147.322	-55.007	1.239
2000	30.940	58.062	33.932	48.260	-147.212	-50.150	4.714
2100	30.949	59.572	35.117	51.355	-147.118	-45.300	4.019
2200	30.937	61.012	36.262	54.450	-147.043	-40.453	3.283
2300	30.920	62.368	37.368	57.246	-146.985	-35.605	2.581
2400	30.907	63.661	38.437	60.000	-146.942	-30.757	1.847
2500	30.896	64.916	39.474	62.711	-146.922	-25.927	1.115
2600	30.984	66.166	40.479	66.839	-146.915	-21.083	0.384
2700	30.989	67.355	41.452	69.238	-146.921	-16.241	0.131
2800	30.997	68.500	42.396	71.036	-146.936	-11.400	0.080
2900	30.997	69.570	43.316	72.936	-146.960	-6.558	0.038
3000	31.000	70.621	44.209	75.236	-146.998	-1.715	0.000

Reference	Range	Points	ΔH° ₂₉₈ kcal/mol	Drift	**ΔH° _{298.15} Be ₃ N ₂ kcal/mol
Yates - 1	1478-1592	9*	364.5±5.9	6.0±3.8	-139.23
Yates - 2	1541-1652	15*	369.6±8.3	4.0±5.3	-141.74
Yates - 3	1438-1661	14	347.7±3.7	374.54	-139.77
Yates - 4	1450-1646	17*	366.7±8.9	375.28	-140.51
Yates	1473-1661	52*	358.3±5.1	375.41	-140.64
Hoenig - 1	1767-1946	14	355.9±3.3	377.77	-143.00
Hoenig - 2	1660-1891	10	395.0±5.6	378.69	-143.92
Hoenig - 3	1648-1893	10	416.9±8.4	383.15	-148.38

*Points rejected due to failure of statistical test.

**Calculated from 3rd law ΔH°₂₉₈.

The data of Yates et al. are seen to be in good agreement with the adopted ΔH°₂₉₈.

Heat Capacity and Entropy.

The low temperature heat capacity of α-Be₃N₂ has been measured, from 25° - 310°K, by B. H. Justice, The Dow Chemical Co., last Quarterly Report under Contract AF04611-67-C-0009, April 1967. These measurements are joined smoothly with the high temperature enthalpies reported by T. B. Douglas and W. H. Payne, Natl. Bur. Std. Report 7587, July 1962. Above 1200°K the values were smoothly extrapolated to a limiting value of 6.2 gibbs/g-atom. The entropy at 298° was calculated by integration of the low temperature data based on S°₂₅ = 0.002 eu.

Melting Data.

See Be₃N₂(1) for details.

BERYLLIUM NITRIDE, ALPHA (α-Be₃N₂)

(CRYSTAL)

OPW = 55.050

$$\Delta H_f^\circ = -136.8 \pm 0.3 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -140.6 \pm 0.3 \text{ kcal/mol}$$

$$\Delta H_m^\circ = [30.9] \text{ kcal/mol}$$

$$S_{298.15}^\circ = 6.157 \text{ gibbs/mol}$$

$$T_m = 2473^\circ\text{K}$$

Heat of Formation.

P. Orsso, C. Hayman, F. D. Oreene and J. T. Bingham, Trans. Faraday Soc. 52, 2719 (1956), have measured the heat of chlorination of α-Be₃N₂ to α-BeCl₂, and the heat of reaction of Be with ammonia. The chlorination reaction (A) α-Be₃N₂(c) + 3Cl₂(g) → 3 α-BeCl₂(c) + N₂(g) had a ΔH°₂₉₈ = -210.3 ± 1.1 kcal/mol, which, combined with the value of -117.1 ± 0.4 kcal/mol for α-BeCl₂ reported in the same paper, yields ΔH°₂₉₈(α-Be₃N₂,c) = -141.0 ± 1.6 kcal/mol. Reaction (B) 3 Be(c) + 2 NH₃(g) = α-Be₃N₂(c) + 3 H₂(g) had a ΔH°₂₉₈ = -214.6 ± 0.3 kcal/mol, which, combined with the JANAP value for NH₃(g), yields ΔH°₂₉₈(α-Be₃N₂,c) = -140.3 ± 0.3 kcal/mol. A weighted mean value of the above two determinations is adopted.

The decomposition Be₃N₂(c) = 3 Be(g) + N₂(g) has been studied by R. E. Yates, M. A. Greenbaum and M. Parber, J. Phys. Chem. 69, 2682 (1964), using the torsion effusion technique. The same decomposition has also been investigated by C. L. Hoenig, UCRL-7521, April 1964, using the Knudsen technique. An analysis of these data sets by 2nd and 3rd law methods is given below.

Reference	Range	Points	ΔH° ₂₉₈ kcal/mol	Drift	**ΔH° _{298.15} Be ₃ N ₂ kcal/mol
Yates - 1	1478-1592	9*	364.5±5.9	6.0±3.8	-139.23
Yates - 2	1541-1652	15*	369.6±8.3	4.0±5.3	-141.74
Yates - 3	1438-1661	14	347.7±3.7	374.54	-139.77
Yates - 4	1450-1646	17*	366.7±8.9	375.28	-140.51
Yates	1473-1661	52*	358.3±5.1	375.41	-140.64
Hoenig - 1	1767-1946	14	355.9±3.3	377.77	-143.00
Hoenig - 2	1660-1891	10	395.0±5.6	378.69	-143.92
Hoenig - 3	1648-1893	10	416.9±8.4	383.15	-148.38

*Points rejected due to failure of statistical test.

**Calculated from 3rd law ΔH°₂₉₈.

The data of Yates et al. are seen to be in good agreement with the adopted ΔH°₂₉₈.



$$\Delta H_f^{298.15} = [-116.4] \text{ kcal/mol}$$

$$\Delta H_m^\circ = [30.9] \text{ kcal/mol}$$

$$S_{298.15}^\circ = [9.425] \text{ gibbs/mol}$$

$$T_m = 2473^\circ \text{K}$$

Heat of Formation.

The heat of formation of Be₃N₂(l) is calculated from $\Delta H_f^{298} \text{ Be}_2\text{N}_2(\text{c})$ by adding ΔH_m° and the difference between $H_{2473}^\circ - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity is estimated to be constant and slightly greater than the maximum for Be₃N₂(c). The entropy at 298°K is estimated in a manner analogous to that of the heat of formation.

Melting Data.

The melting point was reported by P. Fichter and E. Brunner, Z. Anorg. Allgem. Chem. 93, 84 (1915). The heat of melting was calculated on the assumption that each g-atom contributed 2.5 gibbs to ΔS_m° .

T, °K	C _p [°]	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log K _p
0							
100							
200							
298	32.000	9.425	9.425	.000	-116.400	-103.324	75.895
300	32.000	9.623	9.426	.059	-116.375	-103.444	75.359
400	32.000	16.859	10.681	3.250	-115.180	-99.320	54.266
500	32.000	25.959	13.051	6.450	-114.204	-95.489	41.730
600	32.000	31.804	15.705	9.659	-113.342	-91.405	33.440
700	32.000	36.736	18.366	12.859	-112.586	-88.278	27.561
800	32.000	41.009	20.935	16.059	-111.914	-84.852	23.181
900	32.000	44.779	23.379	19.250	-111.324	-81.505	19.782
1000	32.000	48.156	25.691	22.450	-110.818	-78.220	17.095
1100	32.000	51.200	27.873	25.659	-110.398	-74.980	14.897
1200	32.000	53.984	29.935	28.859	-110.066	-71.776	13.072
1300	32.000	56.546	31.885	32.050	-109.813	-68.596	11.532
1400	32.000	58.917	33.732	35.250	-109.642	-65.434	10.215
1500	32.000	61.125	35.485	38.450	-109.551	-62.281	9.074
1600	32.000	63.190	37.153	41.659	-117.804	-59.893	8.044
1700	32.000	65.130	38.742	44.859	-117.526	-57.221	7.099
1800	32.000	66.959	40.260	48.059	-117.269	-54.563	6.261
1900	32.000	68.689	41.711	51.250	-117.031	-51.918	5.512
2000	32.000	70.331	43.101	54.450	-116.813	-49.289	4.860
2100	32.000	71.892	44.435	57.659	-116.614	-46.667	4.232
2200	32.000	73.381	45.717	60.859	-116.434	-44.056	3.681
2300	32.000	74.803	46.951	64.059	-116.272	-41.447	3.178
2400	32.000	76.162	48.140	67.250	-116.127	-38.847	2.718
2500	32.000	77.461	49.288	70.450	-116.004	-36.259	2.298
2600	32.000	78.726	50.396	73.659	-115.895	-33.667	1.905
2700	32.000	79.934	51.468	76.859	-115.800	-31.083	1.545
2800	32.000	81.098	52.505	80.059	-115.812	-28.502	1.211
2900	32.000	82.221	53.511	83.250	-115.841	-25.931	.901
3000	32.000	83.306	54.486	86.450	-115.887	-23.361	.616
3100	32.000	84.355	55.433	89.659	-115.950	-20.801	.356
3200	32.000	85.371	56.352	92.859	-116.030	-18.251	.121
3300	32.000	86.356	57.247	96.059	-116.127	-15.711	.000
3400	32.000	87.301	58.117	99.250	-116.241	-13.181	.000
3500	32.000	88.238	58.964	102.450	-116.370	-10.661	.000
3600	32.000	89.140	59.790	105.659	-116.514	-8.151	.000
3700	32.000	90.017	60.595	108.859	-116.673	-5.651	.000
3800	32.000	90.870	61.381	112.059	-116.846	-3.161	.000
3900	32.000	91.701	62.146	115.250	-117.034	-0.681	.000
4000	32.000	92.511	62.897	118.450	-117.236	1.801	.000

Beryllium Oxide, Trimeric (Be_3O_3)
(Ideal Gas) Mol. Wt. = 75.039

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f kcal. mole ⁻¹	ΔF° _f	Log K _p
0	8.009	52.009	INFINITE	-250.668	-250.668	INFINITE
100	8.159	59.926	66.588	-251.350	-251.350	271.927
200	11.980	65.304	0.000	-252.000	-247.515	181.425
298	15.167	65.304	0.000	-252.000	-247.515	181.425
300	15.226	65.308	0.028	-252.012	-247.487	180.286
400	18.578	70.707	5.675	-253.337	-244.084	106.684
500	20.961	74.588	8.723	-253.337	-244.084	106.684
600	23.091	78.606	66.802	-253.337	-244.084	88.208
700	24.745	82.295	70.470	-253.337	-244.084	74.985
800	26.018	85.686	72.163	-253.337	-244.084	65.049
900	27.011	88.771	73.461	-253.337	-244.084	57.104
1000	27.770	91.596	75.484	-253.337	-244.084	51.104
1100	28.376	94.372	77.081	-256.119	-231.639	46.020
1200	28.861	96.863	78.627	-256.595	-229.394	41.776
1300	29.253	99.189	80.120	-257.110	-227.106	38.178
1400	29.573	101.369	81.561	-257.673	-224.779	35.088
1500	29.838	103.418	82.951	-258.268	-222.403	32.403
1600	30.060	105.351	84.291	-258.895	-220.000	30.016
1700	30.246	107.180	85.584	-259.555	-217.670	27.868
1800	30.405	108.913	86.832	-260.245	-215.399	25.955
1900	30.540	110.551	88.041	-260.965	-213.179	24.261
2000	30.658	112.130	89.204	-261.715	-211.000	22.697
2100	30.759	113.629	90.331	-262.495	-208.865	21.297
2200	30.848	115.062	91.423	-263.305	-206.765	20.022
2300	30.926	116.435	92.481	-264.135	-204.705	18.856
2400	31.003	117.758	93.505	-264.985	-202.685	17.795
2500	31.078	119.031	94.502	-265.855	-200.715	16.795
2600	31.151	120.258	95.469	-266.745	-198.785	15.886
2700	31.221	121.431	96.408	-267.655	-196.895	15.040
2800	31.287	122.547	97.321	-268.585	-195.045	14.254
2900	31.350	123.607	98.208	-269.535	-193.235	13.524
3000	31.409	124.612	99.076	-270.505	-191.465	12.844
3100	31.464	125.569	99.919	-271.495	-189.735	12.214
3200	31.516	126.478	100.741	-272.505	-188.045	11.634
3300	31.565	127.338	101.543	-273.535	-186.395	11.104
3400	31.611	128.153	102.326	-274.585	-184.785	10.624
3500	31.654	128.925	103.090	-275.655	-183.215	10.194
3600	31.694	129.657	103.837	-276.745	-181.685	9.814
3700	31.731	130.347	104.567	-277.855	-180.195	9.484
3800	31.765	130.993	105.278	-278.985	-178.745	9.204
3900	31.796	131.603	105.967	-280.135	-177.335	8.974
4000	31.824	132.178	106.633	-281.305	-175.965	8.794
4100	31.849	132.718	107.278	-282.495	-174.635	8.664
4200	31.871	133.233	107.898	-283.705	-173.345	8.574
4300	31.890	133.723	108.493	-284.935	-172.095	8.514
4400	31.907	134.188	109.063	-286.185	-170.885	8.474
4500	31.921	134.628	109.608	-287.455	-169.715	8.444
4600	31.933	135.043	110.128	-288.745	-168.585	8.424
4700	31.943	135.433	110.623	-290.055	-167.495	8.414
4800	31.951	135.798	111.093	-291.385	-166.445	8.414
4900	31.957	136.138	111.538	-292.735	-165.435	8.424
5000	31.961	136.453	111.958	-294.105	-164.465	8.434
5100	31.964	136.743	112.353	-295.495	-163.535	8.444
5200	31.966	137.008	112.723	-296.905	-162.645	8.454
5300	31.967	137.248	113.068	-298.335	-161.795	8.464
5400	31.968	137.463	113.388	-299.785	-160.985	8.474
5500	31.969	137.653	113.683	-301.255	-160.215	8.484
5600	31.969	137.818	113.953	-302.745	-159.485	8.494
5700	31.969	137.958	114.198	-304.255	-158.795	8.504
5800	31.969	138.073	114.418	-305.785	-158.145	8.514
5900	31.969	138.163	114.613	-307.335	-157.535	8.524
6000	31.969	138.228	114.783	-308.905	-156.965	8.534

Dec. 31, 1960; Sept. 30, 1963



MOL. WT. = 75.039

BERYLLIUM OXIDE TRIMERIC (Be_3O_3) (IDEAL GAS)

Point Group [D_{3h}]
 $\Delta H_f^0 = -250.7 \pm 9 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = -252 \pm 9 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = 11

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}
[730] (1)	[1390] (2)
[990] (1)	[1450] (2)
[1480] (1)	[610] (2)
[1100] (1)	[320] (2)

Bond Distances: Be-O = [1.63] Å $\sigma = [6]$

Bond Angle: Be-O-Be = [120°] O-Be-O = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [9.0658] \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

W. A. Chupka, J. Barkowitz, and C. P. Glease, J. Chem. Phys. **30**, 827 (1959) measured the change in the intensity of the $(\text{BeO})_3^+$ ion with temperature and obtained a second law heat of vaporization of $161 \pm 6 \text{ kcal. mole}^{-1}$ at 2150° K. The uncertainty is large because of an approximate correction of $8 \text{ kcal. mole}^{-1}$ and the neglect of fragmentation effects. We adopted a heat of sublimation at 2150° K. of $163 \text{ kcal. mole}^{-1}$ in order to bring the equilibrium vapor pressure into agreement with that measured by Chupka, at al.

Heat Capacity and Entropy.

The assumed D_{3h} symmetry implies eight vibrational frequencies of the types $2A_1$, A_2 , A_2' , $3E'$, and E_2' . The frequencies were estimated by comparison with the values for the $\text{Be}_2\text{O}(0^-)$ skeleton as given by J. L. Parsons, J. Chem. Phys. **33**, 1860 (1960) and the partial assignment of Borokina by S. K. Gupta and R. P. Porter, J. Phys. Chem. **67**, 1286 (1963). The bond length was taken as that in $\text{Be}_2\text{O}_2(\text{g})$, while the bond angle was arbitrarily taken as 120° . The individual moments of inertia were $I_A = I_B = 16.550$, $I_C = 33.010 \times 10^{-39} \text{ g. cm.}^2$



(Ideal Gas) Mol. Wt. = 100.052

BERYLLIUM OXIDE TETRAMERIC (Be₄O₄) (IDEAL GAS)

MOL. WT. = 100.052

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔF°	Log K _p
0	-0.000	INFINITE	-	-377.924	INFINITE
100	10.385	56.378	87.199	-375.876	821.287
200	15.434	65.025	74.054	-379.162	407.429
298	21.364	72.292	60.000	-389.614	270.921
300	21.473	72.425	60.000	-389.569	269.203
400	26.784	79.358	73.202	-380.769	194.932
500	30.818	85.792	85.085	-381.357	158.294
600	33.745	91.684	97.168	-381.799	130.497
700	35.860	97.053	107.903	-382.157	110.622
800	37.259	101.943	117.466	-382.460	98.490
900	38.259	106.423	126.000	-382.761	88.090
1000	39.434	110.533	133.688	-383.073	74.792
1100	40.110	114.325	140.394	-383.428	67.178
1200	40.642	117.898	146.202	-383.842	60.827
1300	41.064	121.265	151.111	-384.314	55.485
1400	41.412	124.465	155.828	-384.865	50.829
1500	41.694	127.433	160.167	-385.491	46.820
1600	41.924	129.731	164.075	-386.180	43.264
1700	42.110	131.369	167.500	-386.931	40.011
1800	42.261	132.312	170.450	-387.742	37.011
1900	42.383	132.682	172.925	-388.612	34.231
2000	42.485	133.162	174.920	-389.540	31.667
2100	42.560	133.741	176.437	-390.521	29.320
2200	42.612	134.410	177.571	-391.551	27.142
2300	42.648	135.150	178.319	-392.629	25.121
2400	42.669	135.954	178.677	-393.744	23.242
2500	42.676	136.817	178.747	-394.894	21.503
2600	42.672	137.733	178.623	-396.076	19.893
2700	42.658	138.703	178.309	-397.287	18.403
2800	42.635	139.729	177.800	-398.525	17.019
2900	42.603	140.813	177.100	-399.786	15.734
3000	42.563	141.957	176.210	-401.065	14.545
3100	42.516	143.161	175.137	-402.360	13.445
3200	42.463	144.425	173.980	-403.669	12.432
3300	42.404	145.749	172.741	-404.989	11.495
3400	42.340	147.133	171.420	-406.317	10.632
3500	42.271	148.576	170.019	-407.650	9.835
3600	42.198	150.078	168.540	-408.985	9.099
3700	42.121	151.639	166.980	-410.320	8.422
3800	42.040	153.260	165.330	-411.653	7.799
3900	41.955	154.941	163.600	-412.983	7.226
4000	41.867	156.672	161.790	-414.307	6.700
4100	41.776	158.453	159.900	-415.624	6.219
4200	41.682	160.284	157.930	-416.932	5.781
4300	41.585	162.165	155.880	-418.230	5.384
4400	41.485	164.096	153.750	-419.517	5.026
4500	41.382	166.077	151.540	-420.792	4.704
4600	41.276	168.107	149.260	-422.054	4.414
4700	41.167	170.186	146.910	-423.302	4.154
4800	41.055	172.314	144.480	-424.535	3.921
4900	40.940	174.491	142.000	-425.752	3.711
5000	40.822	176.716	139.470	-426.952	3.523
5100	40.701	178.989	136.900	-428.134	3.356
5200	40.577	181.310	134.290	-429.297	3.209
5300	40.451	183.680	131.640	-430.441	3.080
5400	40.322	186.100	128.960	-431.564	2.967
5500	40.191	188.570	126.250	-432.665	2.869
5600	40.058	191.090	123.510	-433.742	2.785
5700	39.923	193.660	120.740	-434.794	2.714
5800	39.786	196.280	117.950	-435.824	2.654
5900	39.647	198.950	115.140	-436.831	2.604
6000	39.506	201.670	112.310	-437.814	2.564

Dec. 31, 1960; Sept. 30, 1963

Point Group [D_{4h}]
ΔH_f° 0 = -376 ± 12 kcal. mole⁻¹
S_{298.15}° = [72.3] cal. deg.⁻¹ mole⁻¹
ΔH_f° 298.15 = -380 ± 12 kcal. mole⁻¹
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[700] (1)	[200] (2)
[850] (1)	[900] (1)
[1400] (1)	[400] (1)
[1000] (1)	[500] (1)
[800] (1)	[1150] (2)
[1000] (1)	[1200] (2)
[800] (1)	[600] (2)

Bond Distance: Be-O = [1.63] Å

σ = [9]

Bond Angle: Be-O-Be = [115°] O-Be-O = [155°]

Product of the Moments of Inertia: I_AI_BI_C = [1.11656] X 10⁻¹¹² g.³ cm.⁶

Heat of Formation

W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. 30, 827 (1959) measured the variation of intensity of the (BaO)₄ ion with temperature in a mass spectrometer. They reported a second law heat of vaporization of 177 ± 8 kcal. mole⁻¹ at 2150°K., which included an approximate correction of 9 kcal. mole⁻¹, and this value was adopted here.

Heat Capacity and Entropy

The assumed D_{4h} structure has 14 vibrational frequencies of the type 2A_{1g}, A_{2g}, 2B_{1g}, 2B_{2g}, E_g, A_{2u}, B_{2u}, E_{2u}, and 3E_u. The frequencies were estimated by comparison with (BaO)₃ and cyclobutane from G. W. Rathjens, N. K. Freeman, W. D. Olinn, and K. S. Fitzer, J. Am. Chem. Soc. 75, 5634 (1953). The estimated structure and frequencies gave an entropy which was in excellent agreement with the experimental heat and equilibrium constant determined by Chupka, et al.

The bond lengths were taken equal to those in Be₂O₂(g) and the angles were chosen so that O-Be-O was almost linear. The individual moments of inertia were calculated to be I_A = I_B = 38.219, I_C = 76.438 X 10⁻³⁹ g. cm.²

Beryllium Oxide, Pentameric (Be_5O_5)
(Ideal Gas) Mol. Wt. = 125.065

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _f
0	0.00	INFINITE	0	0	INFINITE
100	10.823	58.498	502.935	502.935	10.823
200	18.621	68.262	503.429	493.455	18.621
298	26.773	77.240	505.400	488.104	26.773
300	26.917	77.406	505.018	487.998	26.917
400	33.085	84.292	505.937	482.161	33.085
500	38.985	89.762	506.623	476.116	38.985
600	42.853	101.770	507.113	470.015	42.853
700	45.571	108.591	507.489	463.801	45.571
800	47.557	114.813	507.788	457.542	47.557
900	48.935	120.593	508.085	451.239	48.935
1000	50.156	125.750	508.390	444.896	50.156
1100	51.223	130.253	508.747	438.540	51.223
1200	52.175	135.023	509.174	432.141	52.175
1300	52.949	139.184	509.678	425.700	52.949
1400	53.571	142.783	510.271	419.222	53.571
1500	54.051	145.871	510.960	412.696	54.051
1600	54.391	148.494	512.023	405.726	54.391
1700	54.603	150.676	513.462	398.229	54.603
1800	54.815	152.467	515.191	390.712	54.815
1900	54.953	153.915	517.170	383.176	54.953
2000	55.053	155.062	519.452	375.624	55.053
2100	55.128	155.942	522.080	368.045	55.128
2200	55.185	156.598	524.999	360.441	55.185
2300	55.228	157.078	528.254	352.829	55.228
2400	55.262	157.402	531.896	345.187	55.262
2500	55.285	157.592	535.965	337.534	55.285
2600	55.300	157.668	540.494	329.892	55.300
2700	55.308	157.725	545.522	322.281	55.308
2800	55.312	157.768	551.199	314.724	55.312
2900	55.315	157.799	557.574	307.246	55.315
3000	55.318	157.818	564.600	299.869	55.318
3100	55.320	157.828	572.324	292.604	55.320
3200	55.322	157.831	580.704	285.469	55.322
3300	55.324	157.835	589.794	278.472	55.324
3400	55.326	157.839	599.649	271.624	55.326
3500	55.328	157.843	610.324	264.934	55.328
3600	55.330	157.847	621.784	258.404	55.330
3700	55.332	157.851	634.094	252.034	55.332
3800	55.334	157.855	647.314	245.824	55.334
3900	55.336	157.859	661.504	239.774	55.336
4000	55.338	157.863	676.734	233.884	55.338
4100	55.340	157.867	693.074	228.154	55.340
4200	55.342	157.871	710.594	222.574	55.342
4300	55.344	157.875	729.364	217.144	55.344
4400	55.346	157.879	749.464	211.864	55.346
4500	55.348	157.883	770.964	206.734	55.348
4600	55.350	157.887	793.934	201.754	55.350
4700	55.352	157.891	818.434	196.924	55.352
4800	55.354	157.895	844.534	192.244	55.354
4900	55.356	157.899	872.304	187.714	55.356
5000	55.358	157.903	901.804	183.334	55.358
5100	55.360	157.907	933.004	179.104	55.360
5200	55.362	157.911	965.984	175.024	55.362
5300	55.364	157.915	1000.824	171.094	55.364
5400	55.366	157.919	1037.604	167.414	55.366
5500	55.368	157.923	1076.414	163.884	55.368
5600	55.370	157.927	1117.344	160.504	55.370
5700	55.372	157.931	1160.484	157.274	55.372
5800	55.374	157.935	1205.834	154.194	55.374
5900	55.376	157.939	1253.494	151.264	55.376
6000	55.378	157.943	1303.474	148.484	55.378

Dec. 31, 1960; Sept. 30, 1963

Beryllium Oxide Pentameric (Be_5O_5)
(Ideal Gas) MOL. WT. = 125.065

Point Group [D_{5h}]
 $\Delta H_f^\circ = -502 \pm 18$ kcal. mole⁻¹
 $\Delta F_f^\circ = -505 \pm 18$ kcal. mole⁻¹
 $S_{298.15}^\circ = [77.24]$ cal. deg.⁻¹ mole⁻¹
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
[700] (1)	[1200] (2)
[850] (1)	[600] (2)
[1400] (1)	[500] (2)
[1100] (2)	[900] (1)
[900] (2)	[200] (2)
[1000] (2)	[400] (2)
[1200] (2)	[500] (2)

Bond Distances: Be-O = [1.63] Å $\sigma = [10]$

Bond Angle: Be-O-Be = [110°] O-Be-O = [178°]

Product of the Moment of Inertia: $I_A I_B I_C = [6.9653] \times 10^{-112}$ g.³ cm.⁶

Heat of Formation.

W. A. Chupka, J. Berkowitz, and C. F. Giese, *J. Chem. Phys.* **30**, 827 (1959) measured the variation in intensity of the $(\text{BeO})_5^+$ ion with temperature in a mass spectrometer. They calculated a second law heat of vaporization of 193 ± 12 kcal. mole⁻¹ at 2150°K., the uncertainty reflects the inclusion of an approximate correction of 10 kcal. mole⁻¹. This value was adopted here.

Heat Capacity and Entropy.

The assumed D_{5h} structure has 14 vibrations of the type $2A_1$, A_2 , $3E_1$, $4E_2$, E_1' , and $2E_2'$. These were estimated by comparison with similar motions in other ring structures including $(\text{BaO})_3$ and $(\text{BeO})_4$. The estimated structure and frequencies gave an entropy in good agreement with the experimental heat and equilibrium constant determined by Chupka, et al.

The bond length was assumed to be the same as in Be_2O_3 (g) and the angles were chosen so as to make O-Be-O almost linear. The individual moments of inertia are calculated to be $I_A = I_B = 70.356$, $I_C = 140.713 \times 10^{-39}$ g.² cm.²

(Ideal Gas) Mol. Wt. = 150.078

BERYLLIUM OXIDE HEXAMERIC (Be₆O)₆ (IDEAL GAS)

MOL. WT. = 150.078

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	12.000	0.000	INFINITE	-	5.133	-632.101	-632.101	1NF/MITE
100	21.063	60.631	102.456	-	4.223	-626.017	-626.017	1370.000
200	21.158	71.620	84.566	-	2.585	-634.619	-634.619	677.463
298	31.459	82.000	87.000	0.000	-836.000	-612.538	-612.538	448.991
300	31.664	82.195	87.000	0.000	-836.023	-612.594	-612.594	446.106
400	40.551	92.573	83.155	1.687	-637.161	-604.336	-604.336	330.177
500	47.149	102.371	86.100	8.091	-637.974	-596.025	-596.025	260.510
600	51.861	111.408	89.651	13.054	-638.528	-587.581	-587.581	214.016
700	57.682	127.216	97.126	25.070	-638.742	-570.086	-570.086	155.862
800	59.499	134.117	100.858	29.933	-639.523	-561.079	-561.079	136.434
900	60.874	140.461	104.506	35.955	-639.822	-553.225	-553.225	120.901
1000	61.945	146.315	108.004	42.098	-640.180	-545.549	-545.549	109.186
1100	62.769	150.721	111.477	50.646	-641.153	-537.082	-537.082	88.606
1200	63.434	154.752	114.757	59.646	-641.553	-527.882	-527.882	88.606
1300	63.972	161.513	117.930	61.017	-641.790	-518.288	-518.288	80.905
1400	64.413	165.943	120.086	67.437	-642.543	-509.543	-509.543	74.222
1500	64.778	170.112	123.026	73.897	-643.948	-500.069	-500.069	68.303
1600	65.085	173.021	125.426	80.712	-645.098	-490.938	-490.938	63.481
1700	65.344	175.776	127.491	86.913	-646.046	-482.066	-482.066	58.723
1800	65.565	178.401	129.491	93.458	-646.849	-473.406	-473.406	54.050
1900	65.754	180.881	131.315	100.024	-647.431	-465.052	-465.052	50.259
2000	65.919	183.250	132.909	106.608	-647.840	-456.986	-456.986	46.816
2100	66.062	185.534	134.297	113.207	-648.185	-449.271	-449.271	43.685
2200	66.187	187.769	135.596	119.820	-648.468	-441.948	-441.948	40.824
2300	66.297	189.964	136.824	126.444	-648.698	-435.066	-435.066	38.198
2400	66.395	192.129	137.999	133.079	-648.871	-428.566	-428.566	35.783
2500	66.482	194.268	139.123	139.723	-648.994	-422.448	-422.448	33.550
2600	66.559	196.381	140.197	146.373	-649.066	-416.691	-416.691	31.481
2700	66.629	198.470	141.226	153.035	-649.094	-411.294	-411.294	29.566
2800	66.692	200.539	142.210	159.701	-649.084	-406.246	-406.246	27.801
2900	66.749	202.588	143.151	166.373	-649.044	-401.546	-401.546	26.181
3000	66.800	204.620	144.050	173.050	-648.974	-397.186	-397.186	24.696
3100	66.846	206.634	144.906	179.733	-648.874	-393.166	-393.166	23.336
3200	66.887	208.630	145.726	186.420	-648.744	-389.486	-389.486	22.096
3300	66.924	210.600	146.509	193.111	-648.584	-386.146	-386.146	20.976
3400	66.956	212.546	147.254	199.806	-648.394	-383.146	-383.146	19.966
3500	66.984	214.470	147.964	206.506	-648.174	-380.486	-380.486	19.066
3600	66.997	216.380	148.639	213.216	-647.924	-378.146	-378.146	18.266
3700	67.007	218.276	149.276	220.036	-647.644	-376.026	-376.026	17.566
3800	67.014	220.159	149.884	226.866	-647.334	-374.126	-374.126	16.966
3900	67.019	222.030	150.464	233.706	-647.004	-372.446	-372.446	16.466
4000	67.022	223.890	151.016	240.556	-646.654	-370.976	-370.976	16.066
4100	67.024	225.740	151.546	247.416	-646.284	-369.716	-369.716	15.766
4200	67.025	227.580	152.056	254.286	-645.894	-368.656	-368.656	15.566
4300	67.026	229.410	152.546	261.166	-645.484	-367.796	-367.796	15.466
4400	67.027	231.230	153.016	268.056	-645.054	-367.126	-367.126	15.466
4500	67.028	233.040	153.466	274.956	-644.604	-366.646	-366.646	15.566
4600	67.029	234.840	153.896	281.866	-644.134	-366.346	-366.346	15.766
4700	67.030	236.630	154.306	288.786	-643.644	-366.126	-366.126	16.066
4800	67.031	238.410	154.696	295.716	-643.134	-366.076	-366.076	16.466
4900	67.032	240.180	155.066	302.656	-642.604	-366.196	-366.196	16.966
5000	67.033	241.940	155.416	309.606	-642.054	-366.376	-366.376	17.566
5100	67.034	243.690	155.746	316.566	-641.484	-366.616	-366.616	18.266
5200	67.035	245.430	156.056	323.536	-640.894	-366.916	-366.916	19.066
5300	67.036	247.160	156.346	330.516	-640.284	-367.276	-367.276	19.966
5400	67.037	248.880	156.616	337.506	-639.654	-367.696	-367.696	20.966
5500	67.038	250.590	156.866	344.506	-639.004	-368.176	-368.176	22.066
5600	67.039	252.290	157.096	351.516	-638.334	-368.716	-368.716	23.266
5700	67.040	253.980	157.306	358.536	-637.644	-369.316	-369.316	24.566
5800	67.041	255.660	157.496	365.566	-636.934	-369.976	-369.976	25.966
5900	67.042	257.330	157.666	372.606	-636.204	-370.696	-370.696	27.466
6000	67.043	258.990	157.816	379.656	-635.454	-371.476	-371.476	29.066

Dec. 31, 1960; Sept. 30, 1963

Point Group [D_{6h}]
 $\Delta H_f^\circ 0 = -632 \pm 22$ kcal. mole⁻¹
 $\Delta H_f^\circ 298.15 = -636 \pm 22$ kcal. mole⁻¹
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies			
ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
[700] (1)	[600] (2)	[900] (1)	[1100] (2)
[850] (1)	[750] (2)	[1100] (1)	[1200] (2)
[1400] (1)	[850] (2)	[1000] (1)	[500] (2)
[500] (1)	[850] (2)	[800] (1)	[200] (2)
[400] (1)	[950] (2)	[1400] (1)	[250] (2)

Bond Distance: Be-O = [1.63] Å

Bond Angle: Be-O-Be = [110°] O-Be-O = [190°]

Product of the Moments of Inertia: $I_A I_B I_C = [3.1266] \times 10^{-111}$ g.³ cm.⁶

Heat of Formation.

W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. **30**, 827 (1959) measured the temperature dependence of the (BeO)₆⁺ ion in a mass spectrometer. They calculated a second law heat of vaporization of 203 ± 15 kcal. mole⁻¹ which was adopted here. The uncertainty reflects in part an approximate correction of 10 kcal. mole⁻¹ and the small observed intensities.

Heat Capacity and Entropy.

The assumed symmetry D_{6h} has 20 vibrational frequencies of the type 2A_{1g}, A_{2g}, B_{1g}, B_{2g}, E_{1g}, 4E_{2g}, 2E_{1u}, 2E_{2u}, 3A_{1u}, and 2E_{2u}. The frequencies were estimated by comparison with similar motions in other ring molecules including benzene, (BeO)₃ and (BeO)₄. The assumed structure and vibrational frequencies gave an entropy in good agreement with the heat and equilibrium constant determined by Chupka, et al. The bond length was taken equal to that in BeO₂(s) the angles were chosen so that the O-Be-O angle was almost linear but with the Be-O-Be angle less than 120°. The individual moments of inertia were calculated to be I_A = I_B = 116.089, I_C = 232.118 X 10⁻³⁹ g. cm.²

Bromine, Monatomic (Br)
(Ideal Gas) Mol. Wt. = 79.916

T, K.	C _p	S°	(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	4.000	0.000	INFINITE	1.481	28.188	INFINITE	
100	4.968	36.378	46.222	9.844	25.357	55.415	
200	4.968	41.805	41.805	0.000	26.740	18.440	
298	4.968	41.805	41.805	0.000	26.740	18.440	
300	4.968	41.836	41.805	-0.009	26.733	19.658	14.319
400	4.968	43.265	42.000	1.508	23.110	16.044	9.858
500	4.971	44.374	42.368	1.003	23.165	16.771	7.330
600	4.979	45.261	42.780	1.500	23.216	15.407	5.641
700	4.997	46.050	43.194	1.999	23.271	14.194	4.431
800	5.028	46.719	43.593	2.500	23.324	12.894	3.522
900	5.063	47.313	43.974	3.005	23.379	11.587	2.814
1000	5.107	47.848	44.335	3.513	23.436	10.274	2.245
1100	5.153	48.337	44.677	4.026	23.500	8.954	1.779
1200	5.199	48.788	45.001	4.544	23.566	7.629	1.369
1300	5.243	49.206	45.309	5.066	23.633	6.299	1.059
1400	5.284	49.596	45.601	5.592	23.709	4.962	0.775
1500	5.320	49.961	45.880	6.122	23.785	3.620	0.527
1600	5.351	50.306	46.146	6.656	23.864	2.274	0.311
1700	5.377	50.631	46.400	7.192	23.945	0.922	0.116
1800	5.398	50.939	46.644	7.731	24.029	-0.435	0.053
1900	5.415	51.231	46.878	8.272	24.113	-1.796	0.207
2000	5.428	51.509	47.102	8.814	24.199	-3.162	0.346
2100	5.437	51.775	47.319	9.357	24.285	-4.532	0.472
2200	5.443	52.028	47.527	9.901	24.371	-5.907	0.587
2300	5.446	52.270	47.728	10.446	24.457	-7.284	0.692
2400	5.447	52.501	47.922	10.991	24.543	-8.666	0.789
2500	5.448	52.724	48.110	11.535	24.628	-10.052	0.879
2600	5.442	52.937	48.291	12.080	24.712	-11.440	0.962
2700	5.438	53.143	48.467	12.624	24.796	-12.833	1.039
2800	5.432	53.340	48.638	13.167	24.878	-14.228	1.110
2900	5.425	53.531	48.803	13.710	24.959	-15.626	1.178
3000	5.418	53.715	48.964	14.252	25.039	-17.027	1.240
3100	5.410	53.892	49.120	14.794	25.116	-18.430	1.299
3200	5.402	54.064	49.272	15.334	25.195	-19.836	1.355
3300	5.393	54.230	49.420	15.874	25.271	-21.243	1.407
3400	5.384	54.391	49.563	16.413	25.346	-22.656	1.456
3500	5.375	54.547	49.704	16.951	25.419	-24.068	1.503
3600	5.366	54.698	49.840	17.488	25.490	-25.484	1.547
3700	5.357	54.845	49.971	18.024	25.561	-26.901	1.589
3800	5.348	54.988	50.104	18.559	25.630	-28.319	1.629
3900	5.339	55.126	50.231	19.093	25.697	-29.739	1.666
4000	5.330	55.261	50.355	19.627	25.763	-31.163	1.703
4100	5.321	55.393	50.476	20.159	25.827	-32.587	1.737
4200	5.312	55.521	50.595	20.691	25.890	-34.012	1.770
4300	5.304	55.648	50.711	21.222	25.952	-35.436	1.801
4400	5.295	55.768	50.824	21.752	26.013	-36.866	1.831
4500	5.287	55.887	50.935	22.281	26.072	-38.297	1.860
4600	5.279	56.003	51.044	22.809	26.130	-39.727	1.887
4700	5.271	56.116	51.151	23.337	26.186	-41.159	1.914
4800	5.264	56.227	51.256	23.863	26.241	-42.594	1.939
4900	5.256	56.336	51.359	24.389	26.295	-44.027	1.964
5000	5.249	56.442	51.459	24.915	26.346	-45.463	1.987
5100	5.242	56.546	51.557	25.439	26.399	-46.901	2.010
5200	5.236	56.647	51.654	25.963	26.449	-48.336	2.032
5300	5.229	56.747	51.749	26.486	26.498	-49.776	2.052
5400	5.223	56.845	51.843	27.009	26.546	-51.217	2.073
5500	5.217	56.940	51.935	27.531	26.593	-52.656	2.092
5600	5.211	57.034	52.025	28.052	26.636	-54.099	2.111
5700	5.205	57.126	52.114	28.573	26.683	-55.540	2.129
5800	5.199	57.217	52.201	29.093	26.726	-56.982	2.147
5900	5.194	57.306	52.287	29.613	26.769	-58.426	2.164
6000	5.189	57.393	52.371	30.132	26.810	-59.873	2.181

September 30, 1961

Bromine, Monatomic (Br) (Ideal Gas) MOL. WT. = 79.916

ΔH°_f 298 = 28.188 ± 0.70 kcal. mole⁻¹
ΔH°_f 298 = 28.740 kcal. mole⁻¹
S°₂₉₈ = 41.805 cal. mole⁻¹ deg.⁻¹
Ground State = ²S_{1/2}

Electronic Levels and Multiplicities

ω, cm. ⁻¹	g _l	ω, cm. ⁻¹	g _l	ω, cm. ⁻¹	g _l
0.00	4	74686	6	86430	2
3685.00	2	75531	22	87500	10
83429.82	6	76736	4	88561	38
64900.50	4	77317	10	89700	56
66877.16	2	78540	14	90371	44
67176.87	4	79517	10	91737	70
68963.52	2	85724	30	92733	12

Thermodynamic Functions.

Thermodynamic functions were calculated using electronic levels and multiplicities listed by C. E. Moore [Nat'l. Bur. Standards Circ. 467 (1949)]. Higher levels were averaged. The results are in good agreement with W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Nat'l. Bur. Standards 55, 147 (1955)], who used essentially the same data.

Heat of Formation.

The heat of formation is calculated from the dissociation energy of bromine selected by Evans, Munson, and Wagman (loc. cit.) and the heat of sublimation derived for diatomic bromine. Evans, Munson, and Wagman list experimental vapor density measurements from the literature which agree with the spectroscopic value within their estimated uncertainty.

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f kcal. mole ⁻¹	ΔF° _f	Log K _p
0	∞.000	∞.000	∞.000	∞.000	5.279	5.279	∞.000
100	7.101	48.826	2.247	1.550	5.292	3.303	7.218
200	7.484	54.939	1.560	1.512	5.287	3.303	7.218
298	8.363	57.337	∞.000	∞.000	5.287	3.303	7.218
300	8.369	57.389	∞.015	∞.015	5.287	3.303	7.218
400	8.611	59.833	57.669	8.666	5.287	3.303	7.218
500	8.744	61.771	58.302	1.734	5.287	3.303	7.218
600	8.826	63.373	59.018	2.613	5.287	3.303	7.218
700	8.881	64.738	59.740	3.459	5.287	3.303	7.218
800	8.921	65.926	60.440	4.389	5.287	3.303	7.218
900	8.952	66.979	61.109	5.282	5.287	3.303	7.218
1000	8.977	67.923	61.744	6.179	5.287	3.303	7.218
1100	8.998	68.780	62.346	7.078	5.287	3.303	7.218
1200	9.016	69.563	62.915	7.978	5.287	3.303	7.218
1300	9.033	70.286	63.454	8.881	5.287	3.303	7.218
1400	9.048	70.956	63.967	9.785	5.287	3.303	7.218
1500	9.063	71.581	64.454	10.690	5.287	3.303	7.218
1600	9.076	72.166	64.918	11.597	5.287	3.303	7.218
1700	9.089	72.717	65.360	12.506	5.287	3.303	7.218
1800	9.102	73.236	65.784	13.415	5.287	3.303	7.218
1900	9.114	73.729	66.189	14.326	5.287	3.303	7.218
2000	9.126	74.197	66.578	15.238	5.287	3.303	7.218
2100	9.137	74.642	66.951	16.151	5.287	3.303	7.218
2200	9.148	75.068	67.311	17.065	5.287	3.303	7.218
2300	9.160	75.474	67.657	17.981	5.287	3.303	7.218
2400	9.171	75.865	67.991	18.897	5.287	3.303	7.218
2500	9.182	76.239	68.313	19.815	5.287	3.303	7.218
2600	9.192	76.599	68.625	20.734	5.287	3.303	7.218
2700	9.203	76.947	68.927	21.653	5.287	3.303	7.218
2800	9.214	77.281	69.219	22.574	5.287	3.303	7.218
2900	9.224	77.605	69.503	23.496	5.287	3.303	7.218
3000	9.235	77.918	69.778	24.419	5.287	3.303	7.218
3100	9.245	78.221	70.046	25.343	5.287	3.303	7.218
3200	9.256	78.514	70.306	26.268	5.287	3.303	7.218
3300	9.266	78.799	70.559	27.194	5.287	3.303	7.218
3400	9.276	79.076	70.805	28.121	5.287	3.303	7.218
3500	9.287	79.345	71.045	29.050	5.287	3.303	7.218
3600	9.297	79.607	71.280	29.979	5.287	3.303	7.218
3700	9.307	79.862	71.508	30.909	5.287	3.303	7.218
3800	9.317	80.110	71.731	31.840	5.287	3.303	7.218
3900	9.328	80.352	71.949	32.772	5.287	3.303	7.218
4000	9.338	80.589	72.162	33.706	5.287	3.303	7.218
4100	9.348	80.819	72.371	34.640	5.287	3.303	7.218
4200	9.358	81.045	72.574	35.575	5.287	3.303	7.218
4300	9.368	81.265	72.774	36.512	5.287	3.303	7.218
4400	9.378	81.481	72.969	37.450	5.287	3.303	7.218
4500	9.389	81.691	73.161	38.387	5.287	3.303	7.218
4600	9.399	81.898	73.349	39.327	5.287	3.303	7.218
4700	9.409	82.100	73.533	40.267	5.287	3.303	7.218
4800	9.419	82.298	73.713	41.208	5.287	3.303	7.218
4900	9.429	82.492	73.891	42.151	5.287	3.303	7.218
5000	9.439	82.683	74.064	43.094	5.287	3.303	7.218
5100	9.449	82.870	74.235	44.039	5.287	3.303	7.218
5200	9.459	83.054	74.404	44.984	5.287	3.303	7.218
5300	9.469	83.234	74.568	45.931	5.287	3.303	7.218
5400	9.479	83.411	74.729	46.876	5.287	3.303	7.218
5500	9.490	83.585	74.890	47.824	5.287	3.303	7.218
5600	9.500	83.756	75.046	48.776	5.287	3.303	7.218
5700	9.510	83.925	75.201	49.726	5.287	3.303	7.218
5800	9.520	84.090	75.353	50.676	5.287	3.303	7.218
5900	9.530	84.254	75.503	51.626	5.287	3.303	7.218
6000	9.540	84.413	75.649	52.584	5.287	3.303	7.218

Sept. 30, 1962; Sept. 30, 1965

Ground State Configuration $1\Sigma^+$
 $S_{298.15}^{\circ} = 57.337 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{\circ} 0 = 5.28 \pm 0.30 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = 3.50 \pm 0.3 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

ϵ , cm.⁻¹ g_i
0 1
 $\omega_e x_e = 1.8 \text{ cm.}^{-1}$
 $\omega_e = 443.1 \text{ cm.}^{-1}$
 $\alpha_e = 0.000757 \text{ cm.}^{-1}$
 $r_e = 2.136 \text{ \AA}$
 $\sigma = 1$

Heat of Formation.

The average $\Delta H_f^{\circ} 298.15 = -0.406 \text{ kcal. mole}^{-1}$ for the reaction $\text{Br}_2(\text{g}) + \text{Cl}_2(\text{g}) = 2\text{BrCl}(\text{g})$ and the $\Delta H_f^{\circ} 298.15 = -3.694 \text{ kcal. mole}^{-1}$ for $1/2 \text{ Br}_2(\text{g})$ from JANAP tables were used to calculate the $\Delta H_f^{\circ} 298.15 = 3.5 \pm 0.3 \text{ kcal. mole}^{-1}$. Other equilibrium measurements not included below have been summarized by Beeson and Yost, loc. cit.

Third Law $\Delta H_f^{\circ} 298.15$

Source	T°K	Method	kcal. mole ⁻¹
1	301	Light absorption	-0.51
2	298	Light absorption	-0.34
3	372-492	Total pressure Run III	-0.39
3	372-492	Total pressure Run II	-0.47
4	313-45	Mass spectrometric	-0.32
Average			-0.406

Source

- 1 H. G. Verper and G. K. Rollefson, J. Am. Chem. Soc. 56, 620 (1934).
- 2 G. Braune and E. Victor, Z Elektrochem. 41, 508 (1935).
- 3 C. M. Beeson and D. M. Yost, J. Am. Chem. Soc. 61, 1432 (1939).
- 4 H. C. Matraw, C. P. Pachucki and N. J. Hawkins, General Electric Co., Report No. KAPL-1016 (1953) Knolls Atomic Power Laboratory, Schenectady, New York.

Heat Capacity and Entropy.

All spectroscopic and molecular constants were obtained from W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Natl. Bur. of Standards, 55, 147 (1955) except r_e which was calculated from B_e. The value of r_e was reported to be 2.13 Å by C. M. Beeson and D. M. Yost, J. Am. Chem. Soc. 61, 1432 (1939) and L. O. Cole and G. W. Elverum Jr., J. Chem. Phys., 20, 1543 (1952), respectively. Ground state configuration was taken from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

Bromine Monofluoride (BrF)

(Ideal Gas) Mol. Wt. = 98.9074

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	Log K _p
0	6.000	INFINITE	2.156	-12.144	INFINITE
100	6.970	46.743	1.460	-12.130	10.872
200	7.352	51.663	0.748	-12.354	17.529
298	7.877	54.700	0.000	-13.073	12.927
300	7.885	54.749	0.015	-13.082	12.863
400	8.285	55.014	0.742	-13.589	7.903
500	8.488	56.491	1.661	-14.257	7.937
600	8.640	60.503	2.518	-14.689	6.682
700	8.744	61.843	3.387	-14.956	5.762
800	8.850	63.015	4.266	-15.094	5.071
900	8.957	64.087	5.154	-15.158	4.583
1000	9.022	64.995	6.041	-15.198	4.105
1100	9.060	65.848	6.935	-15.211	3.753
1200	9.092	66.659	7.833	-15.203	3.460
1300	9.119	67.449	8.733	-15.170	3.212
1400	9.143	68.216	9.634	-15.116	2.995
1500	9.167	68.964	10.542	-15.041	2.805
1600	9.187	69.229	11.450	-14.947	2.654
1700	9.207	69.781	12.359	-14.834	2.511
1800	9.226	70.302	13.271	-14.708	2.385
1900	9.243	70.792	14.186	-14.571	2.276
2000	9.260	71.295	15.099	-14.428	2.169
2100	9.276	71.713	16.016	-14.277	2.077
2200	9.292	72.140	16.935	-14.119	1.993
2300	9.307	72.549	17.855	-13.955	1.916
2400	9.322	72.937	18.776	-13.786	1.842
2500	9.237	73.318	19.699	-13.612	1.782
2600	9.252	73.680	20.623	-13.434	1.722
2700	9.266	74.030	21.549	-13.251	1.666
2800	9.280	74.367	22.477	-13.064	1.613
2900	9.294	74.694	23.406	-12.872	1.562
3000	9.309	75.008	24.336	-12.676	1.512
3100	9.322	75.314	25.267	-12.475	1.461
3200	9.336	75.610	26.200	-12.269	1.411
3300	9.349	75.897	27.134	-12.058	1.361
3400	9.362	76.177	28.067	-11.842	1.311
3500	9.377	76.448	29.007	-11.621	1.261
3600	9.390	76.713	29.945	-11.395	1.211
3700	9.404	76.970	30.885	-11.164	1.161
3800	9.417	77.221	31.826	-10.928	1.111
3900	9.430	77.466	32.766	-10.687	1.061
4000	9.444	77.705	33.712	-10.441	1.011
4100	9.457	77.938	34.657	-10.190	0.961
4200	9.470	78.166	35.604	-9.934	0.911
4300	9.483	78.389	36.551	-9.673	0.861
4400	9.496	78.607	37.500	-9.407	0.811
4500	9.509	78.821	38.451	-9.136	0.761
4600	9.523	79.030	39.402	-8.860	0.711
4700	9.536	79.235	40.355	-8.584	0.661
4800	9.549	79.436	41.308	-8.303	0.611
4900	9.562	79.633	42.265	-8.017	0.561
5000	9.575	79.826	43.222	-7.726	0.511
5100	9.588	80.016	44.180	-7.431	0.461
5200	9.601	80.202	45.139	-7.132	0.411
5300	9.614	80.384	46.098	-6.828	0.361
5400	9.627	80.565	47.057	-6.520	0.311
5500	9.640	80.742	48.025	-6.207	0.261
5600	9.653	80.916	48.990	-5.890	0.211
5700	9.666	81.086	49.956	-5.568	0.161
5800	9.679	81.256	50.922	-5.242	0.111
5900	9.691	81.420	51.892	-4.912	0.061
6000	9.704	81.583	52.861	-4.577	0.011

June 30, 1962; Sept. 30, 1965

BROMINE MONOFLUORIDE (BrF)

(IDEAL GAS)

MOL. WT. = 98.9074

Ground State Configuration $1\sum^+$ $\Delta H_f^o = -12.1 \pm 0.4$ kcal. mole⁻¹

$S_{298.15}^o = 54.700$ cal. deg.⁻¹ mole⁻¹ $\Delta H_f^o 298.15 = -14.0 \pm 0.4$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

ϵ , cm.⁻¹ g_i

0 1

$\omega_e x_e = 4$ cm.⁻¹

$\omega_e = 0.005206$ cm.⁻¹

$\sigma = 1$

$r_e = 1.7555$ Å

Heat of Formation.

The equilibrium constant for the reaction $\text{Br}_2(\text{g}) + \text{BrF}_3(\text{g}) = 3\text{BrF}(\text{g})$ has been measured over the temperature range 328-380°K. by R. K. Steunenberg, R. C. Vogel and J. Fischer, J. Am. Chem. Soc. **79**, 1320 (1957). Third law analysis of the data yields a $\Delta H_f^o 298 = 11.785 \pm 0.2$ kcal. mole⁻¹, with a drift of -0.6 ± 1.2 cal. mole⁻¹ deg.⁻¹. Second law analysis yields $\Delta H_f^o 298 = 11.98 \pm 0.45$ kcal. mole⁻¹, thus it is obvious that the data is thermodynamically self consistent. There is uncertainty in the entropy of $\text{BrF}_3(\text{g})$ of ± 1 cal. mole⁻¹ deg.⁻¹ but this corresponds only to ± 0.35 kcal. mole⁻¹ in $\Delta H_f^o 298$, thus a best value of $\Delta H_f^o 298 = 11.78 \pm 0.5$ kcal. mole⁻¹ is adopted. This yields $\Delta H_f^o 298 \text{ BrF} = -13.973 \pm 0.4$ kcal. mole⁻¹, the uncertainty in the heat of formation being a maximum value comprising the sum of the uncertainties in Br_2 , BrF_3 and ΔH_f^o .

Attempts have been made to analyze the spectra of BrF to obtain a D^o value. P. H. Broderick and J. E. Sicra, Z. Physik **141**, 515 (1955) obtained two dissociation limits for BrF of 66.52 kcal. mole⁻¹ and 54.98 kcal. mole⁻¹. The difference corresponds to the $\text{Br}(^2P_{1/2}) - \text{Br}(^2P_{3/2})$ excitation energy, indicating that the upper state goes to $\text{F}(^2P_{3/2})$ and $\text{Br}(^2P_{3/2})$. This yields a heat of formation of BrF of -10.23 kcal. mole⁻¹. Since this value is well outside the possible uncertainty limits of the equilibrium data we must conclude that the extrapolation is in error. W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Natl. Bur. Std. **55**, 147 (1955) have also analyzed the spectra and conclude that a heat of formation of -14.4 kcal. mole⁻¹ is possible. However M. H. Evans, private communication Nov. 1965, now believes that the dissociating state was too strongly perturbed for meaningful extrapolation.

Heat Capacity and Entropy.

All molecular constants were obtained from W. H. Evans, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. of Standards **55**, 147 (1955) except r_e and ground state configuration which were taken from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

BROMINE TRIFLUORIDE (BrF₃)

(IDEAL GAS)

MOL. WT. = 136.9042

Point Group C_{2v}

$$\Delta H_f^\circ = -58.4 \pm 0.7 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = 69.867 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^\circ = 298.15 = -61.1 \pm 0.7 \text{ kcal. mole}^{-1}$$

Vibrational Frequencies and Degeneracies

$\bar{\nu}$, cm. ⁻¹	$\bar{\nu}$, cm. ⁻¹
674 (1)	613 (1)
[528] (1)	[384] (1)
[300] (1)	[289] (1)

$$\text{Bond Distances: Br-F}_1 = \text{Br-F}_3 = 1.8081 \text{ \AA} \quad \text{Br-F}_2 = 1.721 \text{ \AA}$$

$$\text{Bond Angle: F}_1\text{-Br-F}_2 = 86^\circ 12.6' \quad \text{F}_2\text{-Br-F}_3 = 86^\circ 12.8' \quad \text{F}_3\text{-Br-F}_1 = 187^\circ 34.8'$$

$$\text{Product of the Moment of Inertia: } I_A I_B I_C = 4.519225 \times 10^{-114} \text{ g.}^3 \text{ cm.}^3$$

Heat of Formation.

The ΔH_f° 298.15 = -61.087 $\pm$ 0.7 kcal. mole⁻¹ is from L. Stein, J. Phys. Chem. 66, 288 (1962) and was derived from heats of reaction of F₂ with Br₂ which were measured in an adiabatic calorimeter. Stein's value for the ΔH_f° 298.15 = -64.78 kcal. mole⁻¹ was based upon gaseous Br₂, which has been adjusted to the liquid Br₂ reference state at 298.15°K.

Heat Capacity and Entropy.

D. W. Magnuson, Report No. K-1173, Carbide and Carbon Chemicals Co., K-25 plant, Oak Ridge, Tennessee (December, 1954) determined the moments of inertia and quadrupole coupling coefficients of both Br⁷⁹F₃ and Br⁸¹F₃ from a number of microwave transitions. From the moment of inertia of the bromine trifluoride molecule was found to have a distorted -T_h structure with one short, 1.721 Å, and two long, 1.810 Å Br-F bonds. The FBrF angle was found to be 86° 12.6'.

H. H. Claassen, B. Weinatock, and J. G. Malm, J. Chem. Phys. 28, 285 (1958), observed two of the six vibrational levels in the vapor, and calculated the other four levels from a normal coordinate treatment of the molecule. They also obtained a measured entropy of BrF₃(g), from low temperature data combined with vapor pressure data and an approximate correction for dimerization. This value is 71.9 e.u. at 316.27°K. compared with a value of 70.82 e.u. from this table, the difference is probably within the uncertainty of the data. The three principal moments of inertia are: I_A = 7.7514 $\times$ 10⁻³⁹, I_B = 2.05791 $\times$ 10⁻³⁸ and I_C = 2.83308 $\times$ 10⁻³⁸ g. cm.²

June 30, 1962; Sept. 30, 1965

Bromine Pentafluoride (BrF₅)
(Ideal Gas) Mol. Wt. = 174.901

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH°	ΔF°	Log K _p
0	∞	∞	∞	∞	∞	∞
100	11.313	58.201	4.584	-98.846	-98.846	INFINITE
200	16.311	68.612	9.529	-100.043	-95.045	207.712
298	24.236	77.337	12.611	-102.466	-98.004	98.004
300	24.304	77.487	12.738	-102.473	-98.004	98.004
400	27.005	84.888	17.328	-105.939	-98.004	98.004
500	28.524	91.092	20.444	-105.614	-98.004	98.004
600	29.439	96.380	22.562	-105.237	-98.004	98.004
700	30.229	100.966	24.262	-104.835	-98.004	98.004
800	30.919	105.002	25.562	-104.425	-98.004	98.004
900	31.524	108.602	26.562	-104.007	-98.004	98.004
1000	32.059	111.847	27.364	-103.590	-98.004	98.004
1100	32.550	114.709	28.000	-103.173	-98.004	98.004
1200	33.000	117.200	28.500	-102.756	-98.004	98.004
1300	33.412	119.356	28.900	-102.340	-98.004	98.004
1400	33.793	121.224	29.200	-101.924	-98.004	98.004
1500	34.150	122.846	29.400	-101.508	-98.004	98.004
1600	34.488	124.256	29.500	-101.092	-98.004	98.004
1700	34.811	125.500	29.500	-100.676	-98.004	98.004
1800	35.121	126.600	29.400	-100.260	-98.004	98.004
1900	35.418	127.576	29.200	-99.844	-98.004	98.004
2000	35.703	128.440	28.900	-99.428	-98.004	98.004
2100	35.976	129.200	28.500	-99.012	-98.004	98.004
2200	36.237	129.876	28.000	-98.596	-98.004	98.004
2300	36.486	130.476	27.400	-98.180	-98.004	98.004
2400	36.723	131.000	26.700	-97.764	-98.004	98.004
2500	36.948	131.456	25.900	-97.348	-98.004	98.004
2600	37.161	131.840	25.000	-96.932	-98.004	98.004
2700	37.361	132.156	24.000	-96.516	-98.004	98.004
2800	37.548	132.400	23.000	-96.100	-98.004	98.004
2900	37.723	132.576	22.000	-95.684	-98.004	98.004
3000	37.886	132.680	21.000	-95.268	-98.004	98.004
3100	38.037	132.716	20.000	-94.852	-98.004	98.004
3200	38.176	132.680	19.000	-94.436	-98.004	98.004
3300	38.303	132.576	18.000	-94.020	-98.004	98.004
3400	38.418	132.400	17.000	-93.604	-98.004	98.004
3500	38.521	132.156	16.000	-93.188	-98.004	98.004
3600	38.612	131.840	15.000	-92.772	-98.004	98.004
3700	38.691	131.456	14.000	-92.356	-98.004	98.004
3800	38.758	131.000	13.000	-91.940	-98.004	98.004
3900	38.812	130.476	12.000	-91.524	-98.004	98.004
4000	38.853	129.876	11.000	-91.108	-98.004	98.004
4100	38.881	129.200	10.000	-90.692	-98.004	98.004
4200	38.896	128.440	9.000	-90.276	-98.004	98.004
4300	38.899	127.576	8.000	-89.860	-98.004	98.004
4400	38.889	126.600	7.000	-89.444	-98.004	98.004
4500	38.866	125.500	6.000	-89.028	-98.004	98.004
4600	38.831	124.256	5.000	-88.612	-98.004	98.004
4700	38.784	122.846	4.000	-88.196	-98.004	98.004
4800	38.726	121.224	3.000	-87.780	-98.004	98.004
4900	38.657	119.356	2.000	-87.364	-98.004	98.004
5000	38.578	117.200	1.000	-86.948	-98.004	98.004
5100	38.488	114.709	0.000	-86.532	-98.004	98.004
5200	38.388	111.847		-86.116	-98.004	98.004
5300	38.279	108.602		-85.700	-98.004	98.004
5400	38.161	105.002		-85.284	-98.004	98.004
5500	38.034	100.966		-84.868	-98.004	98.004
5600	37.898	96.380		-84.452	-98.004	98.004
5700	37.753	91.092		-84.036	-98.004	98.004
5800	37.599	84.888		-83.620	-98.004	98.004
5900	37.436	77.487		-83.204	-98.004	98.004
6000	37.264	68.612		-82.788	-98.004	98.004

Sapt. 30, 1962 Sept. 30, 1965

BrF₅

MOL. WT. = 174.901

(IDEAL GAS)

BROMINE PENTAFLUORIDE (BrF₅)

Point Group C_{4v}
S^{298.15} = 77.34 cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ = -98.8 ± 0.5 kcal. mole⁻¹
ΔH_f^{298.15} = -102.5 ± 0.5 kcal. mole⁻¹
Vibrational Frequencies and Degeneracies
ν₁, cm.⁻¹ 683 (1) 535 (1) 644 (2) 415 (2) 245 (2)
ν₂, cm.⁻¹ 369 (1) 312 (1)
Bond Distances: Br-F_{axial} = 1.79 Å Br-F_{equatorial} = 1.68 Å
Bond Angles: F_{axial}-Br-F_{equatorial} = [90°] and F_{equatorial}-Br-F_{equatorial} = [90°]
Product of the Moment of Inertia: I_AI_BI_C = 3.2035 X 10⁻¹¹³ g.³ cm.⁶
Heat of Formation.
The ΔH_f^{298.15} = -102.466 ± 0.5 kcal. mole⁻¹ is from L. Stein J. Phys. Chem. 66, 289 (1962) and was derived from heats of reaction of F₂ with Br₂ which were measured in an adiabatic calorimeter. Stein's value for the ΔH_f^{298.15} = -106.16 kcal. mole⁻¹ was based upon gaseous Br₂ which has been adjusted to the liquid Br₂ reference state at 298.15°K.

Heat Capacity and Entropy.

O. M. Begun, W. H. Fletcher and D. P. Smith, J. Chem. Phys. 42, 2235 (1965) report the infrared (gas phase) and Raman (liquid phase) spectra and correlate the observations by means of normal coordinate calculations for the similar molecules BrF₃, IF₃, ClF₃ and XeOF₄. The fundamental frequencies are taken from Begun, et al., except for ν₂ which was beyond the range of their infrared measurements. The value ν₂ = 245 cm.⁻¹ for the gas has been observed by R. S. McDevell and L. B. Asprey, J. Chem. Phys. 37, 165 (1962) and is confirmed by 237 cm.⁻¹ found in the Raman spectra of the liquid. Raman values from the liquid were used for the infrared inactive fundamentals ν₄ and ν₅. One Raman active frequency, presumably ν₆, is not observed in any of the four molecules. The value ν₆ = 261 cm.⁻¹ was obtained from the normal coordinate calculation. Previous Raman studies were reported by C. V. Stephenson and E. A. Jones, J. Chem. Phys. 20, 1830 (1952).

A tetragonal pyramidal structure (C_{4v} symmetry) with the above parameters was used by Begun, et al., in the analysis of the spectra. This symmetry is consistent with the NMR spectra of H. S. Outowsky and C. J. Hoffman, J. Chem. Phys. 19, 1259 (1951), with the dipole moment determined by M. T. Rogers, R. D. Pruett, H. B. Thompson and J. L. Speiser, J. Am. Chem. Soc. 78, 44 (1956), and with the X-ray crystal structure obtained by R. D. Burbank and F. N. Benesey, Jr., J. Chem. Phys. 27, 982 (1957). Bond distances were based on those in the crystal and the bond angle was assumed to be 90°, slightly larger than those in the crystal (90.5-86.5°). Begun, et al., indicate that the angle in the gaseous molecule is probably not exactly 90° but that the normal coordinate calculations are not sensitive to this angle. The three principal moments of inertia are: I_A = 2.61497 X 10⁻³⁸, I_B = 2.61497 X 10⁻³⁸ and I_C = 4.04277 X 10⁻³⁸ g. cm.²

T, °K.	C _p	S° - (F° - H°)/T	H° - H° ₂₉₈	ΔH _f [°]	Log K _p
0	∞.000	INFINITE	-2.067	-6.836	INFINITE
100	6.959	39.861	-1.379	-6.861	19.635
200	6.961	44.685	-0.893	-11.048	12.072
300	6.965	47.465	-0.603	-12.705	9.372
400	6.965	47.508	-0.432	-12.810	8.332
500	6.984	48.514	-0.310	-12.840	7.324
600	7.040	51.078	-0.256	-12.580	5.955
700	7.139	52.369	-0.227	-12.665	5.036
800	7.272	53.479	-0.210	-12.743	4.374
900	7.423	54.460	-0.199	-12.809	3.876
1000	7.576	55.343	-0.190	-12.864	3.486
1100	7.725	56.149	-0.180	-12.908	3.173
1200	7.863	56.892	-0.170	-12.942	2.917
1300	7.989	57.582	-0.160	-12.968	2.702
1400	8.103	58.226	-0.150	-12.988	2.520
1500	8.205	58.830	-0.140	-13.003	2.364
1600	8.296	59.399	-0.130	-13.014	2.229
1700	8.378	59.937	-0.120	-13.024	2.110
1800	8.451	60.448	-0.110	-13.031	2.006
1900	8.517	60.933	-0.100	-13.037	1.913
2000	8.577	61.395	-0.090	-13.041	1.829
2100	8.630	61.836	-0.080	-13.045	1.754
2200	8.679	62.258	-0.070	-13.048	1.686
2300	8.724	62.663	-0.060	-13.052	1.625
2400	8.765	63.052	-0.050	-13.056	1.568
2500	8.803	63.426	-0.040	-13.060	1.517
2600	8.838	63.786	-0.030	-13.065	1.469
2700	8.870	64.133	-0.020	-13.070	1.425
2800	8.900	64.468	-0.010	-13.075	1.384
2900	8.929	64.792	-0.005	-13.080	1.347
3000	8.955	65.106	-0.000	-13.084	1.311
3100	8.980	65.410	0.000	-13.103	1.278
3200	9.004	65.705	0.000	-13.103	1.248
3300	9.027	65.991	0.000	-13.111	1.219
3400	9.048	66.269	0.000	-13.121	1.192
3500	9.068	66.540	0.000	-13.131	1.166
3600	9.088	66.803	0.000	-13.142	1.142
3700	9.107	67.059	0.000	-13.155	1.119
3800	9.125	67.309	0.000	-13.168	1.098
3900	9.143	67.553	0.000	-13.182	1.077
4000	9.160	67.790	0.000	-13.198	1.058
4100	9.176	68.023	0.000	-13.215	1.039
4200	9.192	68.249	0.000	-13.232	1.022
4300	9.208	68.471	0.000	-13.251	1.005
4400	9.223	68.688	0.000	-13.271	0.989
4500	9.238	68.900	0.000	-13.292	0.973
4600	9.252	69.108	0.000	-13.314	0.959
4700	9.266	69.311	0.000	-13.338	0.945
4800	9.280	69.511	0.000	-13.362	0.931
4900	9.294	69.706	0.000	-13.388	0.918
5000	9.308	69.896	0.000	-13.414	0.904
5100	9.333	70.271	0.000	-13.471	0.882
5200	9.346	70.452	0.000	-13.501	0.871
5300	9.360	70.625	0.000	-13.532	0.860
5400	9.373	70.790	0.000	-13.564	0.849
5500	9.383	70.977	0.000	-13.597	0.840
5600	9.395	71.147	0.000	-13.632	0.831
5700	9.407	71.313	0.000	-13.667	0.821
5800	9.419	71.477	0.000	-13.703	0.812
5900	9.431	71.638	0.000	-13.740	0.803
6000	9.442	71.796	0.000	-13.779	0.795

Sept. 30, 1961; Sept. 30, 1965

HYDROGEN BROMIDE (HBr)

(IDEAL GAS)

MOL. WT. = 80.91697

$\Delta H_f^{\circ} 0 = -6.84 \pm 0.13 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = -8.71 \pm 0.10 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{E}{\text{cm}^{-1}} = \frac{g_1}{0} - \frac{g_2}{1}$$

$\omega_e = 2649.218 \pm 0.016 \text{ cm}^{-1}$
 $\omega_e^* = 45.246 \pm 0.008 \text{ cm}^{-1}$
 $\alpha_e = 0.23248 \pm 7 \times 10^{-5} \text{ cm}^{-1}$

Heat of Formation

The enthalpy change, $\Delta H_f^{\circ} 376.2 = -12.47 \pm 0.13 \text{ kcal. mole}^{-1}$, for the reaction $(1) 1/2 \text{ H}_2(\text{g}) + 1/2 \text{ Br}_2(\text{g}) = \text{HBr}(\text{g})$ was reported by J. R. Lacher, L. Casali, and J. D. Park, J. Phys. Chem. **50**, 608 (1956). Using $\Delta H_f^{\circ} 298.15$ (Br_2, g) = $7.59 \text{ kcal. mole}^{-1}$, the $\Delta H_f^{\circ} 298.15$ (HBr, g) was derived as $-8.71 \pm 0.13 \text{ kcal. mole}^{-1}$.

The heat of oxidation of aqueous sulfur dioxide with gaseous chlorine and liquid bromine were determined by calorimetric methods by W. H. Johnson and J. R. Ambrose, J. Res. Natl. Bur. Std. **67A**, 427 (1963) and W. H. Johnson and S. Sumner, Acta Chem. Scand., **11**, 1917 (1957), respectively. The results were given as $\Delta H_f^{\circ} 298.15 = -77.28 \pm 0.14 \text{ kcal. mole}^{-1}$ ($\text{X}_2 = \text{Cl}_2(\text{g})$) and $-55.47 \pm 0.11 \text{ kcal. mole}^{-1}$ ($\text{X}_2 = \text{Br}_2(\text{l})$) for the reaction $\text{X}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + 2 \text{ H}_2\text{O}(\text{l}) = \text{H}_2\text{SO}_4 + 2 \text{ H}_2\text{O}(\text{l}) = \text{H}_2\text{SO}_4 + 2 \text{ H}_2\text{O}(\text{l})$. The enthalpy change for the reaction $\text{Cl}_2(\text{g}) + 2 (\text{HBr} \cdot \infty \text{H}_2\text{O}) = \text{Br}_2(\text{l}) + 2 \text{ H}_2\text{O}(\text{l}) = \text{H}_2\text{SO}_4 + 2 \text{ H}_2\text{O}(\text{l})$ was calculated to be $-21.82 \pm 0.18 \text{ kcal. mole}^{-1}$. Using $\Delta H_f^{\circ} 298.15$ ($\text{HCl} \cdot 1250 \text{ H}_2\text{O}$) = $-39.93 \pm 0.05 \text{ kcal. mole}^{-1}$, the heat of formation for $\text{HBr} \cdot 1250 \text{ H}_2\text{O}$ was derived to be $-28.53 \pm 0.10 \text{ kcal. mole}^{-1}$. Employing $\Delta H_f^{\circ} (\text{HBr} \cdot 1250 \text{ H}_2\text{O}) = -20.350 \pm 0.012 \text{ kcal. mole}^{-1}$, leads to $\Delta H_f^{\circ} 298.15$ ($\text{HBr} \cdot \infty \text{H}_2\text{O}$) = $-29.016 \pm 0.10 \text{ kcal. mole}^{-1}$. Based on the value, $\Delta H_f^{\circ} 298.15 = -20.350 \pm 0.012 \text{ kcal. mole}^{-1}$ for the reaction $\text{HBr}(\text{g}) = \text{HBr}(\infty \text{H}_2\text{O})$ reported by C. E. Vandervee and J. D. Mitter, J. Phys. Chem. **67**, 2521 (1963), the heat of formation ($\Delta H_f^{\circ} 298.15$) for $\text{HBr}(\text{g})$ was evaluated as $-8.67 \pm 0.10 \text{ kcal. mole}^{-1}$.

The heats of oxidation of As_2O_3 to As_2O_5 in aqueous solution with $\text{Br}_2(\text{l})$ and $\text{Cl}_2(\text{g})$ were measured by L. Bjellerup, S. Sumner and I. Wedberg, Acta Chem. Scand., **11**, 1761 (1957) and S. Thoren, Symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July, 1963. Using the values $\Delta H_f^{\circ} = -56.61 \pm 0.11 \text{ kcal. mole}^{-1}$ ($\text{X}_2 = \text{Br}_2(\text{l})$) and $-100.09 \pm 0.08 \text{ kcal. mole}^{-1}$ ($\text{X}_2 = \text{Cl}_2(\text{g})$) for the reaction $\text{As}_2\text{O}_3(\text{aq.}) + 2 \text{X}_2 + 2 \text{ H}_2\text{O}(\text{aq.}) \rightarrow \text{As}_2\text{O}_5(\text{aq.}) + 4 \text{ HX}(\text{aq.})$ obtained from H. A. Skinner, Pure Appl. Chem. **9**, 95 (1964), the enthalpy change for the reaction $2\text{HBr}_2(\text{l}) + 4\text{HCl}(\text{aq.}) = 2\text{Cl}_2 + 4\text{HBr}(\text{aq.})$ was calculated to be $+43.48 \pm 0.14 \text{ kcal. mole}^{-1}$. Based on ΔH_f° reaction $2\text{HBr}_2(\text{l}) + 4\text{HCl}(\text{aq.}) = 2\text{Cl}_2 + 4\text{HBr}(\text{aq.})$ was calculated to be $+43.48 \pm 0.14 \text{ kcal. mole}^{-1}$. Based on ΔH_f° ($\text{HCl} \cdot \infty \text{H}_2\text{O}$) = $-39.93 \pm 0.05 \text{ kcal. mole}^{-1}$, the value of $\Delta H_f^{\circ} 298.15$ ($\text{HBr} \cdot \infty \text{H}_2\text{O}$) was derived to be $-29.06 \pm 0.06 \text{ kcal. mole}^{-1}$, yielding $\Delta H_f^{\circ} 298.15$ (HBr, g) = $-8.71 \pm 0.06 \text{ kcal. mole}^{-1}$.

The value of $\Delta H_f^{\circ} 298.15$ (HBr, g) adopted is $-8.71 \pm 0.10 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy

The values of ω_e , ω_e^* , B_e and α_e were taken from T. C. James and R. J. Thibault, J. Chem. Phys. **42**, 1450 (1965), and corrected to the average isotopic species. Submillimeter-wave spectra of HBr were measured by G. Jones and W. Gordy, Phys. Rev. **135**, A 1223 (1964). The molecular constants derived were close to the values adopted. The ground state configuration was obtained from G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand Company, Inc., New York, 1950, in which molecular constants for $\text{HBr}(\text{g})$ were also given. A precise measurement of the infrared fundamental bands of HBr has been made by E. K. Plyler, J. Res. Natl. Bur. Std., **64**, 377 (1960). The corresponding rotational and vibrational constants have been calculated from the observed data. The moment of inertia is $3.30514 \times 10^{-40} \text{ g. cm}^2$.

BrH

Ammonium Bromide (NH₄Br)

(Crystal) Mol. Wt. = 97.94758

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	- 4.052	- 60.939	- 60.939	INFINITE
100	10.584	43.950	- 3.542	- 62.623	- 56.049	122.490
200	18.512	28.975	- 2.053	- 63.277	- 49.203	53.764
298	21.194	26.970	0.000	- 64.900	- 42.005	30.847
300	21.246	27.101	0.039	- 64.910	- 41.943	30.554
400	22.160	33.381	2.224	- 68.581	- 33.532	18.320
500	26.840	38.597	4.942	- 68.095	- 24.908	10.887
600	24.480	43.728	7.213	- 67.084	- 16.270	5.029
700	27.500	47.751	9.814	- 67.597	- 7.607	2.009
800	30.300	51.591	12.707	- 66.935	- 8.827	0.226
900	32.700	55.300	15.859	- 66.036	- 9.247	- 2.245
1000	34.900	58.861	19.241	- 64.927	- 17.554	- 5.836
1100	36.831	62.279	22.820	- 63.636	- 35.741	- 8.114
1200	38.600	65.561	26.602	- 62.189	- 53.805	- 9.154
1300	40.183	68.714	30.542	- 60.589	- 71.759	- 7.017
1400	41.650	71.746	34.634	- 58.868	- 89.547	- 7.734
1500	43.000	74.667	38.868	- 57.035	- 107.228	- 8.338

MOL. WT. = 97.94758

(CRYSTAL)

AMMONIUM BROMIDE (NH₄Br)



ΔH_f^o 0 = -60.9 ± 0.3 kcal. mole⁻¹
 ΔH_f^o 298.15 = -84.9 ± 0.3 kcal. mole⁻¹
 ΔH_f^o = 0.77 kcal. mole⁻¹
 ΔH_m^o = Unknown

S_{298.15} = 26.97 cal. deg.⁻¹ mole⁻¹

T_c = 411°K.

T_m = 815.2°K.

T_d = 670°K.

Heat of Formation.

The equilibrium pressures for the reaction NH₄Br(c) → NH₃(g) + HBr(g) have been measured by several investigators. Using the densi-tensimeter, A. Smith and R. Purcell, J. Chem. Soc. 2944 (1928), determined both the equilibrium pressures and vapor densities of the decomposition products, simultaneously, at several temperatures. In order to check the density values obtained, the authors applied the "extrapolation method", from which it was calculated that the corresponding vapor density agreed with complete dissociation. Based on this conclusion, the reported equilibrium pressures were employed to evaluate the enthalpy changes (ΔH_f^o) of the decomposition reaction by both the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	Equipment Used
Smith and Calvert (1)	576.40-676.02	45.12 ± 0.13	44.93	Isotenoscope
Smith and Purcell (2)	604.95-668.15	45.50 ± 0.17	45.08	Densi-tensimeter
Johnson (3)	573.15-667.75	45.41 ± 0.44	44.85	Spiral Manometer
(1) A. Smith and R. P. Calvert, J. Am. Chem. Soc. 56, 1363 (1934).				
(2) A. Smith and R. Purcell, J. Chem. Soc. 2944 (1928).				
(3) F. M. G. Johnson, Z. Physik. Chem. 65, 38 (1909).				

The value of ΔH_f^o 298.15 adopted is 45.2 ± 0.2 kcal. mole⁻¹. Using ΔH_f^o 298.15 = -10.97 and -8.71 kcal. mole⁻¹ for NH₃(g) and HBr(g), respectively, the value of ΔH_f^o 298.15 for NH₄Br(c) is evaluated as -64.9 ± 0.3 kcal. mole⁻¹. The corresponding ΔH_f^o 298.15 value evaluated from solution data, selected by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NBS-RS-NBS2, National Bureau of Standards, April 1, 1965, is 45.5 ± 0.2 kcal. mole⁻¹.

The vapor densities (573-661°K.) of dissociation products of NH₄Br(c) were also measured by A. Smith and R. H. Lombard, J. Am. Chem. Soc. 57, 38 (1935). Using the equilibrium pressures reported by A. Smith and R. P. Calvert, loc. cit., they derived the corresponding degrees of dissociation of NH₄Br(c) at different temperatures. The calculated results indicated that only 46% of NH₄Br(c) decomposed at 573°K. and as reaction temperatures increased to 661°K. the degree of dissociation decreased to 10%. This conclusion was stated to be erroneous by Smith and Purcell, loc. cit., probably because of incorrect density determinations.

Heat Capacity and Entropy.

The low temperatures (13-305°K.) heat capacities and S_{298.15} were obtained from M. Sorri, H. Suga and S. Seki, Bull. Chem. Soc. Japan, 38, 1125 (1965). The C_p values above 305°K. were estimated by comparison with those for NaCl(c), NaBr(c) and NH₄Cl(c). The low temperature heat capacities were also measured by R. Enald, Ann. Physik, 44, 1213 (1914), 139-301°K., and P. Simon, C. V. Simon and M. Ruhemann, Z. phys. Chem. 129, 339 (1927), 201.2-277.1°K.

Transition Data.

The temperature (T_c) and heat of transition (ΔH_f^o) were given by P. W. Bridgman, Proc. Am. Acad. Arts Sci. 52, 91 (1916-17). T_c = 419.5 ± 0.6°K. was reported by M. M. Markowitz and D. A. Boryta, J. Phys. Chem. 66, 1477 (1962), which was determined by differential thermal analysis. According to Sorri, Suga and Seki, loc. cit., there are 3 solid phase transitions, namely Phase IV (CaCl) → Phase III (tetragonal) at 108°K., Phase III (tetragonal) → Phase II (CaCl) at 235°K. and Phase II (CaCl) → Phase I (NaCl) at 411°K.

Melting Temperature.

The value of T_m was taken from H. Rasmus, Z. anorg. Chem. 114, 117 (1920), determined under pressure.

Mar. 31, 1962; Sept. 30, 1965

Temperatures of Decomposition.

The temperature of decomposition (T_d) was calculated as the temperature at which the total pressure of the decomposition products for the reaction NH₄Br(c) → NH₃(g) + HBr(g) equals 1 atm. T_d = 674 and 688.4°K. were reported by N. W. Laft. Ind. Chemist, 31, 502 (1955) and M. M. Markowitz and D. A. Boryta, loc. cit., respectively.



INTERIM TABLE

Mercurous Bromide (HgBr²)
(Ideal Gas) Mol. Wt. = 280.526

T, °K.	C _p ⁰	S ⁰ - (V ⁰ - H ₂₉₈ ⁰)/T	H ⁰ - H ₂₉₈ ⁰	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	8.009	INF	2.450	27.612	27.612	INF
100	8.728	55.000	2.450	27.612	27.612	INF
200	8.728	55.000	2.450	27.612	27.612	INF
298	8.694	55.000	2.450	27.612	27.612	INF
300	8.694	55.000	2.450	27.612	27.612	INF
400	8.694	55.000	2.450	27.612	27.612	INF
500	8.694	55.000	2.450	27.612	27.612	INF
600	8.694	55.000	2.450	27.612	27.612	INF
700	8.694	55.000	2.450	27.612	27.612	INF
800	8.694	55.000	2.450	27.612	27.612	INF
900	8.694	55.000	2.450	27.612	27.612	INF
1000	8.694	55.000	2.450	27.612	27.612	INF
1100	8.694	55.000	2.450	27.612	27.612	INF
1200	8.694	55.000	2.450	27.612	27.612	INF
1300	8.694	55.000	2.450	27.612	27.612	INF
1400	8.694	55.000	2.450	27.612	27.612	INF
1500	8.694	55.000	2.450	27.612	27.612	INF
1600	8.694	55.000	2.450	27.612	27.612	INF
1700	8.694	55.000	2.450	27.612	27.612	INF
1800	8.694	55.000	2.450	27.612	27.612	INF
1900	8.694	55.000	2.450	27.612	27.612	INF
2000	8.694	55.000	2.450	27.612	27.612	INF
2100	8.694	55.000	2.450	27.612	27.612	INF
2200	8.694	55.000	2.450	27.612	27.612	INF
2300	8.694	55.000	2.450	27.612	27.612	INF
2400	8.694	55.000	2.450	27.612	27.612	INF
2500	8.694	55.000	2.450	27.612	27.612	INF
2600	8.694	55.000	2.450	27.612	27.612	INF
2700	8.694	55.000	2.450	27.612	27.612	INF
2800	8.694	55.000	2.450	27.612	27.612	INF
2900	8.694	55.000	2.450	27.612	27.612	INF
3000	8.694	55.000	2.450	27.612	27.612	INF
3100	8.694	55.000	2.450	27.612	27.612	INF
3200	8.694	55.000	2.450	27.612	27.612	INF
3300	8.694	55.000	2.450	27.612	27.612	INF
3400	8.694	55.000	2.450	27.612	27.612	INF
3500	8.694	55.000	2.450	27.612	27.612	INF
3600	8.694	55.000	2.450	27.612	27.612	INF
3700	8.694	55.000	2.450	27.612	27.612	INF
3800	8.694	55.000	2.450	27.612	27.612	INF
3900	8.694	55.000	2.450	27.612	27.612	INF
4000	8.694	55.000	2.450	27.612	27.612	INF
4100	8.694	55.000	2.450	27.612	27.612	INF
4200	8.694	55.000	2.450	27.612	27.612	INF
4300	8.694	55.000	2.450	27.612	27.612	INF
4400	8.694	55.000	2.450	27.612	27.612	INF
4500	8.694	55.000	2.450	27.612	27.612	INF
4600	8.694	55.000	2.450	27.612	27.612	INF
4700	8.694	55.000	2.450	27.612	27.612	INF
4800	8.694	55.000	2.450	27.612	27.612	INF
4900	8.694	55.000	2.450	27.612	27.612	INF
5000	8.694	55.000	2.450	27.612	27.612	INF
5100	8.694	55.000	2.450	27.612	27.612	INF
5200	8.694	55.000	2.450	27.612	27.612	INF
5300	8.694	55.000	2.450	27.612	27.612	INF
5400	8.694	55.000	2.450	27.612	27.612	INF
5500	8.694	55.000	2.450	27.612	27.612	INF
5600	8.694	55.000	2.450	27.612	27.612	INF
5700	8.694	55.000	2.450	27.612	27.612	INF
5800	8.694	55.000	2.450	27.612	27.612	INF
5900	8.694	55.000	2.450	27.612	27.612	INF
6000	8.694	55.000	2.450	27.612	27.612	INF

December 31, 1961

BrHg

Iodine Monobromide (IBr)
(Ideal Gas)

GFW = 206.8134

IODINE MONOBROMIDE (IBr)

(IDEAL GAS)

GFW = 206.8134

Ground State Configuration $1\Sigma^+$

$$\Delta H_f^\circ = 11.91 \pm 0.02 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = 9.77 \pm 0.02 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 61.86 \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

ϵ_1 , cm^{-1}	ϵ_2	ϵ_3 , cm^{-1}	ϵ_4 , cm^{-1}	ϵ_5
0	1	16880	1	
12230	6	[51677]	2	
[16155]	5	[56349]	2	

$$w_e = 267.38 \text{ cm}^{-1}$$

$$w_e^x = 0.774 \text{ cm}^{-1}$$

$$w_e^y = 0.00568 \text{ cm}^{-1}$$

$$r_e = 2.485 \text{ \AA}$$

Heat of Formation

The equilibrium constants for the reaction (A) $I_2(g) + Br_2(g) = 2 IBr(g)$ were determined to be 0.0124 and 0.01303 at 547.7 and 578°K, respectively, by W. Müller, Z. Physik. Chem. 123, 1 (1926), who studied the rate of reaction between $H_2(g)$ and $Br_2(g)$ in the presence of $I_2(g)$. M. Bodenstein and A. Schmidt, Z. Physik. Chem. 123, 28 (1926), derived two values of the equilibrium constants at 1495°K for the same reaction by vapor density studies on the system I_2 , I , Br_2 , Br and BrI . The equilibrium between $CuBr_2(c)$, $I_2(g)$, $CuBr(c)$ and $IBr(g)$ was investigated by J. Morris and D. M. Yost, J. Am. Chem. Soc. 53, 2625 (1931), and the equilibrium constants at 115.0, 151.2 and 176.0°C for reaction (A) were evaluated. Based on these reported equilibrium constants, the corresponding enthalpy changes for reaction (A) are calculated by both the second and third law methods.

R. M. Badger and D. M. Yost, Phys. Rev. 37, 1548 (1931), observed the infrared bands of IBr and classified them as the $A''\pi_2 - X\Sigma^+$ transition. They have shown that the dissociation products of the upper state are normal atoms. M. O. Brown, Phys. Rev. 42, 355 (1932), assigned a faint set of bands in the red as the $B''\pi_0 - X\Sigma^+$ system. By means of a vibrational analysis he found that the absorption spectrum of IBr is analogous to that of ICl . The heat of dissociation for IBr was evaluated to be $14,560 \pm 5 \text{ cm}^{-1}$ or 1.817 eV . Hence the enthalpy change for the reaction (B) $IBr(g) = I(g) + Br(g)$ is calculated as 41.92 kcal/mol .

The heats of formation for $BrI(g)$ derived from the enthalpy changes for reaction (A) and (B) are presented in the following table. The value of $\Delta H_{298.15}^\circ (IBr, g)$ adopted is $9.77 \pm 0.02 \text{ kcal/mol}$.

Investigator	Reaction	Temperature °K	No. of Points	$\Delta H_{298.15}^\circ$, kcal/mol	Drift eu	$\Delta H_{298.15}^\circ$, kcal/mol
Müller (1926)	(A)	547.7, 578	2	-3.07	-0.55	9.47
Bodenstein and Schmidt (1926)	"	1495	1	-2.92	-	9.70
McMorris and Yost (1931)	(B)	388.2-449.2	14	-2.46	-0.9 $\pm$ 0.4	9.73
Brown (1932)	"	298	-	-	41.92**	9.77**

*Calculation based on third law $\Delta H_{298.15}^\circ$ value.

**The value is derived from $D_0^0(I-Br)$.

Heat Capacity and Entropy

The ground state configuration, electronic levels, quantum weights, w_e and w_e^x are obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Inc., New York, 1950. The values of B_e , α_e (corrected to the average isotopic species) and r_e were reported by T. S. Jaseja, J. Mol. Spectry. 5, 445 (1960), who analyzed the microwave spectrum of IBr , corresponding to the transitions $J = 4-5$ and $J = 5-6$, for the two isotopic species, $^{127}\text{Br}^{79}\text{I}$ and $^{127}\text{Br}^{81}\text{I}$. The moment of inertia is $5.007 \times 10^{-38} \text{ g cm}^2$.

The infrared absorption spectrum of IBr at 8000 - 6800 $\text{\AA}$, associated with a ${}^3\Pi_1 - {}^1\Sigma^+$ transition, was observed by L. E. Selin, Arkiv Fysik 21, 479 (1962). The derived rotational constants are different from those reported by Jaseja, loc. cit.

T, °K	C_p°	$S^\circ - (G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°	Log Kp
0	-0.00	INFINITE	-2.370	11.906	11.906	INFINITE
100	7.425	52.834	69.408	11.921	8.010	17.505
200	8.657	58.428	82.656	11.958	4.624	2.650
298	9.173	61.864	91.770	9.770	0.687	0.650
300	9.173	61.864	91.770	9.770	0.687	0.650
400	9.734	61.818	91.664	9.758	1.833	0.606
500	9.919	61.832	91.682	9.762	1.838	0.608
600	10.061	61.846	91.696	9.766	1.842	0.610
700	10.179	61.859	91.709	9.769	1.845	0.611
800	10.278	61.871	91.721	9.771	1.847	0.612
900	10.361	61.882	91.732	9.772	1.848	0.613
1000	10.430	61.892	91.742	9.773	1.849	0.614
1100	10.488	61.901	91.751	9.774	1.850	0.615
1200	10.536	61.909	91.759	9.775	1.851	0.616
1300	10.575	61.916	91.766	9.776	1.852	0.617
1400	10.607	61.922	91.772	9.777	1.853	0.618
1500	10.633	61.927	91.777	9.778	1.854	0.619
1600	10.655	61.931	91.781	9.779	1.855	0.620
1700	10.673	61.935	91.784	9.780	1.856	0.621
1800	10.688	61.938	91.787	9.781	1.857	0.622
1900	10.701	61.941	91.790	9.782	1.858	0.623
2000	10.712	61.943	91.792	9.783	1.859	0.624
2100	10.721	61.945	91.794	9.784	1.860	0.625
2200	10.728	61.947	91.796	9.785	1.861	0.626
2300	10.734	61.949	91.798	9.786	1.862	0.627
2400	10.739	61.951	91.800	9.787	1.863	0.628
2500	10.743	61.952	91.802	9.788	1.864	0.629
2600	10.746	61.953	91.804	9.789	1.865	0.630
2700	10.748	61.954	91.805	9.790	1.866	0.631
2800	10.750	61.955	91.806	9.791	1.867	0.632
2900	10.751	61.956	91.807	9.792	1.868	0.633
3000	10.752	61.957	91.808	9.793	1.869	0.634
3100	10.753	61.958	91.809	9.794	1.870	0.635
3200	10.754	61.959	91.810	9.795	1.871	0.636
3300	10.755	61.960	91.811	9.796	1.872	0.637
3400	10.756	61.961	91.812	9.797	1.873	0.638
3500	10.757	61.962	91.813	9.798	1.874	0.639
3600	10.758	61.963	91.814	9.799	1.875	0.640
3700	10.759	61.964	91.815	9.800	1.876	0.641
3800	10.760	61.965	91.816	9.801	1.877	0.642
3900	10.761	61.966	91.817	9.802	1.878	0.643
4000	10.762	61.967	91.818	9.803	1.879	0.644
4100	10.763	61.968	91.819	9.804	1.880	0.645
4200	10.764	61.969	91.820	9.805	1.881	0.646
4300	10.765	61.970	91.821	9.806	1.882	0.647
4400	10.766	61.971	91.822	9.807	1.883	0.648
4500	10.767	61.972	91.823	9.808	1.884	0.649
4600	10.768	61.973	91.824	9.809	1.885	0.650
4700	10.769	61.974	91.825	9.810	1.886	0.651
4800	10.770	61.975	91.826	9.811	1.887	0.652
4900	10.771	61.976	91.827	9.812	1.888	0.653
5000	10.772	61.977	91.828	9.813	1.889	0.654
5100	10.773	61.978	91.829	9.814	1.890	0.655
5200	10.774	61.979	91.830	9.815	1.891	0.656
5300	10.775	61.980	91.831	9.816	1.892	0.657
5400	10.776	61.981	91.832	9.817	1.893	0.658
5500	10.777	61.982	91.833	9.818	1.894	0.659
5600	10.778	61.983	91.834	9.819	1.895	0.660
5700	10.779	61.984	91.835	9.820	1.896	0.661
5800	10.780	61.985	91.836	9.821	1.897	0.662
5900	10.781	61.986	91.837	9.822	1.898	0.663
6000	10.782	61.987	91.838	9.823	1.899	0.664

Potassium Bromide (KBr)

POTASSIUM BROMIDE (KBr)

(CRYSTAL)

OPW = 119.011

(Crystal) GFW = 119.011

T, °K	Cp°	gphbs/mol S°	-(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	Kcal/mol ΔHf°	ΔGf°	Log Kp
0	-0.00	0.00	INFINITE	-2.919	-92.417	-92.417	INFINITE
100	10.312	10.265	33.595	-2.333	-92.579	-92.111	201.307
200	11.920	18.047	24.052	-1.201	-92.652	-91.615	100.112
298	12.500	22.930	22.930	-0.000	-94.120	-90.924	66.649
300	12.510	23.007	22.930	-0.023	-94.126	-90.908	66.223
400	12.660	26.655	23.425	1.292	-98.292	-86.616	37.882
500	13.205	29.558	24.371	2.593	-98.175	-86.666	37.882
600	13.470	31.988	25.484	3.927	-98.011	-86.378	30.735
700	13.660	34.055	26.532	5.299	-97.800	-85.921	25.439
800	13.800	35.981	27.527	6.708	-97.553	-85.307	21.827
900	15.222	37.725	28.656	8.188	-97.233	-84.570	18.870
1000	16.255	39.380	29.620	9.760	-96.833	-83.561	16.514
1100	17.460	40.987	30.500	11.448	-95.283	-82.190	14.190
1200	18.400	42.405	32.420	13.113	-93.488	-80.577	12.490
1300	19.030	43.085	34.420	15.113	-91.346	-78.704	10.894
1400	19.530	45.474	37.302	17.042	-88.866	-76.086	9.536
1500	20.000	46.839	38.159	19.020	-86.159	-73.434	8.371

Dec. 31, 1951, Mar. 31, 1957

$$\Delta H_f^\circ = -92.42 \pm 0.1 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = -94.12 \pm 0.1 \text{ kcal/mol}$$

$$\Delta G_m^\circ = 8.1 \text{ kcal/mol}$$

$$\Delta H_a^\circ_{298.15} \text{ (to monomer)} = 51.08 \text{ kcal/mol}$$

$$\Delta H_a^\circ_{298.15} \text{ (to dimer)} = 59.04 \text{ kcal/mol}$$

Heat of Formation.

The heat of solution (ΔH_{sol}) of KBr(c) in $H_2O(l)$ has been measured by many investigators. The results were reviewed in detail by V. B. Parker, U. S. Natl. Bur. Std. NBS-NSR-2, 1955. Eight pertinent ΔH_{sol}° values are reproduced in the table below. Adopting the best value, $\Delta H_{sol}^\circ = 4.75 \pm 0.02 \text{ kcal/mol}$, for the reaction $KBr(c) + K^+(\infty H_2O) + Br^-(\infty H_2O) = -94.12 \text{ kcal/mol}$ for KBr(c). The auxiliary values $\Delta H_{sol}^\circ = -60.32$ and -29.05 kcal/mol for $K^+(\infty H_2O)$ and $Br^-(\infty H_2O)$, respectively, are obtained from U. S. Natl. Bur. Std. Tech. Note 270-1, 1955.

ΔH_{sol}° , Kcal/mol	Temperature, °C	m*	Investigator
4.727	16.6	0.28	P. T. Walden, Z. Physik. Chem. 59, 479 (1907).
4.777	25	0.37	J. Wlat and E. Lange, Z. Physik. Chem. 118, 161 (1925).
4.753	25	0.09	H. R. Chipman, F. M. O. Johnson, and O. Maass, Proc. Trans. Nova Scotian Inst. Sci. 17, 149 (1929).
4.884	20	0.19	M. M. Popov, A. Bundel, and V. Choller, Z. Physik. Chem. 147, 302 (1930).
4.889	23.5	0.14	A. S. Podorov and G. F. Silchenko, Ukrain. Khim. Zhur. 12, 53 (1937).
4.783	25	0.13	E. Lange and W. Martin, Z. Physik. Chem. 190, 233 (1937).
4.542	20.5	0.12	M. M. Popov, S. M. Skuratov, and M. M. Strel'tsova, Zhur. Obanchei Khim. 10, 2023 (1940).
4.739	25	0.28	J. Hietala, Ann. Acad. Sci. Fennicae Ser. A VI No. 63, 1 (1960).

*Values are adjusted to 298.15°K and to infinite dilution.

**Lowest experimental molelity.

Heat Capacity and Entropy.

The low temperature heat capacities, 2.9 - 272.2°K, were measured by W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) A 242, 467 (1957), using an adiabatic calorimeter. The high temperature heat capacities, 325.25 - 711.75°K, are taken from A. Mustajoki, Ann. Acad. Sci. Fennicae, Ser. A I, 98, 7 (1951). These two sets of Cp data are joined smoothly at 298°K. The Cp values at temperatures, 720 - 1007°K, are extrapolated graphically, so that the derived antherly change ($H^\circ_{1007} - H^\circ_{298}$) = 9.9 kcal/mol agrees with that determined by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tennessee, Dec. 1, 1964. The derived enthalpies at 700, 800 and 900°K are also in good agreement with those measured by S. M. Skuratov and S. A. Lapushkin, J. On. Chem. USSR (Eng. Transl.) 21, 2485 (1951). The Cp values above 1007°K are obtained by graphical extrapolation.

The S°_{298} is calculated from the adopted low temperature Cp, based on $S^\circ_{2.9} = 0.0015 \text{ eu}$.

The heat capacities of KBr(s) were also measured by W. Nernst and F. A. Lindemann, Z. Elektrochem. 17, 817 (1911), 78.7 - 89.2°K; F. Korf, Ann. Physik 4, 49 (1911), 137 - 234°K; and K. Clausen, J. Goldmann, and A. Parlick, Z. Naturforsch. 4b, 424 (1949). The enthalpies of KBr(c) were determined by A. Magnus, Phys. Z. 14, 5 (1913), and C. B. Cooper, J. Chem. Phys. 21, 777 (1953). The results are in reasonable agreement with the adopted functions except for those reported by Cooper.

Melting Data.

See KBr(1) table for details.

Heat of Sublimation.

The heat of sublimation to monomer and dimer are calculated as the enthalpy changes for the following two reactions: $KBr(c) = KBr(g)$ and $2 KBr(c) = K_2Br_2(g)$.

BrK

Potassium Bromide (KBr)

(Liquid) GFW = 119.011

T, °K	C _p ^a	gibbs/mol S ^b	-(G ^c -H ²⁹⁸)/T	H ^c -H ²⁹⁸	kcal/mol ΔH ^c	ΔG ^c	Log K _p
0							
100							
200							
298	16.700	25.225	25.225	.000	- 89.984	- 87.472	64.119
300	16.700	25.328	25.225	.031	- 89.983	- 87.456	63.712
400	16.700	30.133	25.880	1.701	- 93.747	- 85.826	46.893
500	16.700	33.959	27.117	3.371	- 93.261	- 83.903	36.674
600	16.700	36.904	28.502	5.041	- 92.761	- 82.077	29.897
700	16.700	39.478	29.891	6.711	- 92.254	- 80.336	25.082
800	16.700	41.708	31.232	8.381	- 91.744	- 78.670	21.492
900	16.700	43.675	32.507	10.051	- 91.235	- 77.065	18.714
1000	16.700	45.435	33.714	11.721	- 90.736	- 75.519	16.505
1100	16.700	47.026	34.853	13.391	- 90.154	- 72.994	14.503
1200	16.700	48.479	35.929	15.061	- 89.432	- 69.740	12.701
1300	16.700	49.816	36.946	16.731	- 87.712	- 66.546	11.187
1400	16.700	51.054	37.910	18.401	- 86.092	- 63.406	9.898
1500	16.700	52.206	38.825	20.071	- 84.473	- 60.318	8.788
1600	16.700	53.284	39.696	21.741	- 82.854	- 57.277	7.824
1700	16.700	54.296	40.525	23.411	- 81.237	- 54.283	7.076
1800	16.700	55.251	41.317	25.081	- 79.621	- 51.330	6.232
1900	16.700	56.154	42.074	26.751	- 77.999	- 48.417	5.569
2000	16.700	57.010	42.800	28.421	- 76.379	- 45.540	4.976
2100	16.700	57.825	43.496	30.091	- 74.759	- 42.700	4.444
2200	16.700	58.602	44.165	31.761	- 73.139	- 39.893	3.963
2300	16.700	59.344	44.809	33.431	- 71.519	- 37.119	3.527
2400	16.700	60.055	45.430	35.101	- 69.899	- 34.375	3.130
2500	16.700	60.737	46.028	36.771	- 68.279	- 31.662	2.768

POTASSIUM BROMIDE (KBr)

(LIQUID)

GFW = 119.011

 $S_{298.15}^{\circ} = 25.225$ gibbs/mol $\Delta H_f^{\circ} = -89.984$ kcal/mol $T_m = 1007^{\circ}\text{K}$ $\Delta H_m^{\circ} = 6.1$ kcal/mol $T_b = 1671^{\circ}\text{K}$ $\Delta H_v^{\circ} = 35.65$ kcal/mol

Heat of Formation.

The heat of formation (ΔH_f°) for KBr(l) is obtained from ΔH_f° (KBr, c) by adding ΔH_m° and the difference between $H_{1007}^{\circ} - H_{298}^{\circ}$ for crystal and liquid.

J. Togruri, H. Flood and T. Forland, Acta Chem. Scand. **17**, 1502 (1963), studied the chemical equilibrium for the reaction $\text{KBr(l)} + \text{HCl(g)} = \text{KCl(l)} + \text{HBr(g)}$. They obtained $\Delta H_{1073}^{\circ} = 3.50 \pm 0.08$ and 3.54 kcal/mol from partial pressure data and emf data, respectively. The corresponding value calculated from these tables is 3.78 kcal/mol. Combination of the experimental results with JANAF auxiliary data leads to -89.70 and -89.74 kcal/mol for ΔH_f° .

Heat Capacity and Entropy.

The heat capacity of 16.7 gibbs/mol was derived by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tennessee, Dec. 1, 1964, from enthalpy data in the range $1010 - 1100^{\circ}\text{K}$. This Cp value is adopted here for the temperature range $298 - 2500^{\circ}\text{K}$.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data.

The adopted T_m and ΔH_m° were determined by J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604 (1958), and A. S. Dworkin and M. A. Bredig, J. Phys. Chem. **64**, 269 (1960), respectively.

Heats of melting of 6.2 kcal/mol from phase diagram studies and 6.7 kcal/mol from calorimetric measurements were obtained by E. Aukrust, B. Bjorge, H. Flood, and T. Forland, Annals of the New York Academy of Sciences **79**, Art. 11, 830 (1960).

Vaporization Data.

The boiling point, $T_b = 1671^{\circ}\text{K}$, is calculated as the temperature at which the sum of the partial pressures of KBr(g) and $\text{K}_2\text{Br}_2(\text{g})$ over KBr(l) equals one atmosphere. The value of ΔH_v° is calculated as the heat required to produce one mole of vapor mixture, which contains 19.5% dimer (K_2Br_2) and 80.5% monomer (KBr).

T_b was reported to be 1648 and 1668°K by H. von Wartenberg and P. Albrecht, Z. Elektrochem. **27**, 162 (1921), and O. Ruff and S. Mugdan, Z. Anorg. Chem. **117**, 147 (1921), respectively.

GFW = 119.011

Ground State Configuration $1^1\Sigma^+$ $\Delta H_f^\circ = -40.83 \pm 0.5 \text{ kcal/mol}$ $\Delta H_f^{298.15} = -43.04 \pm 0.5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

ϵ , cm ⁻¹	$\frac{g_i}{1}$
0	1
$w_e = 218.47 \text{ cm}^{-1}$	$w_{x_e} = 0.7533 \text{ cm}^{-1}$
$w_e = 0.0807 \text{ cm}^{-1}$	$w_{e_e} = 0.000401 \text{ cm}^{-1}$
	$\tau_e = 2.821 \text{ Å}$

Heat of Formation.

The heat of formation is derived from the sublimation and vaporization data analyzed below. Numerous investigators have obtained total pressures by static methods or "apparent" pressures by effusion or transpiration. These pressures are converted to monomer pressures by use of functions [see $K_{2Br}(g)$ table] which are consistent with the dimer-monomer equilibrium data of Hagemark et al.(6). Second and third law analyses of the monomer pressures show remarkable consistency over temperatures from 637 to 1668°K. The selected value of $\Delta H_f^{298} = -43.0 \pm 0.5 \text{ kcal/mol}$ may be compared with -43.8 kcal/mol derived from $D_0 = 3.95 \text{ eV}$ which is reported by Gaydon(14) based on atomic fluorescence data.

Investigator	Reaction	Temperature, °K	No. of Points	ΔH_f^{298} , kcal/mol	Drift kcal/mol	ΔH_f^{298} , kcal/mol
1. Wartenberg-Albrecht	(A)	1368-15-1684-15	14	48.28±0.31	46.70	-1.1±0.2
2. Ruff-Mugdan	"	1361-15-1668-15	10	49.06±0.56	47.16	-1.4±0.4
3. Flock-Rodebush	"	1179-15-1335-75	10	47.80±0.05	46.95	-0.7±0.1
4. Hintz-Jellinek	"	1523-15	1	-	47.34	-
5. Murgulescu-Marta	"	1373-15-1473-15	5	46.20±1.15	47.69	1.1±0.8
6. Hagemark et al.	"	1158-95-1416-02	26	47.15±0.49	46.94	-0.2±0.4
7. Miwa	(B)	823-15-923-15	6	48.04±0.51	51.67	4.1±0.6
8. Mayer-Mintner	"	884-90-929-40	6	56.15±3.17	51.49	-5.2±3.5
9. Zimm-Mayer	"	636-94-900-09	15	50.71±0.21	50.58	-0.1±0.2

*Based on the third law ΔH_f^{298} value. (A) KBr(1) = KBr(g), (B) KBr(c) = KBr(g).

Heat Capacity and Entropy.

Rusk and Gordy(10) have investigated the pure rotational spectra of KBr in the 1.5 to 5.0 mm range of the microwave region by millimeter wave molecular beam spectroscopy. The reported values of w_e , w_{x_e} , B_e and r_e are adopted here and corrected to the average isotopic species. The value of a_e is obtained from Fabre and et al.(11). Molecular constants for KBr(g) have also been reported by Herzberg(12) and Rice and Klemperer(13). They are in good agreement with the values adopted. Herzberg(12) also lists an A state at 31770 cm⁻¹ based on observed electronic spectra. The moment of inertia is $3.4604 \times 10^{-38} \text{ g cm}^2$.

References:

1. H. von Wartenberg and F. Albrecht, Z. Elektrochem. 27, 162 (1921).
2. O. Ruff and S. Mugdan, Z. Anorg. Chem. 117, 147 (1921).
3. E. P. Flock and W. H. Rodebush, J. Am. Chem. Soc. 48, 2522 (1926).
4. H. Hintz and K. Jellinek, Z. Elektrochem. 42, 187 (1936).
5. I. O. Murgulescu and L. Marta, Rev. Roumaine Chim. 11, 457 (1966). The authors adopted total vapor pressures reported by Wartenberg and Albrecht, loc. cit., for the evaluation of the partial pressures of KBr(g) and K₂Br₂(g). We use the KBr partial pressures derived from JANAF table thermodynamic functions for evaluation.
6. K. I. Hagemark, M. Blander and E. B. Luchaninger, J. Phys. Chem. 70, 276 (1966), and K. I. Hagemark, private communication, 3M Company, St. Paul, Minnesota, Feb. 6, 1967.
7. K. Miwa, "Vapor Pressures of Alkali-Halides," J. Fac. Sci., Hokkaido Imperial Univ., Ser. III, 2, 201 (1938).
8. J. E. Mayer and I. H. Wintner, J. Chem. Phys. 5, 301 (1939).
9. B. H. Zimm and J. E. Mayer, J. Chem. Phys. 12, 362 (1944).
10. J. R. Rusk and W. Gordy, Phys. Rev. 127, 817 (1962).
11. P. B. Fabre and R. O. Carlson, C. A. Lee, and I. I. Rabi, Phys. Rev. 91, 1403 (1953).
12. O. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, 1950.
13. S. A. Rice and W. Klemperer, J. Chem. Phys. 27, 573 (1957).
14. A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., London, 1953.

Dec. 31, 1961; Mar. 31, 1967

Lithium Bromide (LiBr)

(Crystal)

GFW = 86.848

T, °K	Cp	$\frac{\text{gkcal/mol}}{S}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	11.692	17.700	17.700	0.000	- 83.870	- 81.650	99.851
300							
400	11.710	17.772	17.700	+0.22	- 83.876	- 81.636	59.472
500	12.245	21.216	18.166	1.220	- 87.419	- 80.155	43.795
600	12.770	24.003	19.063	2.470	- 88.028	- 78.279	34.216
700							
800	13.405	26.385	20.089	3.777	- 87.878	- 76.342	27.607
900	13.785	28.113	21.011	5.068	- 87.443	- 74.423	22.250
1000	14.035	30.493	22.183	6.463	- 87.298	- 72.513	19.826
1100	14.265	32.565	23.217	7.823	- 86.869	- 70.759	17.183
1200	14.470	34.327	24.221	9.306	- 86.315	- 68.998	15.080
1300	14.650	35.778	25.197	11.638	- 85.721	- 67.295	13.370
1400	14.810	37.061	26.146	13.815	- 85.000	- 65.648	12.000
1500	14.970	38.177	27.061	15.232	- 84.407	- 64.095	10.769
1600	15.130	40.139	27.847	17.069	- 83.707	- 62.516	9.759
1700	15.280	41.818	28.603	18.923	- 82.990	- 61.028	8.892
1800	15.430	42.522	29.229	20.788	- 82.261	- 59.587	8.139
1900	15.580	43.829	30.738	24.566	- 81.517	- 58.190	7.480
2000	15.780	45.829	31.698	26.415	- 80.766	- 56.839	6.916
2100	15.810	45.845	31.642	26.415	- 80.766	- 56.839	6.916
2200	15.820	45.810	32.463	28.257	- 80.721	- 56.558	6.588

BrLi

LITHIUM BROMIDE (LiBr)

(CRYSTAL)

OPW = 86.848

 $\Delta H^\circ_f = \text{Unknown}$ $\Delta H^\circ_{298,15} = -83.87 \pm 0.1 \text{ kcal/mol}$ $\Delta H^\circ = -4.22 \text{ kcal/mol}$ $S^\circ_{298,15} = [17.7] \text{ gibbs/mol}$ $T_m = 823^\circ\text{K}$

Heat of Formation.

The heat of formation, $\Delta H^\circ_{298}(\text{LiBr}, c) = -83.87 \text{ kcal/mol}$, was calculated from the heat of solution of lithium bromide (c) at infinite dilution and the ionic heats of formation of $\text{Li}^+(\text{aq}, \text{H}_2\text{O})$ and $\text{Br}^-(\text{aq}, \text{H}_2\text{O})$.

V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-RS-NBS 2, April 1, 1955, reviewed the heat of solution data in the literature and gave the "best" value, $\Delta H^\circ_{\text{sol}} = -11.670 \pm 50 \text{ cal/mol}$ for $\text{LiBr}(c) \rightarrow \text{LiBr}(\text{aq}, \text{H}_2\text{O})$ at 298.15°K . The ionic heat of formation, $\Delta H^\circ_{298}(\text{Li}^+, \text{aq}, \text{H}_2\text{O}) = -66.49 \text{ kcal/mol}$, was calculated from $\Delta H^\circ_{298}(\text{LiOH} \cdot \text{aq}, \text{H}_2\text{O}) = -121.46 \text{ kcal/mol}$ (see JANAF LiOH(c) table, Mar. 31, 1956) with $\Delta H^\circ_{298}(\text{OH}^-, \text{aq}, \text{H}_2\text{O}) = -54.97 \text{ kcal/mol}$ from NBS Technical Note 270-1, "Selected Values of Chemical Thermodynamic Properties," Oct. 1, 1955. The value $\Delta H^\circ_{298}(\text{Br}^-, \text{aq}, \text{H}_2\text{O}) = -29.05 \text{ kcal/mol}$ was also obtained from NBS Technical Note 270-1. Combination of the ionic heats of formation of $\text{Li}^+(\text{aq}, \text{H}_2\text{O})$ and $\text{Br}^-(\text{aq}, \text{H}_2\text{O})$ gives the heat of formation of $\text{LiBr}(\text{aq}, \text{H}_2\text{O})$, $\Delta H^\circ_{298} = -95.54 \text{ kcal/mol}$.

Heat Capacity and Entropy.

A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1964, has measured the enthalpy changes by the drop method ($723\text{--}883^\circ\text{K}$), yielding $H_{298} - H_{298} = 7.0 \text{ kcal/mol}$ for the crystal at the melting point. Heat capacities derived from his data were $C_p 773^\circ = 15.1$ and $C_p 853^\circ = 15.6 \text{ gibbs/mol}$ for the crystal and liquid, respectively. The tabulated heat capacities were estimated based on these values and on the heat capacities of $\text{LiCl}(c)$, $\text{NaCl}(c)$ and $\text{NaBr}(c)$.

The entropy, $S^\circ_{298,15} = 17.7 \text{ eu}$, was estimated by adding the entropy difference between $\text{NaBr}(c)$ and $\text{NaCl}(c)$ to the entropy of lithium chloride (c) at 298.15°K . Comparisons with other alkali halides give results within $\pm 0.5 \text{ eu}$ of this value. K. K. Kelley, U. S. Bur. Min. Bull. 584 (1960) and 592 (1961), has estimated the heat capacities ($C_p = 11.50 + 3.02 \times 10^{-5} T$ gibbs/mol) and the entropy ($S^\circ_{298} = 16.0 \pm 0.5 \text{ eu}$)

Melting Data.

The selected heat of fusion ($\Delta H^\circ_{298} = 4.22 \text{ kcal/mol}$) was obtained from enthalpy measurements in a drop calorimeter by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 54, 269 (1960).

K. K. Kelley, U. S. Bur. Min. Bull. 393 (1936), reviewed some phase diagram studies of the lithium bromide system in the literature, and gave the heat of fusion $\Delta H^\circ_{298} = 2.90 \text{ kcal/mol}$. M. Blanc, Compt. rend. 246, 570 (1958), reported the heat of fusion $\Delta H^\circ_{298} = 3.095 \text{ kcal/mol}$ by a cryoscopic method. Both values are too low.

BrLi

T, °K	C _p ^a	gibbs/mol S ^b	-(G ^c - H ^{298.15})/T	H ^c - H ^{298.15}	kcal/mol ΔH ^c	ΔG ^c	Log K _p
-------	-----------------------------	-----------------------------	--	--------------------------------------	-----------------------------	-----------------	--------------------

0							
100							
200							
298							
300	15.600	70.270	20.270	0.000	- 80.839	- 79.370	98.180
350	15.600	20.316	20.220	0.029	- 80.838	- 79.361	97.814
400	15.600	24.804	20.832	1.369	- 84.019	- 78.190	42.721
500	15.600	28.285	21.988	3.149	- 84.318	- 78.170	33.530
600	15.600	31.130	23.281	4.709	- 83.915	- 75.226	27.401
700	15.600	33.617	24.811	6.129	- 83.582	- 72.511	22.964
800	15.600	35.617	26.431	7.429	- 83.302	- 70.004	19.094
900	15.600	37.435	27.023	8.589	- 82.062	- 71.153	17.278
1000	15.600	39.098	28.130	10.349	- 82.242	- 69.896	15.276
1100	15.600	40.585	29.214	12.309	- 81.821	- 68.682	13.646
1200	15.600	41.918	30.269	14.469	- 81.290	- 67.510	12.274
1300	15.600	43.191	31.169	15.829	- 80.659	- 66.365	11.117
1400	15.600	44.347	32.070	17.169	- 80.557	- 65.257	10.187
1500	15.600	45.424	32.924	18.749	- 80.134	- 64.180	9.351
1600	15.600	46.374	33.717	20.469	- 79.490	- 63.100	8.674
1700	15.600	47.274	34.452	22.329	- 78.734	- 62.070	8.050
1800	15.600	48.268	35.252	24.429	- 77.924	- 61.043	7.474
1900	15.600	49.111	35.959	26.969	- 77.069	- 60.043	6.949
2000	15.600	49.912	36.637	29.949	- 76.169	- 59.043	6.474
2100	15.600	50.673	37.298	33.469	- 75.210	- 58.043	6.042
2200	15.600	51.398	37.913	37.469	- 74.210	- 57.043	5.643
2300	15.600	52.092	38.514	41.929	- 73.169	- 56.043	5.274
2400	15.600	52.756	39.094	46.949	- 72.089	- 55.043	4.943
2500	15.600	53.393	39.653	52.529	- 70.969	- 54.043	4.643
2600	15.600	54.004	40.193	58.669	- 69.810	- 53.043	4.374
2700	15.600	54.593	40.716	65.369	- 68.610	- 52.043	4.134
2800	15.600	55.161	41.222	72.629	- 67.369	- 51.043	3.914
2900	15.600	55.708	41.712	80.469	- 66.089	- 50.043	3.714
3000	15.600	56.237	42.187	88.889	- 64.769	- 49.043	3.534

$S_{298.15}^{\circ} = [20.220]$ gibbs/mol
 $T_m = 823^{\circ}\text{K}$
 $T_b(\text{to equilibrium mixture}) = 1562^{\circ}\text{K}$
 $T_b(\text{to monomer only}) = [1811]^{\circ}\text{K}$

Heat of Formation.
 The heat of formation was calculated from that of the crystal by adding the heat of fusion and the difference between H_{823}° - H_{298}° for crystal and liquid.

Heat Capacity and Entropy.
 A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1964, has derived the heat capacity ($C_p = 15.6$ gibbs/mol) from enthalpy measurements ($823^{\circ} - 803^{\circ}\text{K}$) by the drop method. The liquid heat capacity was assumed to be a constant, 15.6 gibbs/mol. The entropy ($S_{298}^{\circ} = 20.220$ eu) was obtained in a manner analogous to that of the heat of formation.

Melting Data.
 See LiBr(c) table for detail.

Vaporization Data.
 T_b (to monomer only) is taken as the temperature at which the calculated Gibbs energy change is zero for $\text{LiBr(l)} \rightarrow \text{LiBr(g)}$, while ΔH_v° (to monomer only) is the corresponding heat of reaction.

T_b (to equilibrium mixture) is taken as the temperature at which the sum of the calculated partial vapor pressures of LiBr(g) and $\text{Li}_2\text{Br}_2(\text{g})$ reaches one atmosphere (trimer and higher polymers have been neglected in calculation). This value (1562°K) is in good agreement with the boiling point of 1563°K obtained from total vapor pressure measurements by H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 588 (1921), and also the boiling point of 1538°K by O. Ruff and S. Migdan, Z. anorg. Chem. 117, 147 (1921). ΔH_v° (to equilibrium mixture) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 29.23 mole percent of dimer. For detailed information see LiBr(g) and $\text{Li}_2\text{Br}_2(\text{g})$ tables.

Lithium Bromide (LiBr)

(Ideal Gas) GFW = 86.848

T, °K	Cp°	S°	-(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-	34.959	-	INFINITE
100	7.002	45.454	60.429	-1.498	34.716	38.442	84.015
200	7.575	50.460	54.319	-0.772	35.016	42.070	45.972
298	8.115	53.593	53.593	-0.000	35.800	45.281	33.192
300	8.122	53.643	53.593	-0.015	36.812	45.334	33.026
400	8.446	56.028	53.016	-0.845	40.724	47.385	25.890
500	8.637	57.935	54.515	-1.700	41.728	48.045	21.394
600	8.728	59.321	55.238	-2.450	42.015	50.361	18.344
700	8.789	60.403	56.049	-3.150	42.251	51.752	16.151
800	8.803	62.063	56.844	-3.750	42.438	52.981	14.582
900	8.851	63.114	57.303	-4.230	42.781	54.365	13.202
1000	8.990	64.059	57.932	-4.617	43.024	55.639	12.160
1100	9.023	64.918	58.329	-4.928	43.262	56.890	11.303
1200	9.058	65.700	58.586	-5.186	43.497	58.117	10.595
1300	9.078	66.430	59.031	-5.436	43.730	59.318	9.947
1400	9.101	67.103	60.141	-5.747	43.959	60.518	9.447
1500	9.124	67.732	60.626	-6.059	44.185	61.694	8.989
1600	9.145	68.322	61.089	-6.372	44.407	62.853	8.595
1700	9.165	68.872	61.524	-6.685	44.622	63.992	8.257
1800	9.184	69.401	61.934	-6.998	44.832	65.113	7.968
1900	9.202	69.898	62.359	-7.312	45.038	66.218	7.724
2000	9.220	70.370	62.748	-7.624	45.245	67.306	7.519
2100	9.238	70.821	63.122	-7.936	45.452	68.378	7.342
2200	9.256	71.251	63.482	-8.248	45.658	69.435	7.182
2300	9.273	71.663	63.828	-8.559	45.863	70.478	7.036
2400	9.290	72.058	64.163	-8.869	46.068	71.508	6.902
2500	9.306	72.437	64.486	-9.177	46.272	72.524	6.774
2600	9.323	72.803	64.799	-9.483	46.477	73.527	6.650
2700	9.339	73.155	65.102	-9.788	46.681	74.518	6.536
2800	9.356	73.495	65.396	-10.091	46.884	75.497	6.432
2900	9.372	73.823	65.681	-10.393	47.086	76.464	6.338
3000	9.388	74.141	65.958	-10.694	47.287	77.419	6.254
3100	9.404	74.449	66.227	-10.994	47.487	78.362	6.170
3200	9.420	74.748	66.488	-11.292	47.686	79.294	6.096
3300	9.436	75.038	66.743	-11.589	47.884	80.216	6.032
3400	9.452	75.320	66.991	-11.884	48.081	81.128	5.977
3500	9.467	75.594	67.233	-12.177	48.277	82.030	5.932
3600	9.483	75.861	67.469	-12.469	48.472	82.922	5.896
3700	9.499	76.121	67.699	-12.760	48.666	83.804	5.869
3800	9.515	76.375	67.924	-13.049	48.859	84.677	5.849
3900	9.530	76.622	68.144	-13.336	49.051	85.540	5.828
4000	9.546	76.864	68.359	-13.621	49.242	86.392	5.806
4100	9.561	77.100	68.569	-13.904	49.432	87.234	5.784
4200	9.577	77.333	68.777	-14.186	49.621	88.067	5.762
4300	9.592	77.556	68.977	-14.466	49.809	88.891	5.740
4400	9.608	77.777	69.174	-14.744	49.996	89.706	5.718
4500	9.624	77.993	69.368	-15.021	50.182	90.512	5.696
4600	9.639	78.204	69.558	-15.297	50.367	91.309	5.674
4700	9.654	78.412	69.743	-15.572	50.551	92.097	5.652
4800	9.670	78.615	69.927	-15.845	50.734	92.877	5.630
4900	9.685	78.815	70.106	-16.117	50.916	93.648	5.608
5000	9.701	79.011	70.282	-16.388	51.097	94.410	5.586
5100	9.716	79.204	70.455	-16.658	51.277	95.164	5.564
5200	9.732	79.392	70.624	-16.926	51.456	95.910	5.542
5300	9.747	79.577	70.792	-17.193	51.634	96.648	5.520
5400	9.762	79.759	70.957	-17.458	51.811	97.378	5.498
5500	9.778	79.939	71.118	-17.722	51.987	98.100	5.476
5600	9.793	80.115	71.278	-17.985	52.162	98.814	5.454
5700	9.809	80.289	71.435	-18.247	52.336	99.520	5.432
5800	9.824	80.459	71.588	-18.508	52.509	100.218	5.410
5900	9.839	80.627	71.740	-18.768	52.681	100.908	5.388
6000	9.855	80.793	71.890	-19.026	52.853	101.590	5.366

Sept. 30, 1961; June 30, 1966

LITHIUM BROMIDE (LiBr)

Ground State Configuration 1Σ

S^{298.15} = 53.593 gibbs/molΔH_f⁰ = -35.0 ± 3 kcal/molΔH_f^{298.15} = -36.8 ± 3 kcal/mol

Electronic Levels and Quantum Weights

ε, cm ⁻¹	g _i
0	1

ω_ex_e = 3.53 cm⁻¹α_e = 0.00573 cm⁻¹

σ = 1

r_e = 2.1704 Å

Heat of Formation.

The heat of formation (ΔH_f²⁹⁸ (LiBr, g) = -36.8 ± 3 kcal/mol) was calculated from the selected heat of vaporization and the heat of formation for lithium bromide (1). Lithium bromide vaporizes to a mixture of monomeric and diatomic gases. (Higher polymers have been neglected in the calculation.) The heats of vaporization to monomer and to dimer were chosen to satisfy (1) the total vapor pressure data measured by H. von Wartenberg and H. Schulz, Z. Elektrochem. 21, 568 (1921), and O. Ruff and S. Mugdan, Z. anorg. Chem. 117, 147 (1921); (2) the partial vapor pressures of monomer and dimer derived from R. C. Muller and P. Kuch, J. Chem. Phys. 25, 860 (1956), 28, 981 (1958), in an analysis of the velocity distribution of molecules in alkali halide vapor. The selected heats of vaporization are ΔH_v²⁹⁸ (to monomer) = 44.0 ± 3 kcal/mol and ΔH_v²⁹⁸ (to dimer) = 42.0 ± 5 kcal/mol which combine with the heat of formation of lithium bromide (1) (ΔH_f²⁹⁸ = -80.84 kcal/mol) to give the standard heats of formation of LiBr(g) and Li₂Br₂(g) = -36.8 and -119.7 kcal/mol, respectively. The derived heat of dissociation is ΔH₂₉₈⁰ = 46.0 kcal/mol for Li₂Br₂(g) → 2LiBr(g).

J. Berkowitz, H. A. Tassan and W. A. Chupka, J. Chem. Phys. 36, 2170 (1962), have measured mass-spectrometrically the heat of dissociation ΔH₂₉₈⁰ = 45.9 kcal/mol (ΔH₂₉₈⁰ = 46.9 kcal/mol) for Li₂Br₂(g) → 2LiBr(g) in a double open apparatus by the second law method. D. L. Hildenbrand, L. F. Theard, W. F. Hall and N. D. Potter, Philco Report U-2289, under Contract N061-0905-C, Sept. 15, 1963, have determined mass-spectrometrically the heats of sublimation of lithium bromide by the second law method as ΔH_{sub}⁰ (to monomer) = 46.9 and ΔH_{sub}⁰ (to dimer) = 45.0 kcal/mol (equivalent to ΔH_v²⁹⁸ (to monomer) = 45.82 kcal/mol and ΔH_v²⁹⁸ (to dimer) = 41.93 kcal/mol). These values are in reasonable agreement with those selected in the tabulation.

Heat Capacity and Entropy.

The bond distance (r_e) was obtained from the microwave studies by A. Honig, M. Mandel, M. L. Stich and C. H. Townes, Phys. Rev. 95, 623 (1954). The vibrational constants (ω_e and ω_ex_e) were determined from the infrared spectrum by W. Klempner, W. G. Morris, A. Bichler, and A. G. Emile, J. Chem. Phys. 33, 1534 (1960). The rotational constants which have been corrected to the average isotopic species were obtained by A. J. Herbert, P. W. Breivogel, Jr., and K. Street, Jr., J. Chem. Phys. 41, 2368 (1964), using microwave spectra. Their data are in good agreement with those reported by Honig et al., loc. cit., and J. R. Runk and W. Gordy, Phys. Rev. 127, 817 (1962).

The tabulated thermodynamic functions are in reasonable agreement with those calculated by R. L. Wilkins, J. Chem. Eng. Data 5, 337 (1960), who used slightly different molecular constants.

BrLi

BrLi

(Ideal Gas) GFW = 104.221

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o) ₂₉₈ /T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0	+0.00	INFINITE	- 2.289	- 11.166	- 11.166	INFINITE
100	7.234	49.853	65.740	- 10.951	- 15.066	32.926
200	8.104	55.157	59.255	- 11.428	- 19.163	20.941
298	8.517	58.481	58.460	- 11.428	- 22.082	16.627
300	8.522	58.594	58.481	- 11.412	- 22.762	16.588
400	8.715	61.015	58.018	- 10.884	- 25.703	11.770
500	8.820	62.472	59.460	- 10.089	- 27.259	11.015
600	8.884	64.586	60.184	- 9.273	- 28.273	10.663
700	8.924	66.259	60.913	- 8.422	- 29.175	10.475
800	8.962	67.621	61.594	- 7.566	- 30.064	10.331
900	8.989	68.821	62.235	- 6.714	- 30.949	10.218
1000	9.011	69.859	62.835	- 5.876	- 31.826	10.134
1100	9.031	70.818	63.390	- 5.056	- 32.693	10.063
1200	9.049	71.700	63.900	- 4.254	- 33.549	10.000
1300	9.065	72.510	64.366	- 3.470	- 34.396	9.943
1400	9.081	73.263	64.792	- 2.704	- 35.234	9.891
1500	9.095	73.960	65.172	- 1.956	- 36.054	9.844
1600	9.109	74.607	65.503	- 1.226	- 36.856	9.800
1700	9.124	75.200	65.786	- 0.514	- 37.640	9.759
1800	9.137	75.742	66.022	0.180	- 38.406	9.720
1900	9.150	76.235	66.212	0.894	- 39.154	9.683
2000	9.163	76.680	66.356	1.624	- 39.884	9.646
2100	9.175	77.083	66.453	2.368	- 40.596	9.610
2200	9.188	77.443	66.503	3.126	- 41.290	9.574
2300	9.200	77.760	66.508	3.898	- 41.966	9.538
2400	9.213	78.033	66.468	4.684	- 42.624	9.501
2500	9.225	78.258	66.385	5.484	- 43.264	9.464
2600	9.238	78.438	66.258	6.298	- 43.886	9.426
2700	9.250	78.574	66.085	7.126	- 44.490	9.387
2800	9.261	78.668	70.733	7.968	- 45.076	9.347
2900	9.275	78.720	70.733	8.824	- 45.644	9.306
3000	9.288	78.734	70.733	9.694	- 46.194	9.264
3100	9.301	78.709	70.733	10.578	- 46.726	9.221
3200	9.314	78.642	70.733	11.476	- 47.240	9.177
3300	9.328	78.533	70.733	12.388	- 47.736	9.132
3400	9.342	78.380	70.733	13.314	- 48.214	9.087
3500	9.356	78.183	70.733	14.254	- 48.674	9.041
3600	9.371	77.943	70.733	15.208	- 49.116	8.994
3700	9.386	77.659	70.733	16.176	- 49.540	8.946
3800	9.402	77.332	70.733	17.158	- 49.946	8.897
3900	9.419	76.963	70.733	18.154	- 50.334	8.847
4000	9.436	76.550	70.733	19.164	- 50.704	8.796
4100	9.454	76.093	70.733	20.188	- 51.056	8.744
4200	9.472	75.593	70.733	21.226	- 51.390	8.691
4300	9.493	75.050	70.733	22.278	- 51.706	8.637
4400	9.514	74.463	70.733	23.344	- 52.004	8.582
4500	9.535	73.832	70.733	24.424	- 52.284	8.526
4600	9.558	73.157	70.733	25.518	- 52.546	8.469
4700	9.581	72.438	70.733	26.626	- 52.790	8.411
4800	9.606	71.675	70.733	27.748	- 53.016	8.352
4900	9.631	70.868	70.733	28.884	- 53.224	8.292
5000	9.658	70.015	70.733	30.034	- 53.414	8.231
5100	9.685	69.117	70.733	31.198	- 53.586	8.169
5200	9.714	68.174	70.733	32.376	- 53.740	8.106
5300	9.743	67.188	70.733	33.568	- 53.876	8.042
5400	9.774	66.159	70.733	34.774	- 54.004	7.977
5500	9.805	65.088	70.733	35.994	- 54.114	7.911
5600	9.838	63.977	70.733	37.228	- 54.206	7.844
5700	9.871	62.827	70.733	38.476	- 54.280	7.776
5800	9.904	61.539	70.733	39.738	- 54.336	7.707
5900	9.936	60.214	70.733	41.014	- 54.374	7.637
6000	9.971	58.853	70.733	42.304	- 54.394	7.566

June 30, 1968

(IDEAL GAS)

MAGNESIUM MONOBROMIDE (MgBr)

OFW = 104.221

Ground State Configuration $2\sum$

$S_{298.15}^o = 58.481 \pm 0.5$ gibbs/mol

$\Delta H_f^o = -11$ kcal/mol

$\Delta H_f^o_{298.15} = -13 \pm 7$ kcal/mol

Electronic Levels and Quantum Weights

 $\epsilon, \text{ cm}^{-1}$
 g_i
 0
 2
 25800
 4
 39200
 4
 $\omega_e = 373.8 \text{ cm}^{-1}$
 $\omega_e x_e = 1.34 \text{ cm}^{-1}$
 $\alpha_e = [0.000809] \text{ cm}^{-1}$
 $\sigma = 1$
 $r_e = [2.34] \text{ \AA}$

Heat of Formation.

The heat of formation was calculated from that of $\text{MgBr}_2(g)$ using the relation $D(\text{MgBr})/\Delta H_{\text{atom}}(\text{MgBr}_2) = 0.46 \pm 0.04$ which has been shown to apply to several dihalides. This results in $\Delta H_f^o = -13 \pm 7$ and $D_0 = 74.4 \pm 7$ kcal/mol. The selected value is in good agreement with $D_0 \leq 77$ kcal/mol obtained from predissociation by O. Herzberg, "Spectre of Diatomic Molecules," second edition, D. van Nostrand Co., Inc., New York, 1950, and with the linear Birge-Sponner extrapolation of $D_0 = 74$ kcal/mol given by A. O. Aylton, "Dissociation Energies," second edition, Chapman and Hall Ltd. London, 1953. Aylton's selected value of $D_0 = 88 \pm 23$ kcal/mol was discounted since it would require the unlikely ratio $D(\text{MgBr})/\Delta H_{\text{atom}}(\text{MgBr}_2) = 0.28$.

Heat Capacity and Entropy.

The molecular constants ω_e , $\omega_e x_e$ and ground state configuration ($2\sum$) were taken from O. Herzberg, loc. cit., while α_e was calculated from the above constants. The bond distance was estimated to be the same as in $\text{MgBr}_2(g)$.

BrMg

Nitrogen Monobromide (NBr)

(Ideal Gas) Mol. Wt. = 93.924

BrN

NITROGEN MONOBROMIDE (NBr) (IDEAL GAS) MOL. WT. = 93.924

$\Delta H_f^0 = 73.7 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = 71.9 \pm 5 \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = 56.25 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Configuration $3\Sigma^-$

Electronic Level and Multiplicity

$\epsilon, \text{ cm.}^{-1}$	g_i
0	3

$$\omega_e x_e = 4.7 \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$r_e = 1.79 \text{ \AA}$$

$$\omega_e = 699.1 \text{ cm.}^{-1}$$

$$B_e = 0.443 \text{ cm.}^{-1}$$

Heat of Formation

E. R. V. Miller and H. B. Dunford, J. Chem. Phys. 35, 1202 (1961) have extrapolated the ground state vibrational levels and obtain $D_0^0 = 67 \pm 5 \text{ kcal. mole}^{-1}$ or $\Delta H_f^0 = 73.7 \pm 5 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy

Miller and Dunford loc. cit. give all the vibrational and rotational constants, which have been adjusted to the normally occurring isotopic mixture for bromine.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f kcal. mole ⁻¹	ΔF _f kcal. mole ⁻¹	Log K _p
0	-0.000	INFINITE	-2.148	73.700	73.700	INFINITE
100	6.997	48.133	1.145	73.111	73.111	-1.753
200	7.310	53.240	0.696	71.743	71.743	-2.560
298	7.819	56.256	0.000	71.883	65.232	-49.372
300	7.828	56.305	0.014	71.874	67.329	-49.047
400	8.433	60.467	0.813	68.209	66.563	-36.370
500	8.830	63.447	1.643	66.154	66.154	-28.934
600	9.081	65.018	2.400	65.731	65.731	-23.941
700	9.255	65.349	3.164	65.298	65.298	-20.386
800	9.355	65.454	3.854	64.858	64.858	-17.718
900	9.404	65.486	4.484	64.412	64.412	-15.644
1000	9.439	65.478	5.097	63.960	63.960	-13.978
1100	9.461	65.423	5.684	63.504	63.504	-12.616
1200	9.477	65.333	6.245	63.045	63.045	-11.481
1300	9.489	65.216	6.773	62.582	62.582	-10.521
1400	9.498	65.078	7.265	62.117	62.117	-9.696
1500	9.504	64.921	7.723	61.649	61.649	-8.982
1600	9.509	64.750	8.152	61.181	61.181	-8.357
1700	9.512	64.566	8.559	60.711	60.711	-7.805
1800	9.514	64.371	8.944	60.239	60.239	-7.314
1900	9.516	64.166	9.308	59.768	59.768	-6.875
2000	9.517	63.952	9.653	59.293	59.293	-6.479
2100	9.518	63.729	9.979	58.819	58.819	-6.121
2200	9.519	63.500	10.296	58.344	58.344	-5.796
2300	9.520	63.266	10.605	57.868	57.868	-5.498
2400	9.521	63.028	10.907	57.393	57.393	-5.226
2500	9.521	62.786	11.203	56.918	56.918	-4.975
2600	9.522	62.541	11.494	56.443	56.443	-4.744
2700	9.522	62.293	11.780	55.968	55.968	-4.530
2800	9.523	62.043	12.062	55.493	55.493	-4.331
2900	9.523	61.791	12.339	55.018	55.018	-4.145
3000	9.524	61.537	12.612	54.543	54.543	-3.972
3100	9.524	61.281	12.881	54.068	54.068	-3.810
3200	9.525	61.023	13.146	53.593	53.593	-3.659
3300	9.525	60.764	13.407	53.118	53.118	-3.516
3400	9.526	60.504	13.664	52.643	52.643	-3.382
3500	9.526	60.243	13.917	52.168	52.168	-3.255
3600	9.527	60.000	14.166	51.693	51.693	-3.136
3700	9.527	59.756	14.411	51.218	51.218	-3.023
3800	9.528	59.511	14.653	50.743	50.743	-2.916
3900	9.528	59.266	14.892	50.268	50.268	-2.814
4000	9.529	59.021	15.128	49.793	49.793	-2.718
4100	9.529	58.776	15.361	49.318	49.318	-2.626
4200	9.530	58.531	15.592	48.843	48.843	-2.538
4300	9.530	58.286	15.821	48.368	48.368	-2.455
4400	9.531	58.041	16.048	47.893	47.893	-2.375
4500	9.531	57.796	16.273	47.418	47.418	-2.299
4600	9.532	57.551	16.498	46.943	46.943	-2.227
4700	9.532	57.306	16.721	46.468	46.468	-2.157
4800	9.533	57.061	16.943	45.993	45.993	-2.090
4900	9.533	56.816	17.164	45.518	45.518	-2.026
5000	9.534	56.571	17.384	45.043	45.043	-1.965
5100	9.534	56.326	17.603	44.568	44.568	-1.906
5200	9.535	56.081	17.821	44.093	44.093	-1.849
5300	9.535	55.836	18.038	43.618	43.618	-1.794
5400	9.536	55.591	18.254	43.143	43.143	-1.742
5500	9.536	55.346	18.469	42.668	42.668	-1.691
5600	9.537	55.101	18.684	42.193	42.193	-1.642
5700	9.537	54.856	18.898	41.718	41.718	-1.595
5800	9.538	54.611	19.111	41.243	41.243	-1.550
5900	9.538	54.366	19.324	40.768	40.768	-1.505
6000	9.539	54.121	19.537	40.293	40.293	-1.464

Point Group C_{∞}
 $S^{\circ}_{298.15} = 65.35$ gibbs/mol
Round State Quantum Weight = 1

$\Delta H^{\circ}_f = 21.85 \pm 0.2$ kcal/mol
 $\Delta H^{\circ}_{298.15} = 19.83 \pm 0.2$ kcal/mol

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	
1801 (1)	
542 (1)	
[265] (1)	

Bond Distances: O-N = 1.15 ± 0.04 Å
Bond Angle: O-N-Br = $117 \pm 3^{\circ}$

N-Br = 2.14 ± 0.02 Å
 $\sigma = 1$

Product of the Moments of Inertia: $I_A I_B I_C = 5.1631 \times 10^{-115}$ g³ cm⁶

Heat of Formation

The chemical equilibrium of the reaction $2NO(g) + Br_2(g) = 2NOBr(g)$ has been studied by Trautz and Dala¹, Blair, Brea and Yoal², and Kraus³, respectively. Using the reported equilibrium constants, the enthalpy changes ($\Delta H^{\circ}_{298.15}$) of this reaction are evaluated by both the second and third law methods. Based on the third law $\Delta H^{\circ}_{298.15}$ values, the heats of formation for NOBr(g) are derived. The results obtained are presented in the table below. The value of $\Delta H^{\circ}_{298.15}$ (NOBr,g) adopted is 19.63 ± 0.2 kcal/mol.

Investigator	No. of Points	Temperature, °K	Second Law Value	Third Law Value	Drift	$\Delta H^{\circ}_{298.15}$ kcal/mol
1. Trautz and Dala ¹	•	258.2 - 603.2	-11.11	-11.30	-0.4	19.62
2. Blair et al.	30	296.9 - 502.9	-11.74 ± 0.07	-11.26	1.3 ± 0.2	19.64
3. Kraus ³	23	264.0 - 290.1	-13.46 ± 0.50	-9.62	-13.7 ± 1.1	20.46

*The data points employed for evaluation are calculated from a given equation.

1. M. Trautz and V. P. Dala, Z. Anorg. Chem. **110**, 1 (1920).

2. C. M. Blair, Jr., P.D. Brea and D. M. Yoal, J. Am. Chem. Soc. **56**, 1916 (1934).

3. W. Kraus, Z. Physik. Chem. **A175**, 295 (1936).

Heat Capacity and Entropy

The molecular structure of NOBr(g) has been determined by electron diffraction by J. A. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. **59**, 2829 (1937). The results were confirmed later by T. L. Weatherly and Q. Williams, J. Chem. Phys. **25**, 717 (1956), who studied the microwave spectrum of NOBr(g) in the region 20,000 - 40,000 Mc/sec and analyzed the J = 2-3 transition. The values of bond length and angle adopted are obtained from Ketelaar and Palmer, loc. cit. The infrared absorption spectrum of NOBr(g) has been examined from 400 to 5303 cm⁻¹ by W. O. Burns and H. J. Bernalein, J. Chem. Phys. **18**, 1689 (1950). The authors observed the first two fundamental vibrational frequencies and obtained the third from combination and overtone. These assignments are adopted. The three principal moments of inertia are: $I_A = 9.404 \times 10^{-40}$, $I_B = 2.2985 \times 10^{-38}$ and $I_C = 2.3906 \times 10^{-38}$ g cm².

T, °K	C_p°	$g^{\circ} - H^{\circ}_{298}/T$	$H^{\circ} - H^{\circ}_{298}$	kcal/mol ΔH°_f	ΔG°_f	Log Kp
0	-0.000	INFINITE	-2.785	21.868	21.868	INFINITE
100	8.495	94.430	-1.973	20.789	45.426	-
200	10.006	61.182	-1.031	21.293	20.071	-21.933
298	10.868	65.347	-0.000	19.630	19.609	-
300	10.879	65.414	0.070	19.621	19.700	-14.951
400	11.678	71.200	1.253	19.611	21.631	-10.455
500	12.477	75.056	2.059	19.601	22.774	-8.205
600	12.107	73.377	3.488	15.054	23.013	-7.466
700	12.388	75.265	4.713	15.086	25.047	-6.982
800	12.671	76.935	7.563	15.086	27.303	-5.967
900	12.954	78.427	9.828	16.000	28.426	-5.068
1000	13.237	80.104	11.444	16.140	29.546	-5.381
1200	13.204	82.178	13.802	16.216	31.774	-4.960
1400	13.165	84.226	15.141	16.251	32.883	-4.791
1500	13.427	85.131	75.056	16.286	33.001	-4.643
1600	13.479	86.019	75.715	16.318	33.007	-4.512
1700	13.524	86.898	76.345	16.350	33.013	-4.391
1800	13.563	87.719	76.935	16.376	33.019	-4.291
1900	13.594	88.546	77.510	16.401	33.024	-4.196
2000	13.623	89.344	78.059	16.424	33.029	-4.111
2100	13.648	89.709	78.626	16.443	33.033	-4.033
2200	13.670	90.345	79.145	16.458	33.037	-3.961
2300	13.670	90.915	79.626	16.470	33.040	-3.897
2400	13.706	91.536	80.128	16.478	33.042	-3.840
2500	13.722	92.095	80.596	16.483	33.043	-3.787
2600	13.735	92.634	81.049	16.487	33.044	-3.742
2700	13.747	93.152	81.487	16.490	33.045	-3.700
2800	13.757	93.650	81.909	16.491	33.046	-3.660
2900	13.766	94.136	82.326	16.492	33.047	-3.638
3000	13.777	94.603	82.728	16.496	33.049	-3.597
3100	13.785	95.054	83.118	16.490	33.050	-3.558
3200	13.793	95.492	83.498	16.481	33.051	-3.522
3300	13.800	95.917	83.867	16.470	33.052	-3.485
3400	13.806	96.329	84.228	16.458	33.053	-3.445
3500	13.812	96.729	84.580	16.437	33.054	-3.425
3600	13.817	97.118	84.923	16.417	33.054	-3.397
3700	13.822	97.497	85.257	16.395	33.054	-3.370
3800	13.827	97.867	85.582	16.372	33.054	-3.344
3900	13.830	98.229	85.904	16.348	33.054	-3.320
4000	13.834	98.575	86.216	16.315	33.054	-3.297
4100	13.838	98.917	86.522	16.284	33.054	-3.276
4200	13.842	99.250	86.821	16.251	33.054	-3.255
4300	13.844	99.576	87.104	16.218	33.054	-3.235
4400	13.847	99.894	87.401	16.179	33.054	-3.217
4500	13.850	100.205	87.682	16.140	33.054	-3.199
4600	13.853	100.510	87.957	16.099	33.054	-3.182
4700	13.856	100.809	88.226	16.057	33.054	-3.166
4800	13.859	101.099	88.483	16.012	33.054	-3.150
4900	13.861	101.385	88.733	15.966	33.054	-3.135
5000	13.861	101.665	89.008	15.919	33.054	-3.121
5100	13.863	101.946	89.259	15.869	33.054	-3.107
5200	13.865	102.209	89.500	15.818	33.054	-3.092
5300	13.867	102.473	89.748	15.767	33.054	-3.082
5400	13.868	102.732	90.000	15.713	33.054	-3.070
5500	13.870	102.987	90.242	15.658	33.054	-3.058
5600	13.871	103.237	90.450	15.601	33.054	-3.047
5700	13.872	103.482	90.647	15.543	33.054	-3.037
5800	13.874	103.723	90.800	15.485	33.054	-3.026
5900	13.875	103.961	91.119	15.428	33.054	-3.016
6000	13.876	104.194	91.335	15.367	33.054	-3.007

Sodium Bromide (NaBr)

(Crystal) Mol. Wt. = 102.907

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _f
0	0.000	INFINITE	2.770	- 84.680	- 84.680	- 84.680	INFINITE
100	9.000	21.210	2.770	- 84.680	- 84.680	- 84.680	14.421
200	11.950	15.970	2.770	- 84.680	- 84.680	- 84.680	91.864
298	12.285	20.750	2.770	- 84.680	- 84.680	- 84.680	61.187
300	12.295	20.826	2.770	- 84.680	- 84.680	- 84.680	60.796
400	12.775	24.433	2.770	- 84.680	- 84.680	- 84.680	44.633
500	13.110	27.321	2.770	- 84.680	- 84.680	- 84.680	34.739
600	13.400	29.737	2.770	- 84.680	- 84.680	- 84.680	28.153
700	13.700	31.825	2.770	- 84.680	- 84.680	- 84.680	23.458
800	14.000	33.674	2.770	- 84.680	- 84.680	- 84.680	19.945
900	14.300	35.340	2.770	- 84.680	- 84.680	- 84.680	17.221
1000	14.600	36.862	2.770	- 84.680	- 84.680	- 84.680	15.049
1100	14.900	38.268	2.770	- 84.680	- 84.680	- 84.680	13.278
1200	15.200	39.577	2.770	- 84.680	- 84.680	- 84.680	11.725
1300	15.500	40.805	2.770	- 84.680	- 84.680	- 84.680	10.162
1400	15.800	41.965	2.770	- 84.680	- 84.680	- 84.680	8.829
1500	16.096	43.065	2.770	- 84.680	- 84.680	- 84.680	7.681
1600	16.400	44.113	2.770	- 84.680	- 84.680	- 84.680	6.682
1700	16.713	45.117	2.770	- 84.680	- 84.680	- 84.680	5.806
1800	17.033	46.081	2.770	- 84.680	- 84.680	- 84.680	5.033
1900	17.362	47.011	2.770	- 84.680	- 84.680	- 84.680	4.346
2000	17.700	47.910	2.770	- 84.680	- 84.680	- 84.680	3.732

BrNa

MOL. WT. = 102.907

(CRYSTAL)

SODIUM BROMIDE (NaBr)

$\Delta H_f^0 = -84.68 \pm 0.10 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = -86.38 \pm 0.10 \text{ kcal. mole}^{-1}$
 $\Delta H_m^0 = 6.24 \text{ kcal. mole}^{-1}$
 $\Delta H_m^{298.15} = 51.98 \text{ kcal. mole}^{-1} \text{ to monomer gas}$
 $T_m = 1020^\circ \text{K.}$

Heat of Formation.

The heat of solution of NaBr(c) in water has been measured by F. A. Askew, E. Bullock, H. T. Smith, R. K. Tinkler, O. Gatty and J. R. Wolfenden, *J. Chem. Soc.* 1368 (1934) and W. E. Wallace, *J. Am. Chem. Soc.* 71, 2485 (1949) to be +0.01 and -0.14 kcal. mole⁻¹, respectively. Using $\Delta H_f^{298.15}(\text{Na}^+, \text{aq.}) = -57.39$ and $\Delta H_f^{298.15}(\text{Br}^-, \text{aq.}) = -29.05 \text{ kcal. mole}^{-1}$, obtained from D. D. Wagman, National Bureau of Standards, private communication, July 2, 1964, the respective value of $\Delta H_f^{298.15}$ for NaBr(c) was found to be -86.3 and -86.45 kcal. mole⁻¹. The adopted value is the average of these two.

Heat Capacity and Entropy.

The low temperature heat capacities (7.21 - 301.63°K.) were measured by T. E. Gardner and A. R. Taylor, Jr., U. S. Bur. Mines RI 6435 (1964). The high temperature enthalpy changes (280 - 645, 290 - 916°K.) were determined by A. Wagnua, *Phys. Z.* 14, 5 (1913). Based upon the latter data the high temperature heat capacities were derived. The two sets of C_p data were joined smoothly at 298°K. by graphical method. $S_{298.15}^{298.15}$ was obtained from T. E. Gardner and A. R. Taylor, Jr., loc. cit., using $S_{10}^0 = 0.034 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

T_m and ΔH_m^0 were reported by A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.* 54, 269 (1960). The values, $T_m = 1014^\circ \text{K.}$ and $\Delta H_m^0 = 5.52 \text{ kcal. mole}^{-1}$, reported by M. Blanc, *Compt. Rend.*, 246, 570 (1958), were not used.

Heat of Sublimation.

The value of ΔH_m^0 is 298.15 was derived from six sets of vapor pressure data by both the second and third law methods. See NaBr(g) table for detail.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0						
100						
200						
298	14.900	24.940	24.940	0.000	- 81.105	- 79.450
300						58.236
350	14.900	25.032	24.940	0.078	- 81.104	- 79.439
400	14.900	25.116	24.929	1.518	- 85.080	- 78.132
500	14.900	32.543	26.628	3.008	- 84.772	- 76.430
600	14.900	35.360	27.864	4.498	- 84.447	- 74.793
700	14.900	37.657	29.103	5.988	- 84.110	- 73.211
800	14.900	39.481	30.342	7.478	- 83.772	- 71.628
900	14.900	41.002	31.438	8.968	- 83.412	- 70.188
1000	14.900	42.572	32.514	10.458	- 83.062	- 68.737
1100	14.900	44.392	33.531	11.948	- 82.719	- 67.283
1200	14.900	45.988	34.400	13.438	- 82.380	- 65.825
1300	14.900	47.385	35.128	14.928	- 82.040	- 64.365
1400	14.900	48.585	36.258	16.418	- 81.700	- 62.905
1500	14.900	49.613	37.075	17.908	- 81.360	- 61.445
1600	14.900	49.975	37.851	19.398	- 81.020	- 60.000
1700	14.900	50.530	38.578	20.888	- 80.680	- 58.560
1800	14.900	51.230	39.266	22.378	- 80.340	- 57.120
1900	14.900	52.036	39.974	23.868	- 80.000	- 55.680
2000	14.900	52.900	40.621	25.358	- 79.660	- 54.240
2100	14.900	54.027	41.242	26.848	- 79.320	- 52.800
2200	14.900	55.380	42.812	28.338	- 78.980	- 51.360
2300	14.900	56.916	44.467	29.828	- 78.640	- 49.920
2400	14.900	58.624	46.267	31.318	- 78.300	- 48.480
2500	14.900	59.624	48.301	32.808	- 77.960	- 47.040

S_{298.15} = [24.940] cal. deg.⁻¹ mole⁻¹

ΔH_f^o 298.15 = [-81.105] kcal. mole⁻¹

ΔH_m^o = 6.24 kcal. mole⁻¹

T_m = 1020°K.

T_b = [1720]°K. to monomer gas

ΔH_v^o = 39.42 kcal. mole⁻¹ to monomer gas

Heat of Formation.

ΔH_f^o 298.15(l) was obtained from ΔH_f^o 298.15(c) by adding ΔH_m^o and the difference between H° - H°_{298.15} for crystal and liquid. The equilibrium constant of the reaction NaBr(l) + HCl(g) = NaCl(l) + HBr(g) has been determined by J. Toguri, H. Flood and T. Forland, *Acta Chem. Scand.* 17, 1502 (1963). From the reported data, lnK_{900°K} = -1.19 ± 0.01, the heat of reaction (ΔH_r^o 298.15) was derived to be 2.11 kcal. mole⁻¹. Using ΔH_f^o 298.15 (HCl, g) = -22.062, ΔH_f^o 298.15 (NaCl, l) = -92.24 and ΔH_f^o 298.15 (HBr, g) = -8.70 kcal. mole⁻¹, the value of ΔH_f^o 298.15 for NaBr(l) was evaluated to be -81.0 ± 0.5 kcal. mole⁻¹ which is in reasonable agreement with the value adopted. The values of ΔH_f^o 298.15 for HCl(g) and HBr(g) were obtained from D. D. Wagman, National Bureau of Standards, private communication, July 2, 1964.

Heat Capacity and Entropy.

Heat capacity for NaBr(l) was estimated by comparison with those for NaCl(c), AgCl(c) and AgCl(l). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and ΔH_m^o were reported by A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.* 64, 269 (1960). The values, T_m = 1014°K. and ΔH_m^o = 5.52 kcal. mole⁻¹, reported by M. Blanc, *Compt. Rend.*, 246, 570 (1958), were not used.

Vaporization Data.

The boiling point, T_b, was calculated as the temperature at which the value of ΔH_f^o becomes zero for the reaction NaBr(l) → NaBr(g). The difference between ΔH_f^o for NaBr(l) and NaBr(g) at T_b is the heat of vaporization, ΔH_v^o.

Sodium Bromide (NaBr)

(Ideal Gas) Mol. Wt. = 102.907

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	2.344	-32.274	-32.274	INFINITE
100	7.475	48.724	65.090	-32.220	-35.880	78.412
200	8.355	54.221	58.413	-32.504	-39.404	43.056
298	8.681	57.628	57.628	-34.400	-42.491	31.145
300	8.685	57.681	57.628	-34.412	-42.540	30.989
400	8.833	60.203	57.971	-39.000	-44.406	24.261
500	8.915	62.183	58.622	-39.294	-45.722	19.984
600	8.970	63.814	59.356	-39.545	-46.983	17.113
700	9.010	65.200	60.094	-39.768	-48.200	15.048
800	9.043	66.405	60.809	-40.059	-49.380	13.489
900	9.072	67.472	61.491	-40.383	-50.531	12.270
1000	9.098	68.429	62.138	-40.723	-51.655	11.289
1100	9.121	69.297	62.750	-41.070	-52.769	10.482
1200	9.144	70.092	63.329	-41.435	-53.869	9.732
1300	9.166	70.825	63.878	-41.815	-54.956	9.022
1400	9.187	71.505	64.399	-42.204	-56.030	8.350
1500	9.208	72.139	64.894	-42.600	-57.093	7.730
1600	9.228	72.734	65.365	-43.015	-58.143	7.160
1700	9.248	73.294	65.816	-43.445	-59.181	6.630
1800	9.268	73.823	66.246	-43.885	-60.207	6.130
1900	9.287	74.325	66.658	-44.335	-61.221	5.660
2000	9.307	74.802	67.053	-44.795	-62.221	5.210
2100	9.326	75.256	67.433	-45.265	-63.207	4.780
2200	9.345	75.691	67.799	-45.745	-64.179	4.360
2300	9.364	76.106	68.151	-46.235	-65.137	3.950
2400	9.383	76.505	68.481	-46.735	-66.081	3.550
2500	9.402	76.889	68.819	-47.245	-67.011	3.160
2600	9.421	77.258	69.137	-47.765	-67.927	2.780
2700	9.440	77.614	69.444	-48.295	-68.829	2.410
2800	9.459	77.957	69.742	-48.835	-69.717	2.050
2900	9.478	78.290	70.031	-49.385	-70.591	1.700
3000	9.497	78.611	70.312	-49.945	-71.451	1.360
3100	9.515	78.923	70.585	-50.515	-72.297	1.030
3200	9.534	79.225	70.850	-51.095	-73.131	0.710
3300	9.553	79.519	71.108	-51.685	-73.951	0.400
3400	9.572	79.805	71.360	-52.285	-74.757	0.100
3500	9.590	80.082	71.605	-52.895	-75.549	0.000
3600	9.609	80.353	71.844	-53.515	-76.327	0.000
3700	9.628	80.617	72.078	-54.145	-77.091	0.000
3800	9.647	80.873	72.306	-54.785	-77.841	0.000
3900	9.665	81.124	72.529	-55.435	-78.577	0.000
4000	9.684	81.369	72.747	-56.095	-79.301	0.000
4100	9.703	81.608	72.960	-56.765	-80.011	0.000
4200	9.721	81.842	73.169	-57.445	-80.707	0.000
4300	9.740	82.071	73.373	-58.135	-81.391	0.000
4400	9.759	82.296	73.573	-58.835	-82.061	0.000
4500	9.777	82.515	73.770	-59.545	-82.717	0.000
4600	9.796	82.730	73.962	-60.265	-83.361	0.000
4700	9.815	82.941	74.151	-60.995	-84.001	0.000
4800	9.833	83.148	74.336	-61.735	-84.631	0.000
4900	9.852	83.351	74.518	-62.485	-85.251	0.000
5000	9.871	83.550	74.697	-63.245	-85.861	0.000
5100	9.889	83.746	74.872	-64.015	-86.461	0.000
5200	9.908	83.938	75.045	-64.795	-87.051	0.000
5300	9.926	84.127	75.214	-65.585	-87.631	0.000
5400	9.945	84.312	75.381	-66.385	-88.201	0.000
5500	9.964	84.495	75.545	-67.195	-88.761	0.000
5600	9.982	84.675	75.707	-68.015	-89.311	0.000
5700	10.001	84.852	75.865	-68.845	-89.851	0.000
5800	10.019	85.026	76.022	-69.685	-90.381	0.000
5900	10.038	85.197	76.176	-70.535	-90.901	0.000
6000	10.057	85.366	76.332	-71.395	-91.411	0.000

Sept. 30, 1964

SODIUM BROMIDE (NaBr)

(IDEAL GAS)

MOL. WT. = 102.907

Ground State Configuration $1\sum^+ +$ $S^{\circ}_{298.15} = 57.628 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H^{\circ}_f 0 = -32.27 \pm 0.50 \text{ kcal. mole}^{-1}$ $\Delta H^{\circ}_f 298.15 = -34.40 \pm 0.50 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

 $\frac{g_1}{0} \text{ cm.}^{-1}$ $\omega_e x_e = 1.50 \text{ cm.}^{-1}$ $\sigma = 1$ $\alpha_e = 0.000959 \text{ cm.}^{-1}$ $r_e = 2.5020 \pm 0.0001 \text{ \AA}$

Heat of Formation.

The heat of formation ($\Delta H^{\circ}_f 298.15$) was calculated from $\Delta H^{\circ}_f 298.15$ and $\Delta H^{\circ}_f 298.15$ for NaBr(c). The latter was derived from six sets of corrected vapor pressure data, due to the presence of dimeric species in the vapor, by both the second and third law methods. The results are listed as follows.

Investigator	Reaction	Third Law Value	Second Law Value	$\Delta H^{\circ}_f 298.15$, kcal. mole ⁻¹	$\Delta H^{\circ}_f 298.15$, kcal. mole ⁻¹
Niwe ¹	NaBr(c) → NaBr(g)	51.97	50.31	-35.24	-35.24
Cogin and Kimball ²	NaBr(c) → NaBr(g)	52.26	52.14	-34.18	-34.18
Meyer and Wintner ³	NaBr(c) → NaBr(g)	52.59	52.59	-33.79**	-33.79**
Ruff and Muggen ⁴	NaBr(l) → NaBr(g)	46.43	47.48	-34.15	-34.15
Wertheberg and Albrecht ⁵	NaBr(l) → NaBr(g)	46.38	47.54	-34.15	-34.15
Bloom et al. ⁶	NaBr(l) → NaBr(g)	46.23	51.53	-34.88**	-34.88**

*Based on the average of the second and third law values.

**Only the third law value being used.

1 K. Niwe, J. Rec. Sci., Hokkaido Univ., Ser. III, 2, 201 (1938).

2 O. E. Cogin and O. E. Kimball, J. Chem. Phys. 16, 1035 (1948).

3 J. E. Meyer and I. H. Wintner, J. Chem. Phys. 6, 301 (1938).

4 O. Ruff and S. Muggen, Z. anorg. allgem. Chem., 117, 147 (1921).

5 H. von Wertheberg and P. Albrecht, Z. Electrochem., 27, 162 (1921).

6 H. Bloom, J. O. M. Bockris, N. E. Richards and R. O. Taylor, J. Am. Chem. Soc. 80, 2044 (1958).

The value of $\Delta H^{\circ}_f 298.15$ for NaBr(g) adopted is the average value of the six $\Delta H^{\circ}_f 298.15$ values listed in the above table. The dissociation energy (D°_0) was calculated to be 86.28 kcal. mole⁻¹ or 3.74 e.v. which is in good agreement with the value, $D^{\circ}_0 = 3.84 \pm 1$ and 3.65 e.v., reported by A. G. Oeydon, "Disociation Energies", Chapman and Hall Ltd., London, 1953 and O. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, New York, 1950, respectively. According to L. Brewer, private communication, October 23, 1964, Oeydon's original reported value, $D^{\circ}_0 = 3.8$, is an average of the value of 3.84 e.v. from atomic fluorescence and the value of 3.75 e.v. calculated for Oeydon by Brewer from pressure data available at that time.

Heat Capacity and Entropy.

The values of ω_e , $\omega_e x_e$, B_e and α_e were taken from S. A. Rice and W. Klemperer, J. Chem. Phys. 27, 573 (1957). The adopted bond distance (r_e) was reported by A. Honig, M. Mendel, M. L. Sticht and C. H. Townes, Phys. Rev. 96, 629 (1954), which was derived from microwave spectrum. By electron-diffraction method, the Na-Br bond distance was determined as $2.64 \pm 0.01 \text{ \AA}$ by L. R. Maxwell, S. B. Hendricks and V. M. Moaley, Phys. Rev. 52, 968 (1937). The discrepancy may be due to the presence of a large proportion of dimer at the higher pressures used in the electron-diffraction determination. The ground state configuration was reported by O. Herzberg, loc. cit.

BrNa

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	- 2.272	44.519	44.519	INFINITE
100	7.1175	50.995	66.728	44.703	40.487	- 88.479
200	8.010	56.241	60.269	44.652	36.217	- 39.574
298	8.460	59.537	59.537	43.000	32.298	- 23.674
300	8.465	59.599	59.537	42.990	32.232	- 23.480
400	8.777	62.007	59.672	39.195	26.808	- 16.072
500	8.792	62.007	60.511	38.057	26.808	- 11.786
600	8.863	65.616	61.231	38.895	24.589	- 8.956
700	8.912	66.986	61.958	38.704	22.219	- 6.937
800	8.947	68.179	62.663	4.413	14.568	- 3.980
900	8.969	69.145	63.353	18.066	14.568	- 3.980
1000	8.999	70.181	63.973	18.089	13.691	- 2.992
1100	9.019	71.040	64.577	18.096	13.250	- 2.632
1200	9.037	71.825	65.149	18.105	12.809	- 2.333
1300	9.054	72.564	65.691	18.113	12.369	- 2.079
1400	9.069	73.261	66.208	18.121	11.929	- 1.847
1500	9.083	73.847	66.694	18.128	11.484	- 1.633
1600	9.097	74.434	67.159	18.136	11.040	- 1.508
1700	9.111	74.986	67.604	18.143	10.597	- 1.362
1800	9.124	75.511	68.035	18.150	10.154	- 1.217
1900	9.137	76.009	68.451	18.157	9.711	- 1.073
2000	9.149	76.466	68.825	18.167	9.262	- 1.012
2100	9.161	76.916	69.200	18.175	8.817	- .918
2200	9.173	77.343	69.561	18.183	8.372	- .832
2300	9.184	77.753	69.908	18.190	7.927	- .753
2400	9.197	78.147	70.241	18.197	7.482	- .681
2500	9.209	78.518	70.566	18.209	7.033	- .615
2600	9.221	78.879	70.879	20.799	6.584	- .553
2700	9.232	79.227	71.182	21.722	6.136	- .497
2800	9.243	79.565	71.475	22.646	5.689	- .446
2900	9.255	79.888	71.757	23.569	5.240	- .399
3000	9.267	80.202	72.016	24.497	4.793	- .349
3100	9.278	80.506	72.264	25.424	4.345	- .306
3200	9.289	80.800	72.505	26.353	3.894	- .266
3300	9.299	81.091	72.741	27.282	3.446	- .226
3400	9.309	81.376	72.972	28.213	2.994	- .186
3500	9.323	81.634	73.207	29.144	2.544	- .159
3600	9.334	81.897	73.542	30.077	2.092	- .127
3700	9.346	82.153	73.772	31.011	1.641	- .097
3800	9.357	82.409	74.002	31.945	1.191	- .067
3900	9.368	82.666	74.214	32.885	0.741	- .032
4000	9.379	82.883	74.428	33.820	0.285	- .016
4100	9.380	83.115	74.637	34.759	0.167	- .009
4200	9.403	83.542	74.842	35.698	0.106	- .032
4300	9.413	83.778	75.046	36.637	0.046	- .076
4400	9.424	83.778	75.236	37.581	0.000	- .096
4500	9.435	83.991	75.430	38.524	18.442	- .096
4600	9.446	84.198	75.618	39.468	18.457	- .116
4700	9.457	84.402	75.803	40.413	18.472	- .134
4800	9.468	84.606	76.000	41.357	18.487	- .156
4900	9.479	84.796	76.162	42.307	18.503	- .176
5000	9.491	84.988	76.325	43.255	18.519	- .196
5100	9.502	85.176	76.508	44.205	18.534	- .202
5200	9.513	85.350	76.677	45.155	18.551	- .217
5300	9.524	85.524	76.842	46.105	18.567	- .236
5400	9.535	85.720	77.005	47.050	18.585	- .256
5500	9.546	85.895	77.165	48.014	18.603	- .259
5600	9.557	86.067	77.323	48.969	18.620	- .273
5700	9.568	86.236	77.477	49.926	18.638	- .285
5800	9.579	86.406	77.630	50.883	18.656	- .297
5900	9.590	86.567	77.780	51.841	18.676	- .310
6000	9.601	86.728	77.928	52.801	18.694	- .321

June 30, 1963; Dec. 31, 1963

Ground State Configuration [$\sum$]
S^{298.15} = [59.5] cal. deg.⁻¹ mole⁻¹
ΔH_f^o = [45] kcal. mole⁻¹
ΔH_f^{298.15} = [43] kcal. mole⁻¹

Electronic Levels and Multiplicities

$$\frac{\epsilon_f, \text{cm.}^{-1}}{0} \frac{g_f}{(3)}$$

$$\omega_e x_e = [1.5] \text{ cm.}^{-1} \quad \sigma = 1 \quad r_e = [2.23] \text{ \AA}$$

$$\omega_e = [400] \text{ cm.}^{-1} \quad \alpha_e = [0.0008] \text{ cm.}^{-1}$$

$$B_e = [0.1519] \text{ cm.}^{-1}$$

Heat of Formation.

ΔH_f^o 0 was estimated as 40.8 kcal. mole⁻¹ by J. S. Gordon, Astronautics International, Livingston, New Jersey, private communication, August 25, 1961. This ΔH_f^{298.15} was changed from the white (α) to red (V) phosphorus reference state.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit.

INTERIM TABLE

Mol. Wt. = 287.13

(Ideal Gas)

T, K.	C _p ^a	S° ^b	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^c	ΔF _f ^d	Log K _p
0	-0.004	∞	∞	∞	∞	∞	∞
100	7.963	55.664	72.630	2.424	15.449	15.449	INFINITE
200	8.639	61.446	65.739	1.897	15.420	11.377	-24.864
298	8.825	64.936	64.936	.000	15.400	7.464	-8.156
300	8.827	64.991	64.936	.016	13.288	3.922	-2.957
400	8.906	67.542	65.284	.903	9.403	1.586	-.867
500	8.951	69.535	65.942	1.796	9.181	.344	-.150
600	8.982	71.170	66.681	2.493	8.944	-.226	.811
700	9.006	72.546	67.374	3.093	8.674	-.724	1.911
800	9.027	73.750	68.142	4.494	8.376	-1.489	3.156
900	9.046	74.825	68.827	5.398	8.041	-2.407	4.589
1000	9.064	75.779	69.475	6.304	7.667	-3.481	6.176
1100	9.084	76.643	70.088	7.211	7.250	-4.616	7.963
1200	9.095	77.445	70.668	8.121	6.797	-5.811	9.915
1300	9.110	78.184	71.217	9.032	6.308	-7.067	12.020
1400	9.119	78.862	71.737	9.946	5.784	-8.381	14.287
1500	9.191	79.475	72.232	10.864	5.203	-9.750	16.729
1600	9.238	80.059	72.704	11.785	4.563	-11.177	19.355
1700	9.269	80.610	73.154	12.710	3.873	-12.750	22.185
1800	9.314	81.161	73.584	13.639	3.133	-14.467	25.238
1900	9.362	81.666	73.996	14.572	2.353	-16.330	28.543
2000	9.413	82.147	74.392	15.511	1.523	-18.355	32.129
2100	9.466	82.608	74.772	16.455	.653	-20.543	36.029
2200	9.521	83.048	75.142	17.405	-.257	-22.917	40.285
2300	9.576	83.474	75.492	18.359	-1.107	-25.482	44.948
2400	9.632	83.883	75.833	19.320	-1.920	-28.250	50.070
2500	9.687	84.277	76.163	20.286	-2.693	-31.233	55.711
2600	9.742	84.658	76.482	21.257	-3.427	-34.443	61.945
2700	9.796	85.027	76.792	22.231	-4.123	-37.897	68.845
2800	9.847	85.384	77.092	23.216	-4.781	-41.605	76.485
2900	9.898	85.730	77.384	24.203	-5.403	-45.681	84.945
3000	9.946	86.067	77.668	25.196	-5.997	-50.133	94.311
3100	9.992	86.394	77.944	26.193	-6.563	-54.977	104.695
3200	10.036	86.711	78.214	27.193	-7.103	-60.223	116.235
3300	10.078	87.021	78.476	28.200	-7.617	-65.881	128.975
3400	10.117	87.322	78.731	29.209	-8.105	-71.959	143.000
3500	10.154	87.616	78.981	30.223	-8.567	-78.477	158.425
3600	10.189	87.903	79.225	31.240	-9.003	-85.455	175.375
3700	10.221	88.182	79.463	32.260	-9.415	-92.911	193.985
3800	10.251	88.455	79.696	33.284	-9.803	-100.865	214.405
3900	10.279	88.722	79.924	34.311	-10.167	-109.333	236.805
4000	10.306	88.982	80.147	35.340	-10.507	-118.337	261.375
4100	10.330	89.237	80.366	36.372	-10.823	-127.897	288.325
4200	10.353	89.487	80.580	37.405	-11.115	-138.043	317.875
4300	10.373	89.730	80.790	38.442	-11.383	-148.805	350.275
4400	10.393	89.969	80.996	39.481	-11.627	-160.213	385.775
4500	10.410	90.203	81.198	40.521	-11.847	-172.307	424.645
4600	10.427	90.432	81.396	41.563	-12.043	-185.127	467.255
4700	10.442	90.656	81.591	42.607	-12.215	-198.713	513.975
4800	10.456	90.876	81.782	43.651	-12.363	-213.113	565.105
4900	10.469	91.092	81.970	44.697	-12.487	-228.387	621.045
5000	10.480	91.303	82.155	45.745	-12.597	-244.587	682.295
5100	10.491	91.511	82.336	46.793	-12.693	-261.773	749.295
5200	10.501	91.715	82.514	47.841	-12.775	-279.997	822.545
5300	10.511	91.915	82.690	48.893	-12.843	-300.317	902.545
5400	10.519	92.112	82.863	49.945	-12.897	-322.807	990.005
5500	10.527	92.305	83.032	50.997	-12.937	-347.537	1085.645
5600	10.535	92.494	83.200	52.050	-12.963	-373.577	1199.295
5700	10.542	92.681	83.364	53.104	-12.975	-400.997	1331.945
5800	10.548	92.864	83.527	54.159	-12.975	-429.877	1484.695
5900	10.554	93.045	83.686	55.214	-12.963	-460.297	1658.745
6000	10.560	93.222	83.844	56.269	-12.940	-493.347	1855.695

June 30, 1962

Lead Monobromide (PbBr)

(Ideal Gas)

Mol. Wt. = 287.13

ΔH_f° 298.15 = 13.3 ± 9.2 kcal. mole⁻¹S° 298.15 = 64.936 cal. deg.⁻¹ mole⁻¹Ground State Configuration 2Π_{1/2}

Electronic Levels and Multiplicities

ε, cm. ⁻¹	g ₁	g ₂
0	0	2
[8000]	2	2

ω_e = 207.5 cm.⁻¹ω_ex_e = 0.50 cm.⁻¹B_e = [0.04874] cm.⁻¹

σ = 1

Heat of Formation. ΔH_f° 298.15 was calculated from the dissociation energy of PbBr(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ω_e and ω_ex_e were obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950). B_e and α_e were estimated by J. S. Gordon, AstroSystems, Inc., private communication, May, 1962. Electronic levels and multiplicities were estimated from those for Pb(g).

(Ideal Gas)

GFw = 127.809

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ - (G^\circ - H^\circ_{298})/T}$	$\frac{\text{kcal/mol}}{H^\circ - H^\circ_{298}}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
100	7.000	INFINITE	- 2.375	52.506	52.506	INFINITE
100	7.000	53.119	52.747	52.747	52.747	105.502
200	8.466	52.987	- .862	52.508	46.876	- 47.946
298	9.087	62.175	.000	50.800	39.871	- 29.826
300	9.098	62.175	.017	50.789	38.803	- 28.897
400	9.691	67.114	1.932	46.875	26.170	- 15.040
500	10.194	68.943	2.941	46.778	31.924	- 11.628
600	10.333	70.525	3.968	46.672	29.457	- 9.197
700	10.411	71.911	5.005	46.552	27.005	- 7.369
800	10.475	73.282	6.117	46.424	24.681	- 5.849
1000	10.489	75.241	67.838	46.051	19.754	- 3.925
1100	10.500	76.154	68.493	44.897	17.410	- 3.171
1200	10.511	76.975	69.119	44.781	15.844	- 2.603
1300	10.524	77.704	69.719	44.686	14.587	- 2.181
1400	10.539	78.351	70.269	44.505	10.580	- 1.541
1500	10.557	79.182	70.805	44.342	8.325	- 1.137
1600	10.576	79.823	71.317	44.161	6.078	- .781
1700	10.596	80.068	71.806	43.973	3.821	- .487
1800	10.614	80.824	72.275	43.733	1.564	- .202
2000	10.640	81.546	72.775	39.045	- .436	.048
2100	10.662	82.066	73.158	38.803	- 2.403	.250
2200	10.684	82.563	73.574	38.562	- 4.361	.433
2300	10.707	83.049	73.916	38.326	- 6.318	.590
2400	10.727	83.498	74.302	38.083	- 8.260	.750
2500	10.747	83.932	74.737	37.850	- 10.166	.889
2600	10.766	84.354	75.098	37.616	- 12.083	1.016
2700	10.784	84.761	75.449	37.382	- 13.990	1.132
2800	10.801	85.153	75.788	37.148	- 15.896	1.240
2900	10.814	85.533	76.118	36.920	- 17.776	1.340
3000	10.831	85.900	76.438	36.690	- 19.659	1.432
3100	10.845	86.255	76.749	36.461	- 21.532	1.518
3200	10.858	86.599	77.051	36.233	- 23.402	1.598
3300	10.871	86.934	77.344	36.004	- 25.268	1.673
3400	10.881	87.258	77.633	35.779	- 27.114	1.743
3500	10.892	87.574	77.912	35.553	- 28.961	1.808
3600	10.902	87.881	78.185	- 66.299	- 30.538	1.854
3700	10.911	88.180	78.451	35.997	- 32.402	1.905
3800	10.920	88.475	78.711	35.779	- 34.268	1.951
3900	10.929	88.755	78.965	35.553	- 36.129	1.993
4000	10.937	89.031	79.213	35.327	- 37.986	2.031
4100	10.945	89.302	79.456	40.368	- 67.412	1.359
4200	10.952	89.563	79.694	42.553	- 67.941	1.392
4300	10.959	89.819	79.924	44.728	- 68.466	1.424
4400	10.967	90.075	80.154	43.655	- 68.225	1.413
4500	10.975	90.322	80.377	44.752	- 68.518	1.438
4600	10.982	90.563	80.596	- 68.821	- 70.125	1.469
4700	10.989	90.799	80.810	45.850	- 68.821	1.495
4800	10.997	91.031	81.019	46.048	- 69.133	1.521
4900	11.004	91.258	81.227	45.148	- 69.787	1.548
5000	11.012	91.480	81.430	50.249	- 70.125	1.574
5100	11.020	91.698	81.629	51.350	- 70.472	1.601
5200	11.026	91.912	81.817	55.553	- 71.866	1.628
5300	11.032	92.122	82.007	51.553	- 71.866	1.654
5400	11.034	92.329	82.192	51.660	- 71.555	1.672
5500	11.032	92.531	82.392	55.765	- 71.927	1.691
5600	11.031	92.731	82.575	56.870	- 72.307	1.708
5700	11.029	92.926	82.752	55.764	- 72.681	1.725
5800	11.027	93.119	82.932	60.193	- 73.057	1.742
5900	11.024	93.309	83.106	60.193	- 73.470	1.759
6000	11.028	93.495	83.278	61.302	- 73.866	1.776

Dec. 31, 1961; June 30, 1964; Sept. 30, 1964; June 30, 1968

TITANIUM MONOBROMIDE (TiBr)

(IDEAL GAS)

GFw = 127.809

Ground State Configuration [2]

S°_{298.15} = 62.18 ± 2.0 gibbs/mol

ΔH°_f = [52.5 ± 10.0] kcal/mol

ΔH°_f^{298.15} = [50.8 ± 10.0] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[4]
[1000]	[4]
[2000]	[4]
[4000]	[4]
[6000]	[4]
[8000]	[4]
[10000]	[4]

$\omega_e = [295]$ cm⁻¹
 $B_e = [0.0904]$ cm⁻¹
 $\omega_e x_e = [2.21]$ cm⁻¹
 $\alpha_e = [0.00067]$ cm⁻¹

$\sigma = 1$
 $r_e = [2.5]$ Å

Heat of Formation

The heat of formation, ΔH°_f of TiBr (g) is calculated from the dissociation energy, D°₀ which is estimated as 104 kcal/mol. This estimate is obtained from the relation D(TiBr₂) < D°(TiBr₂) < D°(TiBr₃), where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF₂(g) by Zubov and Margrave (1).

Heat Capacity and Entropy

The vibrational frequency, ω_e and the anharmonic vibrational term, $\omega_e x_e$, are estimated from those of TiCl(g) and comparisons of the mercury and alkali monohalides. The interaction distance is estimated from Guggenheimer's relation (2). B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti⁺ (3). α_e is estimated from the Morse potential function.

References

1. K. F. Zubov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).
2. K. M. Guggenheimer, Proc. Phys. Soc. 55, 456 (1946).
3. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Tungsten Monobromide (WBr)

(Ideal Gas) GFW = 263.759

T, °K	C _p ^o	$\frac{\text{gibbs/mol}}{S^o}$	$-(G^o - H^o_{298})/T$	H ^o - H ^o ₂₉₈	keal/mol ΔH^o	ΔG^o	Log K _p
0	.300	.000	INFINITE	- 2.324	181.684	181.584	INFINITE
100	7.389	56.323	72.519	- 1.620	137.350	137.350	- 300.178
200	8.269	65.519	85.119	- .881	104.668	104.668	- 414.668
298	8.512	68.130	88.130	- .000	100.100	100.100	- 494.184
300	8.516	65.183	65.130	.014	100.088	128.361	- 93.511
400	8.767	67.685	65.870	.886	136.249	125.230	- 68.423
500	8.946	69.651	66.117	1.767	136.088	122.493	- 53.542
600	8.995	71.268	66.885	2.654	135.920	119.790	- 43.634
700	8.931	72.642	67.577	3.584	135.744	117.116	- 36.565
800	8.761	73.637	68.287	4.480	135.558	114.466	- 31.271
900	8.592	74.894	68.951	5.388	135.364	111.842	- 27.159
1000	8.025	75.843	69.604	6.239	135.161	109.240	- 23.874
1100	9.062	76.705	70.211	7.183	134.950	106.587	- 21.191
1200	9.102	77.495	70.786	8.051	134.732	104.095	- 18.958
1300	9.144	78.225	71.330	8.963	134.506	101.552	- 17.072
1400	9.189	78.905	71.847	9.880	134.272	99.024	- 15.458
1500	9.234	79.540	72.339	10.801	134.032	96.515	- 14.062
1600	9.279	80.137	72.808	11.727	133.784	94.024	- 12.842
1700	9.324	80.701	73.256	12.657	133.528	91.564	- 11.769
1800	9.369	81.236	73.685	13.592	133.265	89.082	- 10.816
1900	9.413	81.743	74.096	14.531	132.995	86.637	- 9.966
2000	9.458	82.227	74.490	15.474	132.717	84.205	- 9.201
2100	9.503	82.690	74.870	16.422	132.431	81.785	- 8.511
2200	9.549	83.133	75.235	17.375	132.136	79.378	- 7.885
2300	9.596	83.558	75.588	18.332	131.835	76.989	- 7.316
2400	9.646	83.968	75.929	19.294	131.526	74.611	- 6.794
2500	9.698	84.363	76.258	20.261	131.210	72.245	- 6.316
2600	9.753	84.748	76.577	21.234	130.886	69.894	- 5.875
2700	9.811	85.113	76.887	22.212	130.551	67.564	- 5.468
2800	9.872	85.471	77.187	23.196	130.195	65.229	- 5.091
2900	9.937	85.819	77.478	24.187	129.809	62.911	- 4.741
3000	10.005	86.157	77.762	25.184	129.388	60.514	- 4.416
3100	10.077	86.486	78.038	26.188	128.920	58.328	- 4.112
3200	10.151	86.807	78.307	27.199	128.400	56.259	- 3.829
3300	10.228	87.121	78.570	28.218	127.821	54.365	- 3.563
3400	10.307	87.427	78.826	29.245	127.175	51.574	- 3.315
3500	10.388	87.727	79.076	30.280	126.448	49.362	- 3.082
3600	10.471	88.021	79.320	31.322	125.618	47.168	- 2.863
3700	10.554	88.309	79.559	32.374	124.684	45.004	- 2.661
3800	10.638	88.591	79.793	33.433	123.647	42.879	- 2.476
3900	10.722	88.869	80.022	34.501	122.508	40.791	- 2.309
4000	10.805	89.141	80.247	35.578	121.269	38.731	- 2.147
4100	10.888	89.409	80.467	36.662	120.033	36.692	- 1.993
4200	10.969	89.673	80.683	37.755	118.798	34.685	- 1.847
4300	11.049	89.932	80.895	38.856	117.562	32.709	- 1.708
4400	11.127	90.186	81.104	39.965	116.316	30.761	- 1.575
4500	11.202	90.437	81.308	41.081	115.069	28.831	- 1.449
4600	11.275	90.684	81.509	42.205	113.819	26.923	- 1.328
4700	11.345	90.928	81.707	43.336	112.566	25.036	- 1.213
4800	11.411	91.167	81.902	44.474	111.309	23.171	- 1.102
4900	11.475	91.403	82.093	45.618	110.048	21.328	- .996
5000	11.535	91.636	82.282	46.769	108.785	19.507	- .895
5100	11.592	91.865	82.467	47.925	107.518	17.709	- .797
5200	11.645	92.090	82.650	49.087	106.246	16.000	- .704
5300	11.695	92.312	82.831	50.254	104.969	14.393	- .615
5400	11.741	92.531	83.008	51.426	103.686	12.886	- .528
5500	11.783	92.747	83.183	52.602	102.398	11.381	- .445
5600	11.822	92.960	83.356	53.783	101.105	9.876	- .365
5700	11.857	93.170	83.526	54.966	99.808	8.372	- .288
5800	11.889	93.376	83.694	56.154	98.505	6.868	- .214
5900	11.917	93.580	83.860	57.344	97.198	5.364	- .142
6000	11.943	93.780	84.024	58.537	95.886	3.859	- .074

June 30, 1967

TUNGSTEN MONOBROMIDE (WBr)

(IDEAL GAS)

GFW = 263.759

Ground State Configuration [Δ] $\Delta H^o_f = [141.9 \pm 20] \text{ kcal/mol}$ $S^o_{298.15} = [65.1] \text{ gibbs/mol}$ $\Delta H^o_{298.15} = [140.1 \pm 20] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

E_e, cm^{-1}	g_e
0	[4]
[5000]	[2]
[15000]	[20]

 $\omega_e X_e = [0.80] \text{ cm}^{-1}$ $\sigma = 1$ $B_e = [0.05254] \text{ cm}^{-1}$ $r_e = [2.40] \text{ \AA}$

Heat of Formation

The heat of formation, $\Delta H^o_{298}(\text{WBr}, g) = 140.1 \text{ kcal/mol}$, is calculated from the bond dissociation energy. $D^o_{298}(\text{W-Br}) = 90 \pm 20 \text{ kcal/mol}$. This value of D^o_{298} is estimated to be slightly higher than the average bond dissociation energy of $\text{WBr}_2(g)$, by analogy with the WCl_4 system.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in $\text{WBr}_2(g)$. This distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental vibrational frequency, ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 486 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D^o + 0.5 \omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of a_e is calculated from the Morse potential function. The moment of inertia is $53.27 \times 10^{-39} \text{ g cm}^2$.

The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for $\text{WF}_6(g)$. See $\text{WF}_6(g)$ table (March 31, 1967) for details.

(IDEAL GAS) $\Delta H_f^\circ = 171.129$
Ground State Configuration $[^4Z]$
 $S_{298.15}^\circ = [63.4 \pm 2] \text{ gibbs/mol}$
 $\Delta H_f^\circ = [73.9 \pm 10] \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = [72 \pm 10] \text{ kcal/mol}$

ZIRCONIUM MONOBROMIDE (ZrBr₂)

Zirconium Monobromide (ZrBr₂)
(Ideal Gas) $\Delta H_f^\circ = 171.129$

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K _p
0	7.000	0.000	INFINITE	-2.328	73.923	73.923	INFINITE
100	7.404	8.460	70.453	-1.822	66.106	66.106	17.277
200	7.766	16.620	63.443	-1.000	58.414	58.414	11.367
298	8.020	23.843	55.442	-0.000	51.286	51.286	8.052
300	8.024	23.843	55.443	-0.016	51.286	51.286	8.052
400	8.276	31.000	47.443	0.167	43.414	43.414	5.459
500	8.475	37.969	39.443	1.769	35.414	35.414	3.442
600	8.623	44.956	31.443	2.662	27.414	27.414	1.943
700	8.731	51.947	23.443	3.565	19.414	19.414	0.928
800	8.804	58.940	15.443	4.480	11.414	11.414	0.340
900	8.853	65.933	7.443	5.404	3.414	3.414	-0.307
1000	8.882	72.926	-0.557	6.350	-4.586	-4.586	-1.000
1100	8.896	79.919	-8.554	7.306	-12.586	-12.586	-1.741
1200	8.900	86.912	-16.551	8.275	-20.586	-20.586	-2.527
1300	8.896	93.905	-24.548	9.256	-28.586	-28.586	-3.341
1400	8.884	100.898	-32.545	10.248	-36.586	-36.586	-4.184
1500	8.864	107.891	-40.542	11.249	-44.586	-44.586	-5.057
1600	8.836	114.884	-48.539	12.259	-52.586	-52.586	-5.959
1700	8.800	121.877	-56.536	13.274	-60.586	-60.586	-6.889
1800	8.756	128.870	-64.533	14.299	-68.586	-68.586	-7.846
1900	8.704	135.863	-72.530	15.328	-76.586	-76.586	-8.829
2000	8.644	142.856	-80.527	16.360	-84.586	-84.586	-9.837
2100	8.576	149.849	-88.524	17.397	-92.586	-92.586	-10.867
2200	8.500	156.842	-96.521	18.436	-100.586	-100.586	-11.917
2300	8.416	163.835	-104.518	19.474	-108.586	-108.586	-12.984
2400	8.324	170.828	-112.515	20.522	-116.586	-116.586	-14.067
2500	8.224	177.821	-120.512	21.567	-124.586	-124.586	-15.167
2600	8.116	184.814	-128.509	22.614	-132.586	-132.586	-16.282
2700	8.000	191.807	-136.506	23.661	-140.586	-140.586	-17.411
2800	7.876	198.800	-144.503	24.709	-148.586	-148.586	-18.553
2900	7.744	205.793	-152.500	25.754	-156.586	-156.586	-19.707
3000	7.604	212.786	-160.497	26.807	-164.586	-164.586	-20.874
3100	7.456	219.779	-168.494	27.857	-172.586	-172.586	-22.052
3200	7.300	226.772	-176.491	28.907	-180.586	-180.586	-23.241
3300	7.136	233.765	-184.488	29.957	-188.586	-188.586	-24.441
3400	6.964	240.758	-192.485	31.008	-196.586	-196.586	-25.651
3500	6.784	247.751	-200.482	32.058	-204.586	-204.586	-26.871
3600	6.596	254.744	-208.479	33.109	-212.586	-212.586	-28.101
3700	6.400	261.737	-216.476	34.161	-220.586	-220.586	-29.341
3800	6.196	268.730	-224.473	35.212	-228.586	-228.586	-30.591
3900	5.984	275.723	-232.470	36.264	-236.586	-236.586	-31.851
4000	5.764	282.716	-240.467	37.316	-244.586	-244.586	-33.121
4100	5.536	289.709	-248.464	38.368	-252.586	-252.586	-34.401
4200	5.300	296.702	-256.461	39.421	-260.586	-260.586	-35.691
4300	5.056	303.695	-264.458	40.474	-268.586	-268.586	-36.991
4400	4.804	310.688	-272.455	41.526	-276.586	-276.586	-38.301
4500	4.544	317.681	-280.452	42.578	-284.586	-284.586	-39.621
4600	4.276	324.674	-288.449	43.631	-292.586	-292.586	-40.951
4700	4.000	331.667	-296.446	44.681	-300.586	-300.586	-42.291
4800	3.716	338.660	-304.443	45.734	-308.586	-308.586	-43.641
4900	3.424	345.653	-312.440	46.786	-316.586	-316.586	-44.991
5000	3.124	352.646	-320.437	47.839	-324.586	-324.586	-46.351
5100	2.816	359.639	-328.434	48.891	-332.586	-332.586	-47.721
5200	2.500	366.632	-336.431	49.944	-340.586	-340.586	-49.091
5300	2.176	373.625	-344.428	50.996	-348.586	-348.586	-50.471
5400	1.844	380.618	-352.425	52.049	-356.586	-356.586	-51.851
5500	1.504	387.611	-360.422	53.101	-364.586	-364.586	-53.241
5600	1.156	394.604	-368.419	54.154	-372.586	-372.586	-54.641
5700	0.800	401.597	-376.416	55.207	-380.586	-380.586	-56.051
5800	0.436	408.590	-384.413	56.260	-388.586	-388.586	-57.471
5900	0.064	415.583	-392.410	57.313	-396.586	-396.586	-58.891
6000	-0.304	422.576	-400.407	58.366	-404.586	-404.586	-60.321

Sept. 30, 1984; June 30, 1970

Heat Capacity and Entropy
The bond distance is assumed to be the same as that in ZrBr₄(g), which was estimated as 2.47 Å by Godnev, Aleksandrova and Rigina, Optics and Spectroscopy, 1, 172 (1959). The estimated bond distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental frequency ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 416 (1946)). The anharmonicity correction x_e is estimated roughly by assuming x_e = ω_e/4 (0.5 ω_e) = 0.0021. The rotational constant B_e is calculated from the estimated bond distance. The value of a_e is calculated from the Morse potential function. The moment of inertia is 42.148 x 10⁻³⁹ g cm².
The ground state configuration is taken from the ground state multiplet of Zr²⁺ reported by C. E. Moore, "Atomic Energy Levels," Vol. II, Natl. Bur. Std. Circ. 467, 1952. The electronic levels and quantum weights are estimated to be the same as those of Zr²⁺(g).

Heat of Formation
The heat of formation, ΔH₂₉₈^o(ZrBr₂, g) = 72 kcal/mol, is derived from the estimated bond dissociation energy, D₂₉₈^o(Zr-Br) = 103.5 ± 10 kcal/mol. The value of D₂₉₈^o(Zr-Br) is calculated from the relation D₂₉₈^o(Zr-Br)/n₂₉₈^o(Ti-Br) = D₂₉₈^o(Zr-Br₄)^o/n₂₉₈^o(Ti-Br₄)^o where the average bond dissociation energies, D₂₉₈^o(Zr-Br₄) = 102.2 kcal/mol, D₂₉₈^o(Ti-Br₄) = 87.9 kcal/mol and D₂₉₈^o(Ti-Cl) = 89.0 kcal/mol, all calculated from JANAF ΔH₂₉₈^o for ZrBr₄(g), TiBr₄(g), TiCl₄(g), Zr(g), Ti(g) and Br(g).

Tungsten Monobromide (WBr)
(Ideal Gas) GFW = 263.759

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	kcal/mol ΔHf°	Log Kp
0	7.300	INF1MITE	141.594	INF1MITE
100	7.268	56.000	141.594	141.594
200	7.268	61.754	141.594	141.594
298	7.512	65.130	140.100	140.100
300	7.512	65.130	140.088	140.088
400	7.787	67.685	136.249	125.230
500	8.046	69.651	136.088	125.493
600	8.295	71.268	135.920	119.790
700	8.531	72.642	135.744	117.116
800	8.761	73.837	135.558	114.466
900	8.982	74.884	135.364	111.842
1000	9.205	75.843	135.161	109.240
1100	9.402	76.705	134.950	106.557
1200	9.579	77.495	134.732	104.095
1300	9.744	78.225	134.506	101.559
1400	9.899	78.905	134.272	99.024
1500	10.044	79.540	134.032	96.516
1600	10.179	80.137	133.784	94.024
1700	10.304	80.701	133.528	91.546
1800	10.419	81.236	133.265	89.082
1900	10.524	81.743	132.995	86.637
2000	10.619	82.227	132.717	84.205
2100	10.704	82.690	132.431	81.785
2200	10.779	83.133	132.136	79.376
2300	10.844	83.558	131.835	76.989
2400	10.899	83.968	131.526	74.611
2500	10.944	84.363	131.210	72.245
2600	10.979	84.744	130.886	69.894
2700	11.014	85.113	130.551	67.555
2800	11.039	85.471	130.209	65.221
2900	11.064	85.819	129.860	62.911
3000	11.089	86.157	129.506	60.614
3100	11.114	86.486	129.148	58.328
3200	11.139	86.807	128.784	56.059
3300	11.164	87.121	128.416	53.805
3400	11.189	87.427	128.045	51.574
3500	11.214	87.727	127.672	49.362
3600	11.239	88.021	127.298	47.169
3700	11.264	88.309	126.924	45.004
3800	11.289	88.591	126.551	42.869
3900	11.314	88.869	126.178	40.761
4000	11.339	89.141	125.806	38.681
4100	11.364	89.409	125.434	36.632
4200	11.389	89.673	125.062	34.612
4300	11.414	89.932	124.690	32.621
4400	11.439	90.186	124.318	30.660
4500	11.464	90.437	123.946	28.729
4600	11.489	90.684	123.574	26.828
4700	11.514	90.928	123.202	24.957
4800	11.539	91.167	122.830	23.116
4900	11.564	91.403	122.458	21.304
5000	11.589	91.638	122.086	19.522
5100	11.614	91.865	121.714	17.770
5200	11.639	92.090	121.342	16.048
5300	11.664	92.312	120.970	14.356
5400	11.689	92.531	120.598	12.694
5500	11.714	92.747	120.226	11.062
5600	11.739	92.960	119.854	9.460
5700	11.764	93.170	119.482	7.888
5800	11.789	93.376	119.110	6.346
5900	11.814	93.580	118.738	4.834
6000	11.839	93.780	118.366	3.352

June 30, 1967

TUNGSTEN MONOBROMIDE (WBr)

(IDEAL GAS)

GFW = 263.759

Ground State Configuration [2Δ]

 $\Delta H_f^\circ = [141.9 \pm 20] \text{ kcal/mol}$ $S_{298.15}^\circ = [65.1] \text{ gibbs/mol}$ $\Delta H_f^\circ = [140.1 \pm 20] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	[4]
[9000]	[2]
[15000]	[20]

 $\omega_e = [321.4] \text{ cm}^{-1}$ $\omega_e x_e = [0.80] \text{ cm}^{-1}$ $\sigma = 1$ $\alpha_e = [0.00015] \text{ cm}^{-1}$ $r_e = [2.40] \text{ Å}$

Heat of Formation

The heat of formation, $\Delta H_f^\circ(\text{WBr}, g) = 140.1 \text{ kcal/mol}$, is calculated from the bond dissociation energy, $D_{298}^\circ(\text{W-Br}) = 90 \pm 20 \text{ kcal/mol}$. This value of D_{298}° is estimated to be slightly higher than the average bond dissociation energy of $\text{WBr}_2(g)$, by analogy with the WCl_2 system.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in $\text{WBr}_2(g)$. This distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental vibrational frequency, ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D_0 + 0.5 \omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function. The moment of inertia is $53.27 \times 10^{-39} \text{ g cm}^2$.

The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for $\text{WF}_2(g)$. See WF(g) table (March 31, 1967) for details.

ZIRCONIUM MONOBROMIDE (ZrBr)

(IDEAL GAS)

GFW = 171.129

Zirconium Monobromide (ZrBr)

(Ideal Gas) GFW = 171.129

Ground State Configuration $[4f]$ $\Delta H_f^\circ = [73.9 \pm 10] \text{ kcal/mol}$ $S_{298.15}^\circ = [63.4 \pm 2] \text{ gibbs/mol}$ $\Delta H_{298.15}^\circ = [72 \pm 10] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	g_1
0	[4]
[3000]	[4]
[6000]	[4]
[12000]	[4]
[18000]	[4]
[24000]	[4]
[30000]	[4]

 $\omega_e = [317] \text{ cm}^{-1}$ $\omega_e x_e = [0.69] \text{ cm}^{-1}$ $\sigma = 1$ $B_e = [0.065] \text{ cm}^{-1}$ $\alpha_e = [0.00018] \text{ cm}^{-1}$ $r = [2.47] \text{ \AA}$

Heat of Formation

The heat of formation, $\Delta H_f^\circ(\text{ZrBr}, g) = 72 \text{ kcal/mol}$ is derived from the estimated bond dissociation energy, $D_0^\circ(\text{Zr-Br}) = 103.5 \pm 10 \text{ kcal/mol}$. The value of $D_{298}^\circ(\text{Zr-Br})$ is calculated from the relation $D_{298}^\circ(\text{Zr-Br})/D_{298}^\circ(\text{Ti-Br}) = D_{298}^\circ(\text{Zr-Br}_4)/D_{298}^\circ(\text{Ti-Br}_4)$ where the average bond dissociation energies, $D_{298}^\circ(\text{Zr-Br}_4) = 102.2 \text{ kcal/mol}$, $D_{298}^\circ(\text{Ti-Br}_4) = 87.9 \text{ kcal/mol}$ and $D_{298}^\circ(\text{Ti-Cl}) = 89.0 \text{ kcal/mol}$, all calculated from JANAF ΔH_f° for $\text{ZrBr}_4(g)$, $\text{TiBr}_4(g)$, $\text{TiCl}_4(g)$, $\text{Zr}(g)$, $\text{Ti}(g)$ and $\text{Br}(g)$.

Heat Capacity and Entropy

The bond distance is assumed to be the same as that in $\text{ZrBr}_4(g)$, which was estimated as $2.47 \text{ \AA}$ by Godnev, Aleksandrovskaya and Pignia, Optics and Spectroscopy, **2**, 172 (1959). The estimated bond distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental frequency ω_0 (K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 416 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4 (D_0 + 0.5 \omega_e) = 0.0021$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function. The moment of inertia is $42.1488 \times 10^{-39} \text{ g cm}^2$.

The ground state configuration is taken from the ground state multiplet of Zr^+ reported by C. E. Moore, "Atomic Energy Levels," Vol. II, Natl. Bur. Std. Circ. 467, 1952. The electronic levels and quantum weights are estimated to be the same as those of $\text{ZrF}(g)$.

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-2.328	73.923	73.923	INFINITE
100	7.404	54.620	70.483	-1.422	74.002	69.599	-152.108
200	8.252	60.063	64.222	-0.832	74.061	65.297	-71.277
298	8.479	63.443	61.432	-0.600	74.000	61.206	-44.123
300	8.479	63.443	61.432	-0.600	74.000	61.206	-44.123
400	8.624	63.496	61.483	-0.616	71.988	61.220	-44.598
500	8.776	64.000	63.783	-0.887	68.116	58.414	-31.916
600	8.875	67.969	68.430	-1.769	67.904	56.011	-24.442
700	8.973	69.594	65.140	-2.462	67.427	53.656	-19.543
800	9.086	70.987	63.895	-3.155	67.027	51.335	-16.028
900	9.215	72.209	66.609	-4.000	67.161	49.055	-13.401
1000	9.353	73.302	67.293	-5.004	66.874	46.804	-11.367
1100	9.492	74.295	67.850	-6.350	66.582	44.595	-9.746
1200	9.629	75.204	68.546	-7.304	66.270	42.411	-8.424
1300	9.751	76.049	69.153	-8.275	65.907	40.307	-7.341
1400	9.865	76.834	69.714	-9.256	65.492	38.249	-6.430
1500	9.968	77.569	70.249	-10.248	65.028	36.204	-5.652
1600	10.064	78.260	70.760	-11.249	64.591	34.170	-4.979
1700	10.153	78.911	71.249	-12.250	64.184	32.147	-4.391
1800	10.237	79.528	71.714	-13.276	63.802	30.134	-3.874
1900	10.316	80.113	72.169	-14.329	63.446	28.134	-3.414
2000	10.390	80.669	72.602	-15.398	63.117	26.144	-3.007
2100	10.459	81.199	73.018	-16.360	62.816	24.163	-2.640
2200	10.524	81.704	73.420	-17.397	62.541	22.192	-2.310
2300	10.584	82.188	73.809	-18.436	62.286	20.403	-2.027
2400	10.640	82.651	74.182	-19.478	62.039	18.693	-1.776
2500	10.692	83.095	74.544	-20.522	61.804	16.987	-1.547
2600	10.740	83.522	74.895	-21.567	61.577	15.290	-1.337
2700	10.784	83.932	75.235	-22.616	61.356	13.602	-1.143
2800	10.824	84.327	75.564	-23.661	61.139	11.921	-0.945
2900	10.861	84.709	75.884	-24.709	60.920	10.249	-0.807
3000	10.895	85.077	76.195	-25.758	60.707	8.584	-0.647
3100	10.924	85.432	76.497	-26.807	60.494	6.926	-0.505
3200	10.949	85.777	76.790	-27.857	60.281	5.276	-0.372
3300	10.971	86.110	77.077	-28.907	60.068	3.633	-0.248
3400	10.990	86.433	77.355	-29.957	59.854	1.995	-0.132
3500	10.506	86.747	77.627	-31.008	59.641	0.366	-0.023
3600	10.511	87.051	77.892	-32.058	59.428	-1.299	0.079
3700	10.513	87.347	78.150	-33.109	59.215	-2.877	0.175
3800	10.516	87.635	78.403	-34.161	59.004	-4.490	0.265
3900	10.519	87.916	78.649	-35.212	58.793	-6.095	0.351
4000	10.522	88.199	78.891	-36.264	58.584	-7.695	0.431
4100	10.525	88.475	79.126	-37.316	58.376	-9.292	0.508
4200	10.529	88.749	79.357	-38.368	58.168	-10.882	0.580
4300	10.533	89.021	79.583	-39.421	57.961	-12.466	0.649
4400	10.537	89.289	79.804	-40.474	57.754	-14.046	0.714
4500	10.542	89.556	80.021	-41.527	57.548	-15.618	0.776
4600	10.546	89.819	80.233	-42.581	57.342	-17.188	0.835
4700	10.549	89.927	80.441	-43.636	57.136	-18.752	0.891
4800	10.552	90.154	80.646	-44.691	56.930	-20.311	0.944
4900	10.557	90.377	80.846	-45.744	56.724	-21.865	0.995
5000	10.561	90.594	81.043	-46.797	56.518	-23.411	1.042
5100	10.564	90.804	81.236	-47.850	56.312	-24.956	1.083
5200	10.567	91.017	81.426	-48.903	56.106	-26.500	1.122
5300	10.571	91.222	81.612	-49.956	55.900	-28.044	1.159
5400	10.574	91.424	81.795	-51.009	55.694	-29.588	1.194
5500	10.577	91.622	81.976	-52.062	55.488	-31.132	1.229
5600	10.580	91.816	82.153	-53.115	55.282	-32.676	1.263
5700	10.583	92.008	82.327	-54.168	55.076	-34.220	1.297
5800	10.586	92.195	82.496	-55.221	54.870	-35.764	1.331
5900	10.589	92.380	82.667	-56.274	54.664	-37.308	1.365
6000	10.592	92.562	82.833	-57.327	54.458	-38.852	1.399
6100	10.595	92.740	82.997	-58.380	54.252	-40.396	1.433

Sept. 30, 1964; June 30, 1970

Bromine (Br₂)

(Reference State) Mol. Wt. = 159.832

T, °K.	C _p ^o	S ^o	$-(F^o - H_{298}^o)/T$	$H^o - H_{298}^o$	ΔF_i^o	ΔH_i^o	Log K _p
0	.000	.000	INFINITE	5.859	.000	.000	.000
100	10.419	12.870	64.780	5.191	.000	.000	.000
200	12.851	20.484	40.978	4.020	.000	.000	.000
298	16.090	26.384	36.384	.000	.000	.000	.000
300	16.077	36.496	36.384	.033	.000	.000	.000
400	8.775	61.203	40.520	8.273	.000	.000	.000
500	8.857	63.172	44.860	9.156	.000	.000	.000
600	8.908	64.791	46.051	.000	.000	.000	.000
700	8.970	67.167	52.543	10.937	.000	.000	.000
800	8.970	67.363	52.573	11.633	.000	.000	.000
900	8.992	68.421	54.276	12.731	.000	.000	.000
1000	9.011	69.370	55.739	13.631	.000	.000	.000
1100	9.027	70.229	57.018	14.533	.000	.000	.000
1200	9.052	71.755	58.152	15.533	.000	.000	.000
1300	9.056	71.740	59.169	16.341	.000	.000	.000
1400	9.089	72.411	60.092	17.247	.000	.000	.000
1500	9.082	73.037	60.934	18.155	.000	.000	.000
1600	9.094	73.624	61.709	19.064	.000	.000	.000
1700	9.104	74.174	62.428	19.974	.000	.000	.000
1800	9.118	74.696	63.084	20.885	.000	.000	.000
1900	9.128	75.190	63.717	21.797	.000	.000	.000
2000	9.141	75.658	64.303	22.711	.000	.000	.000
2100	9.152	76.104	64.854	23.625	.000	.000	.000
2200	9.163	76.530	65.375	24.541	.000	.000	.000
2300	9.174	76.938	65.869	25.458	.000	.000	.000
2400	9.185	77.329	66.339	26.376	.000	.000	.000
2500	9.196	77.704	66.786	27.295	.000	.000	.000
2600	9.207	78.085	67.213	28.215	.000	.000	.000
2700	9.217	78.462	67.623	29.135	.000	.000	.000
2800	9.228	78.746	68.013	30.058	.000	.000	.000
2900	9.238	79.072	68.368	30.982	.000	.000	.000
3000	9.249	79.385	68.750	31.906	.000	.000	.000
3100	9.260	79.689	69.098	32.832	.000	.000	.000
3200	9.270	79.983	69.433	33.758	.000	.000	.000
3300	9.281	80.268	69.757	34.686	.000	.000	.000
3400	9.291	80.545	70.071	35.614	.000	.000	.000
3500	9.302	80.815	70.374	36.544	.000	.000	.000
3600	9.312	81.077	70.667	37.467	.000	.000	.000
3700	9.323	81.332	70.952	38.406	.000	.000	.000
3800	9.333	81.581	71.229	39.339	.000	.000	.000
3900	9.344	81.824	71.597	40.273	.000	.000	.000
4000	9.354	82.060	71.958	41.208	.000	.000	.000
4100	9.365	82.291	72.312	42.144	.000	.000	.000
4200	9.375	82.517	72.640	43.081	.000	.000	.000
4300	9.386	82.738	72.951	44.019	.000	.000	.000
4400	9.396	82.954	73.236	44.958	.000	.000	.000
4500	9.406	83.165	73.505	45.898	.000	.000	.000
4600	9.417	83.372	73.759	46.839	.000	.000	.000
4700	9.427	83.575	74.008	47.781	.000	.000	.000
4800	9.438	83.773	73.622	48.725	.000	.000	.000
4900	9.448	83.968	73.631	49.669	.000	.000	.000
5000	9.458	84.159	74.036	50.614	.000	.000	.000
5100	9.469	84.348	74.236	51.561	.000	.000	.000
5200	9.479	84.530	74.432	52.501	.000	.000	.000
5300	9.490	84.711	74.625	53.456	.000	.000	.000
5400	9.500	84.888	74.813	54.406	.000	.000	.000
5500	9.510	85.063	74.998	55.356	.000	.000	.000
5600	9.521	85.234	75.179	56.308	.000	.000	.000
5700	9.531	85.403	75.357	57.261	.000	.000	.000
5800	9.542	85.569	75.532	58.214	.000	.000	.000
5900	9.552	85.732	75.703	59.169	.000	.000	.000
6000	9.562	85.892	75.872	60.125	.000	.000	.000

September 30, 1961

Br₂

MOL. WT. = 159.832

(REFERENCE STATE)

0°K to 285.90°K Crystal
 285.90°K to 332.62°K Liquid
 332.62°K to 6000°K Ideal Diatomic Gas

Heat of Formation.

Zero by definition.

Heat Capacity of Crystal and Liquid.

Low temperature thermal data have been adopted from the work of D. L. Hildenbrand, W. R. Kramer, R. A. McDonald, and D. R. Stull [J. Am. Chem. Soc. **80**, 4129 (1958)]. References to older work are given by Hildenbrand, et al., and are not given any weight here.

Heat of Melting and Melting Point.

Hildenbrand, et al., (loc. cit.) report $T_m = 285.90^\circ\text{K}$ and $\Delta H_m = 2.527 \text{ kcal. mole}^{-1}$.

Heat of Sublimation, Ideal Gas Functions.

See ideal gas tables for details.

T, K.	cal. mole ⁻¹ deg. ⁻¹		-(F°-H° ₂₉₈)/T		kcal. mole ⁻¹		Log K _P
	C _p	S°	H°-H° ₂₉₈	T	ΔH _f °	ΔF _f °	
0							
100							
200							
300	18.077	36.384	36.384	.000	.000	.000	.000
400	18.060	41.676	36.384	1.834	6.439	1.372	.749
500	18.000	45.692	36.425	3.634	5.522	3.216	1.406
600	18.000	48.974	39.918	5.434	4.610	4.840	1.777
700	18.000	51.749	41.415	7.234	3.703	6.390	1.995
800	18.000	54.153	42.860	9.034	2.799	7.769	2.122
900	18.000	56.273	44.235	10.834	1.897	9.036	2.194
1000	18.000	58.169	45.535	12.634	.997	10.204	2.230

BROMINE (Br₂)

(LIQUID)

MOL. WT. = 159.832

ΔH_f° 298 = 0

ΔH_m° = 2.527 kcal. mole⁻¹

ΔH_v° = 7.084 kcal. mole⁻¹

T_m = 265.90°K.

T_b = 332.62°K.

Heat of Formation.

The heat of formation at 298.15°K is zero by definition.

Heat Capacity.

The liquid heat capacity data of D. L. Hildenbrand, W. R. Kramer, R. A. McDonald, and D. R. Stull [J. Am. Chem. Soc. 80, 4129 (1958)] were extrapolated to a constant value of 18.0 cal. mole⁻¹ deg.⁻¹

Entropy.

The entropy is that given by Hildenbrand, et al., (loc. cit.) for liquid bromine at 298.15°K.

Vaporization.

See ideal gas tables for details.



Iron Dibromide (FeBr₂)
(Crystal) GFW = 215.665

IRON DIBROMIDE (FeBr₂) (CRYSTAL)

OPW = 215.665

T, °K	Cp°	$\frac{\text{gkcal/mol}}{S^\circ}$	$-(T^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	19.176	33.620	33.620	+0.00	- 59.500	- 56.729	41.584
300	19.186	33.739	33.620	-0.035	- 59.509	- 56.712	41.314
400	19.718	39.331	34.379	1.981	- 66.429	- 54.335	29.687
500	20.250	43.788	35.830	3.979	- 65.989	- 51.363	22.451
600	20.782	47.527	37.476	6.031	- 65.555	- 48.479	17.658
700	21.314	50.864	39.159	10.135	- 65.033	- 45.617	14.750
800	21.846	53.809	40.737	16.074	- 64.416	- 42.750	12.800
900	22.378	56.409	42.304	22.605	- 63.701	- 40.244	10.773
1000	22.910	58.794	43.825	30.869	- 62.894	- 37.584	8.214
1100	23.442	61.003	45.379	39.567	- 61.983	- 34.931	6.040
1200	23.974	63.000	46.877	48.696	- 60.976	- 32.301	4.283
1300	24.506	64.605	48.096	58.171	- 60.053	- 29.708	4.994
1400	25.038	66.841	49.370	68.841	- 59.320	- 27.171	4.242
1500	25.570	68.586	50.594	80.269	- 58.551	- 24.687	3.597

$\Delta H^\circ_{298.15} = 33.62 \pm 0.3$ gibbs/mol
 $T_f = 650^\circ\text{K}$
 $T_m = 964^\circ\text{K}$
 $\Delta H^\circ_{298.15} = -59.5 \pm 0.5$ kcal/mol
 $\Delta H^\circ = 0.1$ kcal/mol
 $\Delta H^\circ_m = [12 \pm 3]$ kcal/mol
 $\Delta H^\circ_{298.15}$ (to monomer) = $[49.6]$ kcal/mol
 $\Delta H^\circ_{298.15}$ (to dimer) = $[58.5]$ kcal/mol

$\Delta H^\circ_{298.15}$ = Unknown

Heat of Formation.

The heats of solution of Fe(c), Br₂(l) and FeBr₂(c) in Br₂-KBr aqueous solution were measured by use of ice calorimeter by (1) W. Hieber and A. Woerner, Z. Elektrochem. 40, 287 (1934). From the results obtained the heat of formation for FeBr₂(c) was reported to be -59.87 kcal/mol.

The heats of solution of FeBr₂(c) in water were determined by (2) J. C. M. Li and N. W. Gregory, J. Am. Chem. Soc. 74, 4670 (1952) and (3) P. Paoletti, Trans. Faraday Soc. 61, 219 (1965), to be -20.1 ± 0.4 and -20.06 ± 0.08 kcal/mol, respectively. Using $\Delta H^\circ_{298.15} = -29.05$ and -21.3 kcal/mol for Br⁻(aq) and Fe²⁺(aq), the corresponding heats of formation for FeBr₂(c) were calculated as -59.3 and -59.34 kcal/mol. The value of $\Delta H^\circ_{298.15}$ (Br⁻, aq) was taken from "Selected Values of Chemical Thermodynamic Properties," Part I, Technical Note 270-1, by D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, National Bureau of Standards, 1965. The value of $\Delta H^\circ_{298.15}$ (Fe²⁺, aq) was derived from heats of solution and formation for FeCl₂(c) using $\Delta H^\circ_{298.15}(\text{Cl}^-, \text{aq}) = -39.552$ kcal/mol from the same source as $\Delta H^\circ_{298.15}$ (Br⁻, aq). The value of $\Delta H^\circ_{298.15}$ (FeBr₂, c) adopted is -59.5 ± 0.5 kcal/mol.

Heat Capacity and Entropy.

The heat capacities, 323-633°K, were measured by N. W. Gregory and H. E. O'Neal, J. Am. Chem. Soc. 81, 2649 (1959). Those for temperatures below 323°K and above 633°K were estimated by linear extrapolation. Low temperature heat capacities, 12-110°K, were reported by G. Miljutin and N. Nachimowitch, Phys. Trans. Ukrain. Acad. Sci. 7, 71 (1940). However, these data are inadequate for obtaining an accurate entropy at 298°K. The adopted $S^\circ_{298.15}$ value was reported by N. W. Gregory and R. O. MacLaren, J. Phys. Chem. 59, 110 (1955). It was obtained from E. F. Westrum, Jr., University of Michigan, Ann Arbor, Michigan, by private communication. A magnetic transition at 11°K was reported by H. Bizette, C. Terrier, and B. Tsai, Compt. rend. 245, 507 (1957).

Transition Data.

T_f and ΔH°_f were taken from N. W. Gregory and H. E. O'Neal, loc. cit.

Melting Data.

T_m adopted was reported by R. O. MacLaren and N. W. Gregory, J. Phys. Chem. 59, 184 (1955). The value was calculated from the vapor pressure equations and is slightly above the previously reported value, 684°C (957°K), by A. Ferreri, A. Celeri and F. Giorgi, Atti accad. Nazl. Lincei 9, 782, 1134 (1929). However, it agrees well with 982 ± 2°K obtained by the differential thermocouple cooling curve analysis by the same authors. The ΔH°_m value was estimated from the vapor pressure data in order to obtain good agreement between the second and third law heats of vaporization. See the FeBr₂(g) table for details.

Heat of Sublimation.

$\Delta H^\circ_{298.15}$ (to monomer) is calculated as the difference between $\Delta H^\circ_{298.15}$ for FeBr₂(g) and FeBr₂(c). $\Delta H^\circ_{298.15}$ (to dimer) is calculated as the difference between those for Fe₂Br₄(g) and 2 FeBr₂(c).

Sept. 30, 1966





Iron Dibromide (FeBr₂)
(Liquid) GFW = 215.665

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° ^c	ΔG°	Log K _p
0							
100							
200							
298	25.500	40.483	40.483	0.000	-50.431	-49.706	36.436
300	25.500	40.541	40.483	0.047	-50.428	-49.702	36.208
400	25.500	40.877	40.482	2.597	-50.744	-48.108	26.285
500	25.500	53.667	43.372	5.147	-55.752	-46.065	20.135
600	25.500	56.316	45.487	7.697	-54.820	-44.217	16.106
700	25.500	62.247	47.608	10.247	-53.952	-42.512	13.245
800	25.500	65.652	49.655	12.800	-53.063	-40.843	11.281
900	25.500	68.542	51.635	15.347	-52.160	-39.194	9.581
1000	25.500	71.342	53.645	17.897	-51.257	-37.565	8.113
1100	25.500	73.772	55.184	20.447	-51.724	-36.647	7.281
1200	25.500	75.991	56.821	22.997	-51.250	-35.206	6.519
1300	25.500	78.022	58.451	25.547	-50.776	-33.765	5.817
1400	25.500	80.022	60.081	28.097	-49.613	-32.776	5.117
1500	25.500	81.681	61.750	30.647	-48.824	-31.602	4.604
1600	25.500	83.327	62.579	33.197	-48.052	-30.479	4.163
1700	25.500	84.873	63.845	35.747	-47.597	-29.528	3.742
1800	25.500	86.270	65.071	38.297	-47.088	-28.608	3.342
1900	25.500	87.709	66.271	40.847	-46.578	-27.146	2.962
2000	25.500	89.017	67.319	43.397	-46.068	-25.962	2.637

IRON DIBROMIDE (FeBr₂) (LIQUID) GFW = 215.665

$S_{298.15}^{\circ} = [40.483] \text{ gibbs/mol}$

$\Delta H_{298.15}^{\circ} = [-50.431] \text{ kcal/mol}$

$\Delta H_m^{\circ} = [12 + 3] \text{ kcal/mol}$

$\Delta H_v^{\circ} = [29.4] \text{ kcal/mol}$

$T_m = 964^{\circ}\text{K}$

$T_b = [1207] ^{\circ}\text{K}$

Heat of Formation.

The value of $\Delta H_{298.15}^{\circ} (l)$ was obtained from $\Delta H_{298.15}^{\circ} (c)$ by adding ΔH_m° and the difference between $H_m^{\circ} - H_m^{\circ}$ for FeBr₂(c) and FeBr₂(l).

Heat Capacity and Entropy.

The heat capacity was assumed to be constant in the temperature range from 298.15 to 2000°K and was estimated on the basis of 8.5 gibbs/g-atom. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See FeBr₂(c) table for details.

Vaporization Data.

T_b is calculated as the temperature at which the total pressure of FeBr₂(g) and Fe₂Br₃(g) over FeBr₂(l) equals one atmosphere. Based on the vapor composition and the value of ΔH_v° for both the monomer and dimer at T_b , the heat of vaporization is derived.



Iron Dibromide (FeBr₂)
(Ideal Gas) GFW = 215.665

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	h ^o - H° ₂₉₈	h ^o - H° ₂₉₈	ΔG°	Log Kp
0	+0.00	INFINITE	-	-	6.705	INFINITE
100	12.721	65.559	3.829	-	6.705	25.394
200	14.081	74.890	8.1919	-	6.705	18.220
298	14.496	80.604	+0.00	-	6.705	15.464
300	14.501	80.604	-0.007	-	6.705	15.464
400	14.609	86.891	1.466	-	6.705	12.814
500	14.752	88.174	2.258	-	6.705	10.917
600	14.802	90.869	4.436	-	6.705	9.645
700	14.862	93.153	7.918	-	6.705	8.727
800	14.939	96.834	12.608	-	6.705	8.077
900	15.004	98.472	16.891	-	6.705	7.677
1000	15.054	99.905	21.079	-	6.705	7.424
1100	15.080	101.251	25.084	-	6.705	7.263
1200	15.095	102.516	28.930	-	6.705	7.163
1300	15.104	103.702	32.649	-	6.705	7.095
1400	15.108	104.819	36.259	-	6.705	7.048
1500	15.108	105.863	39.778	-	6.705	7.014
1600	15.104	106.832	43.216	-	6.705	6.989
1700	15.097	107.726	46.584	-	6.705	6.971
1800	15.088	108.546	49.889	-	6.705	6.958
1900	15.077	109.292	53.134	-	6.705	6.949
2000	15.064	109.967	56.321	-	6.705	6.943
2100	15.050	110.572	59.452	-	6.705	6.940
2200	15.035	111.110	62.527	-	6.705	6.938
2300	15.019	111.582	65.548	-	6.705	6.937
2400	15.002	112.000	68.515	-	6.705	6.936
2500	14.984	112.363	71.428	-	6.705	6.935
2600	14.965	112.672	74.287	-	6.705	6.934
2700	14.945	112.928	77.092	-	6.705	6.933
2800	14.924	113.132	79.844	-	6.705	6.932
2900	14.902	113.286	82.544	-	6.705	6.931
3000	14.879	113.390	85.194	-	6.705	6.930
3100	14.855	113.444	87.794	-	6.705	6.929
3200	14.830	113.458	90.344	-	6.705	6.928
3300	14.804	113.432	92.844	-	6.705	6.927
3400	14.778	113.366	95.294	-	6.705	6.926
3500	14.751	113.260	97.694	-	6.705	6.925
3600	14.724	113.114	100.044	-	6.705	6.924
3700	14.696	112.938	102.344	-	6.705	6.923
3800	14.668	112.732	104.594	-	6.705	6.922
3900	14.639	112.496	106.794	-	6.705	6.921
4000	14.610	112.230	108.944	-	6.705	6.920
4100	14.580	111.934	111.044	-	6.705	6.919
4200	14.549	111.608	113.094	-	6.705	6.918
4300	14.517	111.252	115.094	-	6.705	6.917
4400	14.484	110.866	117.044	-	6.705	6.916
4500	14.450	110.448	118.944	-	6.705	6.915
4600	14.415	110.000	120.794	-	6.705	6.914
4700	14.379	109.522	122.594	-	6.705	6.913
4800	14.342	109.014	124.344	-	6.705	6.912
4900	14.304	108.476	126.044	-	6.705	6.911
5000	14.265	107.908	127.694	-	6.705	6.910
5100	14.225	107.310	129.294	-	6.705	6.909
5200	14.184	106.682	130.844	-	6.705	6.908
5300	14.142	106.024	132.344	-	6.705	6.907
5400	14.099	105.336	133.794	-	6.705	6.906
5500	14.055	104.618	135.194	-	6.705	6.905
5600	14.010	103.870	136.544	-	6.705	6.904
5700	13.964	103.092	137.844	-	6.705	6.903
5800	13.917	102.284	139.094	-	6.705	6.902
5900	13.869	101.446	140.294	-	6.705	6.901
6000	13.820	100.578	141.444	-	6.705	6.900

Sept. 30, 1966



(IDEAL GAS)

(IDEAL GAS)

Point Group [D_{2h}]
S_{298.15} = [80.8] gibbs/mol
ΔH_{f0}° = [-8.8 ± 0.5] kcal/mol
ΔH_{f298.15}° = [-9.9 ± 0.5] kcal/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i
0	[10]
[4450]	[10]
[8900]	[5]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	
[150] (1)	
[35] (2)	
[300] (1)	

Bond Distance: Fe-Br = [2.24] Å

Bond Angle: Br-Fe-Br = [180]°

Rotational Constant: B₀ = [0.02102] cm⁻¹

Heat of Formation.

The vapor pressures of FeBr₂(c) and FeBr₂(l) have been measured in the temperature range from 823.15 to 982.15°K by several investigators. Using the reported data the corresponding enthalpy changes (ΔH^o) for the reactions (A) FeBr₂(c) = FeBr₂(g) and (B) FeBr₂(l) = FeBr₂(g) were evaluated by both the second and third law methods. The results obtained are presented in the following table. The values of ΔH_{f298.15}° for FeBr₂(c) are calculated based on the third law values for ΔH_{f298.15}° for FeBr₂(g) adopted in -9.9 ± 0.5 kcal/mol.

Reference	Reaction	Temperature, °K	Method	ΔH _{f298.15} °, kcal/mol	Drift	ΔH _{f298.15} °, kcal/mol
1	(A)	873.15-982.15	Transpiration	50.04	-0.75	-9.94
1	(A)	823.15-718.15	Effusion	49.21	+1.37	-9.38
1	(A)	873.15-982.15	Diaphragm	59.20	-10.09	-9.85
2	(A)	670.0-740.0	Torsion - Effusion	49.11	+0.71	-9.91
1	(B)	982.15-1182.15	Diaphragm	39.77	+0.93	-9.59

1. R. O. MacLaren and N. W. Gregory, J. Phys. Chem. **59**, 184 (1955).
2. R. J. Sime and N. W. Gregory, J. Phys. Chem. **84**, 86 (1980).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The electronic levels and quantum weights were estimated by comparison with those for FeCl₂(g) reported by C. W. Dekock and D. M. Gruen, J. Chem. Phys. **43**, 4387 (1966). The bond distance was estimated by L. Brewer, O. R. Somayajulu and E. Brackett, Chem. Rev. **93**, 111 (1983). The vibrational frequencies were estimated in order to obtain good agreement between the second and third law heats of sublimation and vaporization. The moment of inertia is 1.33146 x 10⁻³⁷ g cm².



Mercury Dibromide (HgBr₂)

INTERIM TABLE

(Crystal) Mol. Wt. = 360.442

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o ΔH _f ^o	ΔF _f ^o	Log K _f
		cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹		
0					
100					
200					
298	18.000	40.706	40.706	0.000	- 36.371
300	16.013	40.817	40.706	0.033	- 36.385
400	11.713	40.095	40.706	1.070	- 35.857
500	10.414	50.347	49.794	3.776	- 30.007
600	20.114	53.988	44.361	5.752	- 26.609
700	20.614	57.101	45.960	7.799	- 21.117
800	21.114	59.714	47.560	9.846	- 16.644
900	21.614	62.327	49.159	11.893	- 12.171
1000	22.114	64.940	50.759	13.940	- 7.700
1100	23.614	67.094	51.926	16.684	- 5.665
1200	24.314	69.179	53.276	19.081	- 4.426
1300	25.014	71.153	54.706	21.267	- 3.187
1400	25.714	73.059	56.214	23.247	- 1.948
1500	26.414	74.830	57.036	24.690	- 1.751

Br₂Hg

MERCURY DIBROMIDE (HgBr₂) (crystal)

Mol. Wt. = 360.442
 ΔH_f° 298.15 = -40.500 ± 0.5 kcal. mole⁻¹
 $S_{298.15}^\circ$ = [40.706] ± 1.5 cal. deg. ⁻¹ mole⁻¹
 T_m = 514°K
 ΔH_m = 4.280 ± 0.08 kcal. mole⁻¹

Heat of Formation. Taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," (1952).

Heat Capacity and Entropy. C_p was assumed to be a linear function of temperature and was fitted to the data of M. Guinchant, Comp. Rend. 145, 320 (1907) and G. J. Janz and J. Goodkin, J. Phys. Chem. 63, 1975 (1959). The entropy was estimated by adjusting its value until the melting, sublimation and vaporization data were in agreement.

Melting. T_m was taken from National Bureau of Standards (U.S.) Circular 500 (loc. cit.). ΔH_m was given by G. J. Janz and J. Goodkin (loc. cit.).

Br₂Hg

INTERIM TABLE

(Liquid) Mol. Wt. = 360.442

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _f
0									
100									
200									
296	16,000	46,797	46,797	.000	-	37,158	-	34,665	25,541
300	19,013	46,906	46,797	.033	-	37,170	-	34,630	25,372
400	24,400	53,091	47,579	2,205	-	43,699	-	32,606	17,616
500	24,400	56,536	49,246	4,665	-	42,994	-	29,891	13,065
500	24,400	62,984	51,176	7,065	-	42,091	-	27,356	9,964
600	24,400	68,505	53,148	9,522	-	39,172	-	24,926	7,370
700	24,400	73,008	55,168	11,965	-	35,112	-	21,994	5,170
800	24,400	76,678	56,872	14,405	-	31,126	-	18,562	3,541
900	24,400	79,446	58,404	16,845	-	27,063	-	15,356	2,263
1000	24,400	81,250	60,242	19,265	-	23,002	-	12,330	1,236
1100	24,400	82,550	61,723	21,778	-	19,007	-	9,292	.622
1200	24,400	83,458	62,850	24,292	-	15,094	-	6,236	.292
1300	24,400	84,058	63,655	26,805	-	11,364	-	3,167	.078
1400	24,400	84,342	64,076	29,318	-	7,914	-	0,100	.000
1500	24,400	84,342	64,076	31,831	-	4,761	-	-2,974	.000

MERCURY DIBROMIDE (HgBr₂)

(Liquid)

Mol. Wt. = 360.442

ΔH°_f 298.15 = -37.158 ± 0.58 kcal. mole⁻¹S° 298.15 = [46.797] ± 1.5 cal. deg.⁻¹ mole⁻¹T_m = 514°KΔH°_m = 4.280 ± 0.08 kcal. mole⁻¹T_b = 592°KΔH°_v = 14.148 ± 0.25 kcal. mole⁻¹Heat of Formation. Calculated from ΔH°_f(c).Heat Capacity and Entropy. C_p obtained from the data of O. J.

Janz and J. Goodkin, J. Phys. Chem. 63, 1975 (1959) in the range 507-544°K, it was assumed constant above and below this value.

A glassy type transition was assumed at 343°K below which the heat capacity was equal to that of the crystal. The entropy was obtained from S°(c), the entropy of fusion and the estimated heat capacity.

Melting and Vaporization. T_m and T_b were taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," (1952). ΔH°_m was given by O. J. Janz and J. Goodkin (loc. cit.) and ΔH°_v was obtained from the data of E. B. R. Prideaux, J. Chem. Soc. (London) 57, 2032 (1936) and F. M. G. Johnson, J. Amer. Chem. Soc. 53, 777 (1931).

Mercury Dibromide (HgBr₂)
(Ideal Gas) Mol. Wt. = 360.442

INTERIM TABLE

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100	12.900	41.900	IMF	2.742	16.074	16.074	IMF
200	12.740	41.740	2.742	1.156	16.156	16.156	2.742
300	12.600	41.600	1.156	0.000	20.424	20.424	1.156
400	12.480	41.480	0.000	0.027	20.442	27.010	0.027
500	12.380	41.380	0.027	1.400	27.690	15.120	1.400
600	12.300	41.300	1.400	2.947	27.658	12.089	2.947
700	12.240	41.240	2.947	4.422	27.539	10.031	4.422
800	12.200	41.200	4.422	5.901	27.420	8.061	5.901
900	12.180	41.180	5.901	7.383	27.301	6.439	7.383
1000	12.170	41.170	7.383	8.867	27.182	5.185	8.867
1100	12.170	41.170	8.867	10.352	27.063	4.146	10.352
1200	12.180	41.180	10.352	11.838	26.944	3.317	11.838
1300	12.200	41.200	11.838	13.325	26.825	2.627	13.325
1400	12.230	41.230	13.325	14.812	26.706	2.043	14.812
1500	12.270	41.270	14.812	16.298	26.587	1.545	16.298
1600	12.320	41.320	16.298	17.784	26.468	1.113	17.784
1700	12.380	41.380	17.784	19.270	26.349	0.737	19.270
1800	12.450	41.450	19.270	20.756	26.230	0.405	20.756
1900	12.530	41.530	20.756	22.242	26.111	0.111	22.242
2000	12.620	41.620	22.242	23.728	26.000	0.000	23.728
2100	12.720	41.720	23.728	25.214	25.889	-0.111	25.214
2200	12.830	41.830	25.214	26.700	25.778	-0.222	26.700
2300	12.950	41.950	26.700	28.186	25.667	-0.333	28.186
2400	13.080	42.080	28.186	29.672	25.556	-0.444	29.672
2500	13.220	42.220	29.672	31.158	25.444	-0.556	31.158
2600	13.370	42.370	31.158	32.644	25.333	-0.667	32.644
2700	13.530	42.530	32.644	34.130	25.222	-0.778	34.130
2800	13.700	42.700	34.130	35.616	25.111	-0.889	35.616
2900	13.880	42.880	35.616	37.102	25.000	-1.000	37.102
3000	14.070	43.070	37.102	38.588	24.889	-1.111	38.588
3100	14.270	43.270	38.588	40.074	24.778	-1.222	40.074
3200	14.480	43.480	40.074	41.560	24.667	-1.333	41.560
3300	14.700	43.700	41.560	43.046	24.556	-1.444	43.046
3400	14.930	43.930	43.046	44.532	24.444	-1.556	44.532
3500	15.180	44.180	44.532	46.018	24.333	-1.667	46.018
3600	15.450	44.450	46.018	47.504	24.222	-1.778	47.504
3700	15.740	44.740	47.504	48.990	24.111	-1.889	48.990
3800	16.050	45.050	48.990	50.476	24.000	-2.000	50.476
3900	16.380	45.380	50.476	51.962	23.889	-2.111	51.962
4000	16.730	45.730	51.962	53.448	23.778	-2.222	53.448
4100	17.100	46.100	53.448	54.934	23.667	-2.333	54.934
4200	17.490	46.490	54.934	56.420	23.556	-2.444	56.420
4300	17.900	46.900	56.420	57.906	23.444	-2.556	57.906
4400	18.330	47.330	57.906	59.392	23.333	-2.667	59.392
4500	18.780	47.780	59.392	60.878	23.222	-2.778	60.878
4600	19.250	48.250	60.878	62.364	23.111	-2.889	62.364
4700	19.740	48.740	62.364	63.850	23.000	-3.000	63.850
4800	20.260	49.260	63.850	65.336	22.889	-3.111	65.336
4900	20.810	49.810	65.336	66.822	22.778	-3.222	66.822
5000	21.380	50.380	66.822	68.308	22.667	-3.333	68.308
5100	21.980	50.980	68.308	69.794	22.556	-3.444	69.794
5200	22.610	51.610	69.794	71.280	22.444	-3.556	71.280
5300	23.270	52.270	71.280	72.766	22.333	-3.667	72.766
5400	23.960	52.960	72.766	74.252	22.222	-3.778	74.252
5500	24.680	53.680	74.252	75.738	22.111	-3.889	75.738
5600	25.430	54.430	75.738	77.224	22.000	-4.000	77.224
5700	26.210	55.210	77.224	78.710	21.889	-4.111	78.710
5800	27.020	56.020	78.710	80.196	21.778	-4.222	80.196
5900	27.860	56.860	80.196	81.682	21.667	-4.333	81.682
6000	28.730	57.730	81.682	83.168	21.556	-4.444	83.168

March 31, 1962



MERCURY DIBROMIDE (HgBr₂) (Ideal Gas)

Mol. Wt. = 360.442
ΔH_f⁰ 298.15 = -20.424 ± 2.0 kcal. mole⁻¹
S° 298.15 = 76.511 cal. deg.⁻¹ mole⁻¹
Point Group = D_{∞h}

Vibrational Levels and Multiplicities

ω, cm.⁻¹
225 { 1 }
41 { 2 }
233 { 1 }

Hg-Br distance = 2.41 Å

Moment of Inertia = 154.12 X 10⁻³⁹ g. cm.²

σ = 2

Heat of Formation. The heat of formation of the crystal as given in National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952, was combined with the 3rd law heat of sublimation at 298°K from the data of K. Naka and Z. Shibata, J. Fac. Sci. Hokkaido Imp. Univ. Ser. III 2, 193 (1938) and P. M. G. Johnson, J. Amer. Chem. Soc. 53, 777 (1931).

Heat Capacity and Entropy. The vibrational constants were given by W. Klemperer and L. Lindeman, J. Chem. Phys. 25, 397 (1956). The bond length is an average of the values given by H. Braune and S. Knöke, Zeits. phys. Chemie B23, 163 (1933); A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, Trans. Farad. Soc. 33, 852 (1937) and P. A. Akshin, V. P. Spiridinov and A. N. Khodchenkov, Zhur. Fiz. Khim. 33, 20 (1959).



INTERIM TABLE

T, °K.	C _p	S° -(F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0								
100	25.000	32.293	32.293	.000	-48.800	-42.705	31.302	
200	25.025	32.438	32.293	.046	-48.811	-42.666	31.091	
300	26.200	39.805	33.280	2.610	-53.809	-39.158	21.384	
400	27.020	45.744	35.198	5.273	-54.333	-35.049	15.319	
500	27.630	50.728	37.382	8.007	-55.785	-31.044	11.307	
600	28.000	55.028	39.702	10.794	-57.242	-27.992	7.400	
700	28.470	58.799	41.770	13.623	-58.704	-25.734	4.288	
800	28.780	62.171	43.853	16.488	-60.329	-23.433	1.644	
900	29.050	65.217	45.840	19.377	-62.332	-21.433	.095	
1000	29.293	67.997	47.729	22.295	-64.310	-19.341		1.641
1100	29.510	70.556	49.528	25.235	-66.267	-17.193		2.940
1200	29.687	72.924	51.238	28.195	-68.206	-15.040		4.024
1300	29.910	75.132	52.865	31.174	-70.125	-12.804		4.933
1400	30.180	77.205	54.419	34.176	-72.023	-10.488		5.709

March 31, 1962

MERCURY MONOBROMIDE, DIMERIC (Hg₂Br₂) (crystal)

Mol. Wt. = 561.052

ΔH_f 298.15 = -48.800 ± 0.2 kcal. mole⁻¹

S° 298.15 = 52.283 ± 0.75 cal. deg. ⁻¹ mole⁻¹

T_{sub} = 666°K (decomp.)

Heat of Formation. The average of the values obtained from the cell measurements of T. W. Dakin and D. T. Ewing, J. Am. Chem. Soc. 62, 2280 (1940) and those of F. Iahikawa and Y. Ueda, J. Chem. Soc. Japan 51, 59 (1930) was adopted.

Heat Capacity and Entropy. The heat capacity was estimated by analogy with mercurous chloride. The entropy of formation was obtained from the free energy and heat of formation data listed under heat of formation.

Sublimation. The vapor pressure over mercurous bromide reaches one atmosphere at 666°K according to G. Jung and W. Ziegler Zalta. f. physik. Chem. A150, 139 (1930). At this point the vapor is dissociated into Hg(g) and HgBr₂(g).

Potassium Bromide, Dimeric (K₂Br₂)

GF_W = 238.022

(Ideal Gas)

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈ ^o)/T	H ₂₉₈ ^o - H ₀ ^o	ΔH _f ^o	ΔG _f ^o	Log K _p
0	17.000	95.000	0.000	-129.077	-129.077	19.717
100	17.000	95.000	0.000	-129.077	-129.077	19.717
200	19.165	92.165	1.000	-129.077	-129.077	19.717
298	19.546	89.902	0.000	-129.077	-129.077	19.717
300	19.550	89.903	0.036	-129.223	-135.980	99.062
400	19.589	95.669	1.999	-138.128	-136.449	54.552
500	19.734	101.071	3.1972	-138.524	-135.984	54.552
600	19.790	103.676	5.949	-138.887	-135.440	49.334
700	19.812	104.728	9.5401	-139.232	-134.838	42.098
800	19.826	105.375	9.986	-139.570	-134.189	36.659
900	19.835	111.710	96.495	-139.909	-133.494	32.417
1000	19.842	113.801	99.922	-140.267	-132.764	29.016
1100	19.847	115.692	101.271	-140.658	-132.097	25.818
1200	19.851	117.419	102.546	-141.086	-131.486	22.864
1300	19.854	119.008	103.752	-141.551	-130.921	20.161
1400	19.857	120.480	104.895	-142.051	-130.400	17.688
1500	19.859	121.850	105.980	-142.586	-130.000	15.424
1600	19.860	123.131	107.013	-143.156	-129.719	13.319
1700	19.861	124.335	107.996	-143.761	-129.466	11.349
1800	19.863	125.471	108.936	-144.401	-129.236	9.509
1900	19.863	126.545	109.835	-145.076	-129.031	7.869
2000	19.864	127.563	110.696	-145.786	-128.849	6.424
2100	19.865	128.533	111.522	-146.531	-128.686	5.159
2200	19.866	129.457	112.317	-147.311	-128.541	4.049
2300	19.866	130.340	113.081	-148.126	-128.416	3.069
2400	19.867	131.185	113.818	-148.976	-128.311	2.269
2500	19.867	131.996	114.529	-149.861	-128.226	1.629
2600	19.867	132.776	115.216	-150.781	-128.161	1.129
2700	19.868	133.525	115.880	-151.736	-128.116	0.749
2800	19.868	134.248	116.524	-152.726	-128.091	0.469
2900	19.868	134.945	117.147	-153.751	-128.086	0.269
3000	19.868	135.619	117.751	-154.811	-128.101	0.129
3100	19.869	136.270	118.338	-155.906	-128.126	0.049
3200	19.869	136.901	118.909	-157.036	-128.161	0.009
3300	19.869	137.512	119.463	-158.201	-128.206	0.000
3400	19.869	138.106	120.003	-159.401	-128.261	0.000
3500	19.869	138.681	120.528	-160.636	-128.326	0.000
3600	19.869	139.241	121.040	-161.906	-128.401	0.000
3700	19.869	139.786	121.540	-163.211	-128.486	0.000
3800	19.870	140.316	122.027	-164.551	-128.581	0.000
3900	19.870	140.832	122.502	-165.926	-128.686	0.000
4000	19.870	141.335	122.967	-167.336	-128.801	0.000
4100	19.870	141.825	123.421	-168.781	-128.926	0.000
4200	19.870	142.304	123.865	-170.261	-129.061	0.000
4300	19.870	142.772	124.299	-171.776	-129.206	0.000
4400	19.870	143.229	124.724	-173.326	-129.361	0.000
4500	19.870	143.675	125.140	-174.911	-129.526	0.000
4600	19.870	144.112	125.548	-176.531	-129.701	0.000
4700	19.870	144.539	125.948	-178.186	-129.886	0.000
4800	19.870	144.957	126.339	-179.876	-130.081	0.000
4900	19.870	145.367	126.723	-181.601	-130.286	0.000
5000	19.870	145.769	127.100	-183.361	-130.501	0.000
5100	19.871	146.162	127.470	-185.156	-130.726	0.000
5200	19.871	146.548	127.833	-186.986	-130.961	0.000
5300	19.871	146.926	128.190	-188.851	-131.206	0.000
5400	19.871	147.298	128.541	-190.751	-131.461	0.000
5500	19.871	147.662	128.885	-192.686	-131.726	0.000
5600	19.871	148.020	129.223	-194.656	-132.001	0.000
5700	19.871	148.372	129.556	-196.661	-132.286	0.000
5800	19.871	148.718	129.884	-198.701	-132.581	0.000
5900	19.871	149.057	130.206	-200.776	-132.886	0.000
6000	19.871	149.391	130.523	-202.886	-133.201	0.000

Dec. 31, 1961; Mar. 31, 1967

POTASSIUM BROMIDE, DIMERIC (K₂Br₂)

(IDEAL GAS)

GF_W = 238.022

Point Group [D_{2h}]

S_{298.15} = [89.9] gibbs/mol

Ground State Quantum Weight = [1]

ΔH_f^o = -125.0 ± 4 kcal/mol

ΔH_f^o_{298.15} = -129.2 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies	
ω, cm ⁻¹	w, cm ⁻¹
[135] (1)	[80] (1)
[125] (1)	[80] (1)
[150] (1)	[150] (1)

Bond Distances: K-Br = [3.07] Å

Bond Angles: Br-K-Br = [102]°

Product of the Moments of Inertia: I_AI_BI_C = [1.473 x 10⁻¹¹] g³ cm⁶

Heat of Formation

Vapor densities and vapor pressures of KBr were measured, using a liquid gold isothermometer, by K. I. Hagemark, M. Blander, and E. B. Luchinger, J. Phys. Chem. 70, 276 (1966), and K. I. Hagemark, private communication, 3M Company, St. Paul, Minn., Feb. 6, 1967. Based on the equilibrium constants for the reaction 2KBr(g) = K₂Br₂(g) in the temperature range 1267-1434°K, the enthalpy change (ΔH_f^o₂₉₈) of this reaction is evaluated by the second and third law methods to be -42.80 ± 4.26 and -43.12 kcal/mol, respectively. The heat of formation for K₂Br₂(g) is calculated to be -129.2 ± 4 kcal/mol, using the third law ΔH_f^o₂₉₈ value and ΔH_f^o₂₉₈(KBr,g) = -43.04 kcal/mol. The drift in the third law ΔH_f^o₂₉₈ values is 0.01 ± 3.2 eu.

Heat Capacity and Entropy

The molecular structure and bond distances were estimated by J. Berkowitz, J. Chem. Phys. 29, 1386 (1958), and are tentatively adopted. J. Berkowitz, J. Chem. Phys. 32, 1519 (1960), has calculated vibrational frequencies on the basis of the potential function for an ionic model. These values are adjusted so that the third law ΔH_f^o₂₉₈ value for the reaction 2KBr(g) = K₂Br₂(g) agrees with the second law value. The three principal moments of inertia are: I_A = 4.867 x 10⁻³⁸, I_B = 1.513 x 10⁻³⁷, I_C = 2.000 x 10⁻³⁷ g cm².

Br₂K₂

Point Group D_{2h}
 $\Delta H_f^\circ = -115.6 \pm 5 \text{ kcal/mol}$
 $\Delta H_f^\circ = -119.7 \pm 5 \text{ kcal/mol}$
 $S_{298.15}^\circ = [75.15] \text{ gibbs/mol}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
[202](1)	[327](1)	
[203](1)	413 (1)	
[353](1)	295 (1)	

Bond Distance: Li-Br = 2.35 Å

Bond Angle: Br-Li-Br = 110°

Product of the Moments of Inertia: $I_A I_B I_C = 4.220745 \times 10^{-113} \text{ g}^3 \text{ cm}^6$

Heat of Formation

This was obtained from the heat of formation of the liquid and the selected heat of vaporization to the dimer, which derivation has been given in the LiBr(g) table.

Heat Capacity and Entropy

J. Berkowitz, J. Chem. Phys. 29, 1386 (1958), 32, 1519 (1960), has calculated the molecular structure and vibrational frequencies based on an ionic model. The planar rhombic structure for dimeric lithium bromide, proposed by Berkowitz, has been confirmed by the lack of polarity in electric deflection by A. Büchler, J. L. Stauffer and W. Klemperer, J. Am. Chem. Soc. 85, 4544 (1964). The selected bond distances and angle were obtained from the electron diffraction studies of monomer-dimer vapor by P. A. Kikichin and N. G. Rambidi, Z. Physik Chem. 213, 111 (1960). The bond distances ($r_{\text{Br-Br}} = 4.20 \text{ Å}$ and $r_{\text{Li-Li}} = 2.60 \text{ Å}$) calculated by Berkowitz are in reasonable agreement with those selected. The three principal moments of inertia are $I_A = 4.1866 \times 10^{-39}$, $I_B = 98.3352 \times 10^{-39}$ and $I_C = 102.5218 \times 10^{-39} \text{ g cm}^2$.

S. H. Bauer, T. Ino and R. P. Porter, J. Chem. Phys. 33, 685 (1960), have estimated six vibrational frequencies (576, 576, 202, 230, 329 and 365 cm⁻¹) for Li₂Br₂(g) in the electron diffraction studies of Li₂Cl₂(g). W. Klemperer and W. G. Norris, J. Chem. Phys. 34, 1071 (1961), have observed two fundamental vibrational frequencies (413 and 295 cm⁻¹) in the infrared spectrum and tentatively assigned them as B_{2u} and B_{3u} modes and these have been adopted in the tabulation. The remaining four vibrational frequencies were obtained from J. Berkowitz, loc. cit., because his model and derivation are self-consistent.

Sept. 30, 1961; June 30, 1966

Magnesium Dibromide (MgBr₂)
(Crystal) GFW = 184.130

T, °K	Cp ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^c	Log Kp
0							
100	17.515	28.500	28.500	•000	-124.000	-119.320	87.464
200	17.520	28.608	28.500	•032	-124.012	-119.290	86.903
300	18.260	33.754	29.197	1.823	-131.075	-116.250	83.516
400	18.830	37.891	30.535	3.678	-130.745	-112.581	49.209
500	19.330	41.389	32.059	5.586	-130.394	-108.682	30.407
600	19.770	44.139	33.729	7.583	-130.023	-104.442	22.821
700	20.150	46.051	35.126	9.540	-129.647	-101.957	27.853
800	20.510	47.045	36.386	11.572	-129.273	-98.518	23.923
900	20.880	48.045	37.582	13.643	-128.902	-94.958	20.749
1000	21.246	49.045	38.740	15.740	-128.520	-91.352	18.150
1100	21.600	50.045	39.847	17.890	-128.130	-87.769	15.990
1200	21.970	51.045	41.001	20.069	-127.788	-84.281	14.169
1300	22.330	52.045	42.203	22.284	-127.423	-80.818	12.538
1400	22.700	53.045	43.447	24.535	-127.077	-77.476	10.880
1500	23.070	54.045	44.734	26.824	-126.724	-74.251	9.437
1600	23.470	55.045	46.063	29.150	-126.369	-71.141	8.141
1700	23.870	56.045	47.434	31.508	-126.015	-68.090	7.053
1800	24.240	57.045	48.849	33.903	-125.669	-65.098	6.058
1900	24.610	58.045	50.309	36.333	-125.324	-62.169	5.169
2000	24.980	59.045	51.814	38.803	-124.979	-59.303	4.303

OPW = 184.130

(CRYSTAL)

MAGNESIUM DIBROMIDE (MgBr₂)

ΔH_f⁰ = Unknown

ΔH_f⁰298.15 = -124.0 ± 1 kcal/mol

ΔH_m⁰ = 8.3 ± 2 kcal/mol

S_{298.15} = [28.5 ± 2] gibbs/mol

T_m = 984°K

Heat of Formation

The heat of formation was calculated from ΔH_f⁰ values for Mg⁺⁺(H₂O) and Br⁻(H₂O) and ΔHsol⁰(H₂O) for MgBr₂(c). The value for Br⁻ was obtained from D. D. Wagman et al., NBS Tech. Note 270-1, Natl. Bur. of Std., Washington, D.C., 1965. Values for Mg⁺⁺ and ΔHsol⁰ were taken from F. D. Rossini et al., NBS Circ. 500, Natl. Bur. of Std., Washington, D.C., 1952, since a survey of the literature revealed no new data which would significantly change these values. ΔHsol⁰ is based on measurements of Beketoff, Bull. acad. sci. Russ. 34, 291 (1892), while Mg⁺⁺ is presumably based on data for MgCl₂.

The selected heat of formation is confirmed by ΔH_f⁰073 = -0.287 kcal/mol for MgBr₂(l) + HCl(g) = MgCl₂(l) + HBr(g) observed by J. Toguri, H. Flood and T. Forland, Acta Chem. Scand. 17, 1502 (1963). Based on JANAP functions, this leads to ΔH_f⁰298 = -124.9 kcal/mol for MgBr₂(c).

Heat Capacity and Entropy

The entropy and heat capacity were estimated by comparison with the corresponding values for MgCl₂, NaCl and NaBr. W. M. Latimer, "Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, 1952, has estimated S₂₉₈ = 29.4 eu which is also a reasonable value. Use of 29.4 eu would give almost exact agreement between the selected ΔH_f⁰ and the equilibrium data of Toguri et al., but this may be fortuitous because of uncertainties in the enthalpy and heat of melting for MgBr₂.

Melting Data

T_m and ΔH_m⁰ are the values obtained by K. K. Kelley, USNM Bulletin 393, 1956, from phase diagrams for the systems MgBr₂ - NaBr and MgBr₂ - KBr studied by G. Kellner, Z. Anorg. Chem. 99, 137 (1912), and for MgBr₂ - LiBr studied by A. Ferrati and C. Colla, Atti accad. Lincei, ser. 6, 13, 78 (1931).

Magnesium Dibromide (MgBr₂)

(Liquid) GFW = 184.130

T, °K	Cp	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	23.750	31.968	31.968	-	0.000	- 114.691	84.070
300	23.250	32.113	31.968	.043	- 118.238	- 114.667	83.535
400	23.250	38.802	32.881	2.368	- 124.867	- 112.061	81.227
500	23.250	43.990	34.603	4.693	- 124.067	- 108.952	77.623
600	23.250	48.229	36.532	7.018	- 123.299	- 106.903	78.612
700	23.250	51.813	38.465	9.343	- 122.560	- 103.179	72.414
800	23.250	54.918	40.332	11.668	- 121.856	- 100.460	27.444
900	23.250	57.656	42.193	13.993	- 121.190	- 97.623	23.725
1000	23.250	60.106	43.787	16.318	- 120.684	- 95.081	20.780
1100	23.250	62.322	45.373	18.643	- 122.063	- 92.353	18.349
1200	23.250	64.345	46.871	20.968	- 121.468	- 89.678	16.333
1300	23.250	66.206	48.288	23.293	- 120.901	- 87.051	14.635
1400	23.250	67.959	49.630	25.618	- 120.326	- 84.959	13.111
1500	23.250	69.553	50.904	27.943	- 119.668	- 83.222	11.747
1600	23.250	71.033	52.116	30.268	- 118.887	- 81.581	10.187
1700	23.250	72.443	53.270	32.593	- 117.969	- 79.964	8.994
1800	23.250	73.772	54.373	34.918	- 117.052	- 78.404	7.961
1900	23.250	75.029	55.427	37.243	- 116.135	- 76.804	7.064
2000	23.250	76.221	56.437	39.568	- 115.221	- 75.429	6.106

June 30, 1966

MAGNESIUM DIBROMIDE (MgBr₂)

OPW = 184.130

(LIQUID)

S° _{298.15} = [31.968] gibbs/mol	ΔHf° _{298.15} = [-118.337] kcal/mol
Tm = 984°K	ΔHm° = 8.3 kcal/mol
Tb = [1557]*K	ΔHv° = [32.9] kcal/mol

Heat of Formation.

The ΔHf°_{298.15} was obtained from ΔHf°_{298.15(c)} by adding ΔHm° and the difference between H°_m - H°_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was assumed constant and estimated as 23.25 gibbs/mol using 7.75 gibbs/g-atom as suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1959. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See MgBr₂(c) table.

Vaporization Data.

Tb was calculated as the temperature at which ΔGr° = 0 for MgBr₂(c) → MgBr₂(g). ΔHv° is the corresponding enthalpy change.

Br₂Mg

Br₂Mg

Magnesium Dibromide (MgBr₂)

(Ideal Gas) GFW = 184.130



GFW = 184.130

(IDEAL GAS)

MAGNESIUM DIBROMIDE (MgBr₂)

T, °K	Cp ^b	S ^c	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	kcal/mol	ΔGf°	Log Kp
0	+0.00	+0.00	INFINITE	-	3.257	-	70.802	-	INFINITE
100	10.047	54.314	78.938	2.462	-	70.829	-	74.746	163.358
200	12.047	68.760	1.303	-	71.403	-	76.566	-	85.453
298	13.714	67.532	+0.00	-	74.600	-	81.537	-	94.783
300	13.727	67.532	+0.25	-	74.619	-	81.600	-	94.445
400	14.190	71.637	68.077	1.424	-	82.074	-	82.402	45.023
500	14.430	74.432	70.120	2.856	-	82.167	-	82.473	36.049
600	14.568	77.476	70.398	4.307	-	82.273	-	82.526	30.060
700	14.624	79.729	71.489	5.768	-	82.398	-	82.558	25.776
800	14.711	81.690	72.644	7.237	-	82.550	-	82.572	22.558
900	14.751	83.425	73.747	8.710	-	82.736	-	82.563	20.049
1000	14.779	84.980	74.794	10.186	-	85.079	-	82.350	17.998
1100	14.800	86.390	75.785	11.665	-	85.304	-	82.069	16.306
1200	14.817	87.679	76.723	13.144	-	85.553	-	81.764	14.991
1300	14.829	88.865	77.612	14.629	-	85.828	-	81.436	13.691
1400	14.840	89.964	78.456	16.112	-	86.128	-	81.087	12.583
1500	14.848	90.989	79.258	17.597	-	86.446	-	80.749	11.572
1600	14.855	91.947	80.021	19.082	-	86.782	-	80.422	10.631
1700	14.860	92.848	80.749	20.567	-	87.136	-	80.102	9.777
1800	14.865	93.697	81.445	22.054	-	87.506	-	79.796	8.947
1900	14.869	94.501	82.111	23.540	-	87.894	-	79.504	8.185
2000	14.872	95.264	82.750	25.027	-	88.298	-	79.229	7.488
2100	14.875	95.989	83.363	26.515	-	88.716	-	79.000	6.834
2200	14.878	96.682	83.953	28.002	-	89.148	-	78.785	6.217
2300	14.880	97.343	84.521	29.490	-	89.594	-	78.586	5.636
2400	14.882	97.976	85.069	30.978	-	89.957	-	78.394	5.077
2500	14.884	98.584	85.597	32.467	-	90.336	-	78.214	4.546
2600	14.885	99.168	86.108	33.955	-	90.730	-	78.046	4.034
2700	14.886	99.729	86.602	35.444	-	91.138	-	77.892	3.536
2800	14.888	100.271	87.081	36.932	-	91.560	-	77.742	3.052
2900	14.889	100.793	87.545	38.421	-	91.994	-	77.596	2.583
3000	14.890	101.294	87.995	39.910	-	92.440	-	77.454	2.129
3100	14.891	101.786	88.432	41.399	-	92.896	-	77.316	1.686
3200	14.891	102.259	88.856	42.888	-	93.362	-	77.182	1.254
3300	14.892	102.717	89.270	44.377	-	93.838	-	77.052	0.832
3400	14.893	103.162	89.672	45.867	-	94.324	-	76.926	0.420
3500	14.893	103.594	90.063	47.356	-	94.820	-	76.804	0.018
3600	14.894	104.013	90.445	48.845	-	95.326	-	76.686	-0.384
3700	14.894	104.421	90.817	50.335	-	95.842	-	76.572	-0.792
3800	14.895	104.818	91.180	51.824	-	96.368	-	76.462	-1.200
3900	14.895	105.205	91.534	53.314	-	96.904	-	76.356	-1.608
4000	14.896	105.587	91.882	54.803	-	97.450	-	76.254	-2.016
4100	14.896	105.950	92.320	56.293	-	97.996	-	76.156	-2.424
4200	14.897	106.300	92.751	57.782	-	98.552	-	76.062	-2.832
4300	14.897	106.660	93.172	59.272	-	99.108	-	75.972	-3.240
4400	14.897	107.007	93.583	60.762	-	99.674	-	75.886	-3.648
4500	14.897	107.337	93.983	62.252	-	100.240	-	75.804	-4.056
4600	14.898	107.664	94.364	63.741	-	100.816	-	75.726	-4.464
4700	14.898	107.985	94.736	65.231	-	101.402	-	75.652	-4.872
4800	14.898	108.298	95.099	66.721	-	101.998	-	75.582	-5.280
4900	14.898	108.606	95.454	68.211	-	102.604	-	75.516	-5.688
5000	14.899	108.907	95.800	69.701	-	103.220	-	75.454	-6.096
5100	14.899	109.202	96.136	71.190	-	103.846	-	75.396	-6.504
5200	14.899	109.491	96.464	72.680	-	104.482	-	75.342	-6.912
5300	14.899	109.775	96.784	74.170	-	105.128	-	75.292	-7.320
5400	14.899	110.053	97.094	75.660	-	105.784	-	75.246	-7.728
5500	14.900	110.327	97.395	77.150	-	106.450	-	75.204	-8.136
5600	14.900	110.595	97.688	78.640	-	107.126	-	75.166	-8.544
5700	14.900	110.859	97.974	80.130	-	107.812	-	75.132	-8.952
5800	14.900	111.118	98.254	81.620	-	108.508	-	75.102	-9.360
5900	14.900	111.373	98.528	83.110	-	109.214	-	75.076	-9.768
6000	14.900	111.624	98.796	84.600	-	109.930	-	75.054	-10.176

June 30, 1966

Point Group D_{∞h}

S_{298.15} = [67.5 ± 2] gibbs/mol

Ground State Quantum Weight = [1]

ΔHf° = -70.8 kcal/mol

ΔHf°_{298.15} = -74.6 ± 3 kcal/mol

Vibrational Frequencies and Degeneracies

$\frac{\omega_e}{(179)(1)}$
[220](2)
491 (1)

Bond Distance: Mg-Br = 2.34 Å

Bond Angle: Br-Mg-Br = 180°

Rotational Constant: B = 0.019264 cm⁻¹

σ = 2

Heat of Formation.

The ΔHf°_{298.15} was calculated from the ΔHf°_{298.15} = 49.4 kcal/mol for the reaction MgBr₂(c) = MgBr₂(g), based on third law analysis of pressures at 758 and 842°K determined from Knudsen effusion - mass spectrometric studies by J. Berkowitz and J. R. Marquert, J. Chem. Phys. **37**, 1853 (1962). Second law analysis of ion intensities (635 - 850°K) gave ΔHf° = 50.3 kcal/mol at 727°K, corresponding to ΔHf° = 52.2 kcal/mol at 298.15°K. The absolute pressure at 842°K was calibrated by integrating the ion current during complete volatilization of the sample. Data for (MgBr₂)₂ indicate that the dimer mole fraction (about 0.04 at 842°K) over the crystal increases with increasing temperature; this behavior is similar to that of the alkali halides.

Heat Capacity and Entropy.

Bond distance and bond angle were taken from the electron diffraction studies of P. A. Akishin, V. P. Spiridonov, G. A. Sobolev and V. A. Naumov, Zhur. Fiz. Khim. **31**, 461 (1957). Electric deflection experiments of A. Bichler, J. L. Stauffer and W. Klumperer, J. Am. Chem. Soc. **86**, 4544 (1964), also suggest a linear structure for MgBr₂ within the sensitivity of the measurements. The antisymmetric stretching vibration ν₃ is that observed in the infrared spectra of the vapor by S. P. Rendell, P. T. Greene and J. L. Margrave, J. Phys. Chem. **63**, 758 (1959). The other frequencies were estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963), from a valence force model using K = 1.5 and kδ/12 = 0.15 md/Å.



Sodium Bromide, Dimeric (Na₂Br₂)
(Ideal Gas) Mol. Wt. = 205.814



(IDEAL GAS)

SODIUM BROMIDE, DIMERIC (Na₂Br₂)

(IDEAL GAS)

MOL. WT. = 205.814

$$\Delta H_f^0 = -111.93 \pm 0.90 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -116.24 \pm 0.90 \text{ kcal. mole}^{-1}$$

Point Group [D_{2h}]

$$S^{298.15} = [83.384] \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹
[182] (1)	[134] (1)
[120] (1)	[188] (1)
[207] (1)	[228] (1)

Bond Distances: Na-Br = [2.75] Å

Bond Angle: Na-Br-Na = [71]°

Product of the Moments of Inertia: I_AI_BI_C = [3.9701 X 10⁻¹¹²] g³ cm.⁶

Heat of Formation.

The temperature dependence of the equilibrium constants (1293-1434°K.) for the reaction (NaBr)₂(g) ⇌ 2NaBr(g) has been studied by S. Smith, W. T. Smith, Jr. and E. H. Taylor, J. Chem. Phys. **24**, 558 (1956). The dissociation energy (ΔE_{300°K.}) was evaluated to be 42.9 ± 1.3 kcal. mole⁻¹. The vapor mixture contains 37 to 17% of dimers in the temperature range of 1293 to 1434°K. Hence the vapor pressure data on NaBr(g) reported by the previous investigators were reexamined. In other words, the reported vapor pressure of NaBr(g) is the sum of the partial pressures of both the monomer (NaBr) and the dimer (Na₂Br₂). The partial pressures of Na₂Br₂(g) thus obtained were used to evaluate the heats of vaporization by both the second and third law methods. The values of ΔH_f^{298.15} for Na₂Br₂(g) were then calculated. The results are presented as follows.

Investigator	Reaction	Third Law Value	Second Law Value	ΔH _f ^{298.15} , kcal. mole ⁻¹
Niwa ¹	2NaBr(c) → Na ₂ Br ₂ (g)	56.51	54.84	-117.08
Cogin and Kimball ²	2NaBr(c) → Na ₂ Br ₂ (g)	56.80	56.69	-116.01
Mayer and Wintner ³	2NaBr(c) → Na ₂ Br ₂ (g)	57.13	68.78	-115.63**
Ruff and Muggan ⁴	2NaBr(l) → Na ₂ Br ₂ (g)	45.70	46.71	-116.00
Wartenberg and Albrecht ⁵	2NaBr(l) → Na ₂ Br ₂ (g)	45.84	46.77	-116.00
Bloom et al. ⁶	2NaBr(l) → Na ₂ Br ₂ (g)	45.49	53.17	-116.72**

*Based on the average of the second and third law values.

**Only the third law value being used.

1 K. Niwa, J. Fac. Sci., Hokkaido Univ., Ser. III, **2**, 201 (1938).

2 G. E. Cogin and O. E. Kimball, J. Chem. Phys. **16**, 1035 (1948).

3 J. E. Mayer and I. H. Wintner, J. Chem. Phys., **5**, 301 (1938).

4 O. Ruff and S. Muggan, Z. anorg. allgem. Chem., **117**, 147 (1921).

5 H. von Wartenberg and P. Albrecht, Z. Electrochem., **27**, 162 (1921).

6 H. Bloom, J. O.W. Bockris, N. E. Richards and R. O. Taylor, J. Am. Chem. Soc. **80**, 2044 (1958).

The value of ΔH_f^{298.15} for Na₂Br₂(g) adopted is the average of the six ΔH_f^{298.15} values listed in the above table.

Heat Capacity and Entropy.

Bond distance and angles were calculated based on the related data reported by J. Berkowitz, J. Chem. Phys. **29**, 1386 (1958). The vibrational frequencies were calculated by J. Berkowitz, J. Chem. Phys., **32**, 1519 (1960), from an assumed model. The ground state quantum weight was estimated. The three principal moments of inertia are I_A = 1.94452 X 10⁻³⁸, I_B = 1.33619 X 10⁻³⁷ and I_C = 1.53065 X 10⁻³⁷ g. cm.²

Sept. 30, 1984



T, °K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	0.000	0.000	INFINITE	-4.633	-111.932	-111.932	INFINITE
100	15.116	64.123	89.740	-3.962	-112.169	-112.169	253.847
200	18.347	75.880	85.116	-1.847	-112.769	-112.769	131.021
298	19.150	83.384	83.184	0.000	-112.900	-112.900	90.008
300	19.259	83.503	83.186	1.035	-116.262	-122.960	89.572
400	19.683	89.402	84.140	1.969	-126.556	-128.534	67.491
500	19.688	93.422	85.576	3.923	-128.667	-123.051	53.783
600	19.688	97.005	87.191	5.888	-126.032	-122.493	44.616
800	19.768	102.682	90.388	9.835	-126.365	-121.879	38.051
900	19.760	105.011	91.886	11.813	-126.976	-120.516	29.252
1000	19.806	107.097	93.304	13.781	-127.276	-119.779	26.116
1100	19.817	108.986	94.646	15.774	-127.589	-119.019	23.666
1200	19.833	110.239	95.913	17.750	-127.890	-118.309	21.364
1300	19.838	111.776	97.251	19.713	-128.186	-117.596	19.211
1400	19.838	113.707	98.621	21.723	-128.476	-116.891	17.182
1500	19.843	115.136	99.332	23.707	-128.760	-116.186	15.261
1600	19.846	116.417	100.360	25.691	-129.039	-115.481	13.431
1700	19.846	117.655	101.716	27.676	-129.312	-114.776	11.681
1800	19.846	118.755	102.377	29.661	-129.580	-114.071	10.011
1900	19.846	119.828	103.172	31.646	-129.843	-113.366	8.421
2000	19.856	120.867	104.031	33.632	-130.101	-112.661	6.911
2100	19.857	121.816	104.855	35.618	-130.354	-111.956	5.481
2200	19.860	122.622	105.646	37.593	-130.601	-111.251	4.131
2300	19.860	123.432	106.407	39.568	-130.843	-110.546	2.861
2400	19.861	124.167	107.144	41.573	-131.081	-109.841	1.671
2500	19.862	125.278	107.854	43.562	-131.316	-109.136	0.561
2600	19.863	126.037	108.539	45.548	-131.546	-108.431	0.304
2700	19.863	126.750	109.202	47.528	-131.771	-107.726	0.000
2800	19.863	127.426	109.846	49.500	-131.991	-107.021	-0.304
2900	19.865	128.276	110.465	51.507	-132.206	-106.316	-0.608
3000	19.865	128.900	111.069	53.493	-132.416	-105.611	-0.912
3100	19.866	129.531	111.654	55.480	-132.621	-104.906	-1.216
3200	19.866	130.793	112.777	57.455	-132.821	-104.201	-1.520
3300	19.866	130.793	112.777	59.430	-133.016	-103.496	-1.824
3400	19.867	131.386	113.516	61.440	-133.206	-102.791	-2.128
3500	19.867	131.982	113.860	63.426	-133.391	-102.086	-2.432
3600	19.867	132.522	114.352	65.413	-133.576	-101.381	-2.736
3700	19.867	132.956	114.850	67.400	-133.746	-100.676	-3.040
3800	19.868	133.596	115.172	69.387	-133.916	-99.971	-3.344
3900	19.868	134.112	115.611	71.374	-134.081	-99.266	-3.648
4000	19.868	134.615	116.275	73.360	-134.241	-98.561	-3.952
4100	19.869	135.106	116.728	75.347	-134.396	-97.856	-4.256
4200	19.869	135.600	117.030	77.334	-134.546	-97.151	-4.560
4300	19.869	136.508	118.030	79.320	-134.696	-96.446	-4.864
4400	19.869	136.508	118.030	81.308	-134.846	-95.741	-5.168
4500	19.869	136.955	118.445	83.295	-134.996	-95.036	-5.472
4600	19.869	137.392	118.893	85.282	-135.136	-94.331	-5.776
4700	19.869	137.829	119.254	87.269	-135.281	-93.626	-6.080
4800	19.869	138.258	119.623	89.256	-135.421	-92.921	-6.384
4900	19.870	138.667	120.026	91.243	-135.561	-92.216	-6.688
5000	19.870	139.064	120.403	93.230	-135.696	-91.511	-6.992
5100	19.870	139.442	120.772	95.217	-135.831	-90.806	-7.296
5200	19.870	140.257	121.441	97.204	-135.966	-90.101	-7.600
5300	19.870	140.578	121.861	99.191	-136.096	-89.396	-7.904
5400	19.870	140.578	121.861	101.178	-136.226	-88.691	-8.208
5500	19.870	140.743	122.185	103.165	-136.356	-87.986	-8.512
5600	19.870	141.301	122.524	105.152	-136.486	-87.281	-8.816
5700	19.871	141.652	122.854	107.139	-136.616	-86.576	-9.120
5800	19.871	141.908	123.183	109.126	-136.746	-85.871	-9.424
5900	19.871	142.338	123.505	111.113	-136.876	-85.166	-9.728
6000	19.871	142.672	123.822	113.100	-136.996	-84.461	-10.032

Lead Dibromide (PbBr₂)

(Crystal) Mol. Wt. = 367.04

INTERIM TABLE

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H _{298°)/T}	H°-H _{298°}	ΔH _f ^o	ΔF _f ^o	Log K _p
100	16,290	19,003	19,717	3,482	3,482	63,199	63,199	19,717
200	18,495	31,116	40,396	1,856	1,856	63,291	62,740	66,536
298	19,246	39,658	39,658	0.000	0.000	66,073	62,134	45,344
300	19,250	39,777	39,658	0.06	66,082	62,110	65,245	
400	19,470	44,345	39,416	1,972	73,036	59,336	37,410	
500	19,690	48,713	40,454	3,930	72,636	55,936	24,458	
600	19,910	52,823	42,473	5,810	72,234	52,659	13,160	
700	20,130	56,516	44,506	7,614	71,834	49,259	15,372	
800	20,350	59,910	46,559	9,346	71,434	45,859	10,331	
900	20,570	63,020	48,620	11,022	71,034	42,459	8,587	
1000	20,790	65,899	50,699	12,649	70,634	39,059	7,168	
1100	21,010	68,591	52,756	14,222	70,234	35,659	5,993	
1200	21,230	71,036	54,789	15,742	69,834	32,259	5,024	
1300	21,450	73,280	56,799	17,212	69,434	28,859	4,285	
1400	21,670	75,333	58,789	18,632	69,034	25,459	3,725	
1500	21,890	77,197	60,759	20,002	68,634	22,059	3,325	
1600	22,110	78,881	62,709	21,322	68,234	18,659	3,004	
1700	22,330	80,333	64,639	22,592	67,834	15,259	2,753	
1800	22,550	81,586	66,479	23,812	67,434	11,859	2,563	
1900	22,770	82,661	68,209	24,982	67,034	8,459	2,423	
2000	22,990	83,586	69,829	26,102	66,634	5,059	2,323	
2100	23,210	84,371	71,339	27,172	66,234	1,659	2,253	
2200	23,430	85,036	72,759	28,192	65,834	-1,741	2,203	
2300	23,650	85,581	74,109	29,162	65,434	-5,141	2,173	
2400	23,870	86,016	75,389	30,092	65,034	-8,541	2,153	
2500	24,090	86,351	76,609	30,892	64,634	-11,941	2,143	

Lead Dibromide (PbBr₂) (crystal)

Mol. Wt. = 367.04

ΔH_f^o 298.15 = -66.07 ± 0.20 kcal. mole⁻¹

S_{298.15}^o = 38.66 ± 0.5 cal. deg.⁻¹ mole⁻¹

ΔH_f^o 298.15 = 41.90 ± 0.17 kcal. mole⁻¹

T_m = 640°K.

ΔH_m^o = 4.96 kcal. mole⁻¹

Heat of Formation. Recalculated from the data reported by H. Braune and P. Koref, Z. anorg. Chem., 87, 175 (1914) and C. Kramer, Z. Elektrochem., 26, 97 (1920).

Heat Capacity, Entropy, and Melting Data. C_p (18.4° to 297.0°K.) reported by W. M. Latimer and H. D. Hoenel, J. Am. Chem. Soc., 49, 19 (1926). Above 298.15°K., C_p given by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) was used. T_m and ΔH_m^o obtained from M. Blanc and G. Petit, Compt. rend., 248, 1305 (1959).

Heat of Sublimation. Calculated from vapor pressure data of H. Bloom, J. O'M. Bockris, R. E. Richards and R. G. Taylor, J. Am. Chem. Soc., 80, 2044 (1958), H. von Wartenberg and O. Boase, Z. Elektrochem., 28, 384 (1922), F. Volmer, Phys. Z., 30, 590 (1929), and B. Greiner and K. Jellinek, Z. physik. Chem., 165, 97 (1933) which are in good agreement.

INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	ΔH° _f	ΔF° _f	Log K _f
0					
100	19.246	42.699	63.001	60.267	44.175
200	19.250	42.698	63.010	60.250	43.890
300	19.252	42.697	63.016	60.232	43.605
400	19.254	42.696	63.022	60.214	43.320
500	19.256	42.695	63.028	60.196	43.035
600	19.258	42.694	63.034	60.178	42.750
700	19.260	42.693	63.040	60.160	42.465
800	19.262	42.692	63.046	60.142	42.180
900	19.264	42.691	63.052	60.124	41.895
1000	19.266	42.690	63.058	60.106	41.610
1100	19.268	42.689	63.064	60.088	41.325
1200	19.270	42.688	63.070	60.070	41.040
1300	19.272	42.687	63.076	60.052	40.755
1400	19.274	42.686	63.082	60.034	40.470
1500	19.276	42.685	63.088	60.016	40.185
1600	19.278	42.684	63.094	60.000	39.900
1700	19.280	42.683	63.100	59.982	39.615
1800	19.282	42.682	63.106	59.964	39.330
1900	19.284	42.681	63.112	59.946	39.045
2000	19.286	42.680	63.118	59.928	38.760
2100	19.288	42.679	63.124	59.910	38.475
2200	19.290	42.678	63.130	59.892	38.190
2300	19.292	42.677	63.136	59.874	37.905
2400	19.294	42.676	63.142	59.856	37.620
2500	19.296	42.675	63.148	59.838	37.335
2600	19.298	42.674	63.154	59.820	37.050
2700	19.300	42.673	63.160	59.802	36.765
2800	19.302	42.672	63.166	59.784	36.480
2900	19.304	42.671	63.172	59.766	36.195
3000	19.306	42.670	63.178	59.748	35.910

March 31, 1962

Br₂Pb

Lead Dibromide (PbBr₂) (Liquid)

Mol. Wt. = 367.04
 ΔH_f° 298.15 = [-63.00 ± 0.20] kcal. mole⁻¹
 $S_{298.15}^\circ$ = [42.699] cal. deg.⁻¹ mole⁻¹
 T_m = 640°K.
 ΔH_m° = 4.96 kcal. mole⁻¹
 T_b = 1187°K.
 ΔH_v° = 27.44 ± 0.17 kcal. mole⁻¹

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy, and Melting Data. C_p obtained from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). T_m and ΔH_m reported by M. Blanc and G. Petit, Compt. rend. 248, 1305-6 (1959). A glass transition temperature of 400°K. is assumed.

Vaporization Phenomena. T_b and ΔH_v calculated from ΔH_f 298.15 and free energy functions for condensed and gaseous states.

Br₂Pb

Lead Dibromide (PbBr₂)

(Ideal Gas) Mol. Wt. = 367.04

INTERIM TABLE

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	cal. mole ⁻¹	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	13.000	0.000	INFINITE	2.467	20.340	20.340	20.340	INFINITE	
100	13.340	60.022	64.176	1.3333	20.671	20.671	20.671	51.706	
200	13.424	77.009	63.672	1.000	24.176	24.176	24.176	32.233	
298	13.662	82.426	62.827	0.985	24.184	24.184	24.184	33.267	
300	13.685	82.511	62.827	0.985	24.184	24.184	24.184	33.267	
400	13.781	92.663	62.965	1.399	31.714	31.714	31.714	24.289	
500	13.827	99.155	63.984	2.760	31.669	31.669	31.669	19.085	
600	13.853	102.067	65.127	4.164	32.063	32.063	32.063	15.371	
700	13.866	104.204	66.275	5.590	33.460	33.460	33.460	13.241	
800	13.876	105.586	67.384	6.936	33.909	33.909	33.909	11.901	
900	13.885	106.918	68.451	8.201	34.311	34.311	34.311	10.192	
1000	13.890	108.155	69.440	9.714	34.131	34.131	34.131	8.145	
1100	13.893	109.379	70.364	11.104	34.342	34.342	34.342	6.562	
1200	13.896	109.666	71.277	12.493	34.547	34.547	34.547	5.295	
1300	13.898	109.910	72.121	13.879	34.746	34.746	34.746	4.280	
1400	13.900	110.120	72.921	15.263	34.949	34.949	34.949	3.463	
1500	13.901	110.299	73.680	16.643	35.151	35.151	35.151	2.859	
1600	13.903	110.446	74.403	18.023	35.357	35.357	35.357	2.416	
1700	13.904	110.566	75.092	19.403	35.566	35.566	35.566	2.110	
1800	13.905	110.666	75.747	20.784	35.777	35.777	35.777	1.910	
1900	13.906	110.747	76.366	22.164	35.990	35.990	35.990	1.769	
2000	13.906	110.789	76.942	23.545	36.204	36.204	36.204	1.680	
2100	13.906	110.807	77.476	24.926	36.420	36.420	36.420	1.641	
2200	13.906	110.814	77.961	26.307	36.637	36.637	36.637	1.651	
2300	13.907	110.817	78.397	27.688	36.855	36.855	36.855	1.709	
2400	13.907	110.817	78.784	29.069	37.073	37.073	37.073	1.815	
2500	13.907	110.817	79.121	30.450	37.290	37.290	37.290	1.969	
2600	13.908	110.817	79.408	31.831	37.507	37.507	37.507	2.173	
2700	13.908	110.817	79.645	33.212	37.724	37.724	37.724	2.427	
2800	13.908	110.817	79.832	34.593	37.941	37.941	37.941	2.731	
2900	13.908	110.817	79.970	35.974	38.158	38.158	38.158	3.085	
3000	13.909	110.817	80.107	37.355	38.375	38.375	38.375	3.489	
3100	13.909	110.817	80.244	38.736	38.592	38.592	38.592	3.943	
3200	13.909	110.817	80.381	40.117	38.809	38.809	38.809	4.447	
3300	13.909	110.817	80.518	41.498	39.026	39.026	39.026	4.991	
3400	13.909	110.817	80.655	42.879	39.243	39.243	39.243	5.585	
3500	13.909	110.817	80.792	44.260	39.460	39.460	39.460	6.229	
3600	13.909	110.817	80.929	45.641	39.677	39.677	39.677	6.923	
3700	13.909	110.817	81.066	47.022	39.894	39.894	39.894	7.667	
3800	13.909	110.817	81.203	48.403	40.111	40.111	40.111	8.461	
3900	13.909	110.817	81.340	49.784	40.328	40.328	40.328	9.305	
4000	13.909	110.817	81.477	51.165	40.545	40.545	40.545	10.199	
4100	13.910	110.817	81.614	52.546	40.762	40.762	40.762	11.143	
4200	13.910	110.817	81.751	53.927	40.979	40.979	40.979	12.137	
4300	13.910	110.817	81.888	55.308	41.196	41.196	41.196	13.181	
4400	13.910	110.817	82.025	56.689	41.413	41.413	41.413	14.275	
4500	13.910	110.817	82.162	58.070	41.630	41.630	41.630	15.419	
4600	13.910	110.817	82.299	59.451	41.847	41.847	41.847	16.613	
4700	13.910	110.817	82.436	60.832	42.064	42.064	42.064	17.857	
4800	13.910	110.817	82.573	62.213	42.281	42.281	42.281	19.151	
4900	13.910	110.817	82.710	63.594	42.498	42.498	42.498	20.495	
5000	13.910	110.817	82.847	64.975	42.715	42.715	42.715	21.889	
5100	13.910	110.817	82.984	66.356	42.932	42.932	42.932	23.333	
5200	13.910	110.817	83.121	67.737	43.149	43.149	43.149	24.827	
5300	13.910	110.817	83.258	69.118	43.366	43.366	43.366	26.371	
5400	13.910	110.817	83.395	70.499	43.583	43.583	43.583	27.965	
5500	13.910	110.817	83.532	71.880	43.799	43.799	43.799	29.609	
5600	13.910	110.817	83.669	73.261	44.016	44.016	44.016	31.303	
5700	13.910	110.817	83.806	74.642	44.233	44.233	44.233	33.047	
5800	13.910	110.817	83.943	76.023	44.450	44.450	44.450	34.841	
5900	13.910	110.817	84.080	77.404	44.667	44.667	44.667	36.685	
6000	13.910	110.817	84.217	78.785	44.884	44.884	44.884	38.579	

March 31, 1962

Br₂Pb

Lead Dibromide (PbBr₂) (Ideal Gas)

Mol. Wt. = 367.04

ΔH°_f 298.15 = -24.18 ± 0.26 kcal. mole⁻¹

S°_{298.15} = 82.426 cal. deg⁻¹ mole⁻¹

Point Group C_{2v}

Vibrational Levels and Multiplicities

ω, cm⁻¹
[140] (1)
[45] (1)
[200] (1)

Pb-Br distance = 2.60 ± 0.03 Å BrPbBr angle = 95° σ = 2

I_A = 46.245 X 10⁻³⁹ g. cm.² I_B = 97.514 X 10⁻³⁹ g. cm.²

I_C = I_A + I_B = 143.759 X 10⁻³⁹ g. cm.²

Heat of Formation. Calculated from ΔH°_f 298.15 and ΔH°_f 298.15 for PbBr₂(c).

Heat Capacity and Entropy. Molecular dimensions obtained from L. E. Sutton (ed.), "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958. Vibrational frequencies estimated by comparison with the corresponding values for HgBr₂(g).

Br₂Pb

(Crystal)

GFW = 207.718

TITANIUM DIBROMIDE (TiBr₂)

(CRYSTAL)

GFW = 207.718

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0							
100	18.807	25.900	25.900	.000	- 96.900	- 91.590	67.137
200	18.812	26.016	25.900	.035	- 96.900	- 91.557	66.499
300	18.806	26.146	25.900	1.930	- 103.872	- 89.322	48.257
400	19.760	31.754	28.050	3.652	- 103.479	- 84.481	36.927
500	19.634	39.308	29.639	5.602	- 103.083	- 80.719	29.402
600	19.908	42.355	31.243	6.779	- 102.685	- 77.023	24.048
700	20.182	45.032	32.802	11.413	- 101.689	- 69.795	16.949
800	20.456	47.354	34.304	13.474	- 101.494	- 66.250	14.479
1000	20.730	49.584	35.719	15.961	- 101.098	- 62.745	12.466
1100	21.004	51.583	37.072	16.075	- 101.639	- 55.735	10.708
1200	21.278	53.492	38.359	20.586	- 100.582	- 52.254	8.157
1300	21.552	55.139	40.753	24.582	- 100.039	- 48.822	7.113
1400	21.826	56.558	42.781				
1500	22.100	58.258	41.870				

ΔH_f^o = unknownΔH_f^o_{298.15} = -96.9 ± 5.0 kcal/molS_{298.15}^o = [25.9 ± 2.0] gibbs/molT₈ = [1208.8]°KΔH₈^o = [49.29] kcal/mol

Heat of Formation

The heat of formation of TiBr₂ crystal is derived from the data of Hall and Blocher (1) for the reaction 2TiBr₃(c) = TiBr₄(g) + TiBr₂(c). Second and third law analyses of these data are not useful because of the formation of solid solutions in the above process. Hall and Blocher obtained a value of ΔH_f^o₂₉₈ of 31.3 kcal/mol for the reaction by integrating the incremental free energy changes over varying compositions of the solid solutions. The corresponding ΔH_f^o₂₉₈ and ΔH_f^o₂₉₈ are calculated as 34.6 kcal/mol and -96.9 kcal/mol, respectively, using auxiliary JANAF heats of formation and enthalpy data.

Heat Capacity and Entropy

The heat capacity of TiBr₂(c) was estimated by Kelley (2). The value of S_{298.15}^o is estimated from that of TiCl₂(c) and the difference between ionic entropy contributions of Cl⁻ and Br⁻.

Heat of Sublimation

The heat of sublimation of TiBr₂(c) is taken as the difference in the heats of formation of TiBr₂(c) and TiBr₂(g) at the sublimation temperature. The sublimation temperature is taken as the point at which ΔG^o = 0 for the reaction TiBr₂(c) = TiBr₂(g). The heat of formation of TiBr₂(g), upon which these quantities depend, is an estimated quantity.

References

1. E. H. Hall and J. M. Blocher, Jr., J. Phys. Chem. **63**, 1525 (1959).
2. K. K. Kelley, U. S. Bur. Mines Bull. **584**, 1960.

Dec. 31, 1961; June 30, 1964; June 30, 1968

Titanium Dibromide (TiBr₂)

(Ideal Gas)

GFW = 207.718

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	Log K _p
0	∞	∞	∞	∞	∞	∞
100	11.939	59.137	56.056	3.615	39.404	INFINITE
200	13.172	63.752	58.056	2.691	38.282	95.534
298	13.752	67.752	58.056	2.000	42.800	37.936
300	14.353	73.752	58.056	1.027	42.817	51.812
400	14.581	76.005	74.319	1.475	50.227	53.293
500	14.694	77.394	75.394	2.939	50.292	54.053
600	14.756	78.604	76.404	4.412	50.373	54.798
700	14.795	79.625	77.422	5.490	50.474	55.529
800	14.822	80.462	78.000	7.370	50.600	56.243
900	14.844	81.122	78.454	8.854	50.750	56.939
1000	14.867	81.525	81.186	10.339	50.929	57.617
1100	14.894	82.943	82.191	11.827	51.132	58.275
1200	14.930	84.241	83.142	13.318	52.296	58.877
1300	14.975	85.537	84.052	14.810	53.419	59.420
1400	15.030	86.834	84.866	16.314	54.554	59.959
1500	15.096	88.132	85.708	17.820	55.701	60.479
1600	15.171	89.435	86.482	19.333	56.860	60.981
1700	15.254	90.741	87.220	20.855	58.031	61.464
1800	15.343	92.048	87.926	22.384	59.218	61.928
1900	15.437	93.356	88.602	23.923	60.418	62.376
2000	15.532	94.664	89.252	25.472	61.631	62.801
2100	15.628	95.972	89.877	27.030	62.857	63.206
2200	15.722	97.280	90.478	28.597	64.096	63.592
2300	15.815	98.588	91.056	30.174	65.349	63.959
2400	15.905	99.896	91.620	31.760	66.615	64.307
2500	15.990	101.204	92.162	33.355	67.892	64.635
2600	16.072	102.512	92.687	34.958	69.179	64.943
2700	16.149	103.820	93.197	36.569	70.475	65.231
2800	16.222	105.128	93.691	38.188	71.781	65.500
2900	16.290	106.436	94.171	39.813	73.096	65.750
3000	16.354	107.744	94.638	41.446	74.421	65.981
3100	16.414	109.052	95.092	43.084	75.756	66.194
3200	16.470	110.360	95.535	44.728	77.101	66.389
3300	16.523	111.668	95.966	46.378	78.456	66.566
3400	16.573	112.976	96.387	48.033	79.821	66.725
3500	16.620	114.284	96.797	49.692	81.196	66.866
3600	16.665	115.592	97.198	51.356	82.581	66.989
3700	16.707	116.900	97.590	53.025	83.976	67.094
3800	16.748	118.208	97.973	54.698	85.381	67.181
3900	16.787	119.516	98.348	56.375	86.796	67.250
4000	16.825	120.824	98.715	58.055	88.221	67.301
4100	16.861	122.132	99.074	59.739	89.656	67.334
4200	16.896	123.440	99.425	61.427	91.101	67.350
4300	16.930	124.748	99.770	63.119	92.556	67.350
4400	16.963	126.056	100.108	64.813	94.021	67.334
4500	16.995	127.364	100.440	66.511	95.496	67.299
4600	17.026	128.672	100.765	68.212	96.981	67.249
4700	17.056	129.980	101.085	69.916	98.476	67.184
4800	17.085	131.288	101.392	71.623	99.981	67.104
4900	17.113	132.596	101.706	73.333	101.496	67.009
5000	17.140	133.904	102.009	75.046	103.021	66.900
5100	17.166	135.212	102.307	76.761	104.556	66.776
5200	17.191	136.520	102.599	78.479	106.101	66.639
5300	17.214	137.828	102.887	80.199	107.656	66.489
5400	17.237	139.136	103.171	81.922	109.221	66.324
5500	17.258	140.444	103.449	83.647	110.796	66.144
5600	17.279	141.752	103.724	85.373	112.381	65.949
5700	17.297	143.060	103.994	87.102	113.976	65.739
5800	17.315	144.368	104.260	88.833	115.581	65.514
5900	17.331	145.676	104.522	90.565	117.196	65.274
6000	17.346	146.984	104.780	92.299	118.821	65.019

June 30, 1964; June 30, 1968

TITANIUM DIBROMIDE (TiBr₂)

(IDEAL GAS)

Point Group [D_{∞h}]ΔH_f⁰ = -39.4 ± 5.0 kcal/molS_{298.15} = [73.8 ± 3.0] gibbs/molΔH_f⁰ = -42.8 ± 5.0 kcal/mol

Ground State Quantum Weight = [3]

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	g _i
[105] (2)	[105] (2)
[160] (1)	[333] (1)

Bond Distance: Ti-Br = [2.4] Å

Bond Angle: Br-Ti-Br = [180°]

Rotational Constant: B₀ = [0.0183] cm⁻¹

Heat of Formation

The heat of formation of TiBr₂(g) is calculated from the estimated Ti-Br bond energy. The bond energy is estimated as being the same as the average Ti-Cl bond energy of TiCl₂(g). This estimate is used because the measured average bond energies of TiBr₃(g) and TiCl₃(g) and those of TiBr₄(g) and TiCl₄(g) are very nearly equal.

Heat Capacity and Entropy

The interatomic distances are estimated from those of TiCl₂(g), TiCl₄(g) and TiBr₄(g). The vibrational frequencies are estimated from a valence force field model. The force constant k is estimated as 1.2 millidynes Å⁻¹, and the constant k_f/l² is assumed to be 0.06 millidynes Å⁻¹. These values are derived by a correlation with other dihalides.

The electronic levels are assumed to be the same as TiCl₂(g). The levels of TiCl₂(g) are estimated by assuming that they correspond to the inverted states of NiCl₂(g) (1). The linear configuration is adopted since experimental evidence indicates that other transition metal dihalides are linear (2, 3, 4, 5).

References

1. C. W. DeKock and D. M. Gruen, J. Chem. Phys. **44**, 4387 (1966).
2. R. A. Berg and O. Sinanoglu, J. Chem. Phys. **32**, 1082 (1960).
3. J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. **34**, 1670 (1961).
4. G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. **36**, 2879 (1962).
5. A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. **40**, 3471 (1964).



ZIRCONIUM DIBROMIDE (ZrBr₂)

(CRYSTAL)

ZIRCONIUM DIBROMIDE (ZrBr₂)Zirconium Dibromide (ZrBr₂)
(Crystal)

GFW = 251.038

GFW = 251.038

 ΔH_f° = Unknown $\Delta H_f^\circ_{298.15} = [-96.7 \pm 10] \text{ kcal/mol}$ $\Delta H_m^\circ = [15.0 \pm 10] \text{ kcal/mol}$ $\Delta H_{298.15}^\circ = [55.0 \pm 5] \text{ kcal/mol}$ $S_{298.15}^\circ = [27.7 \pm 3] \text{ gibbs/mol}$ $T_m = [900]^\circ\text{K}$ Heat of Formation

The value of $\Delta H_f^\circ(\text{ZrBr}_2, c) = -96.7 \text{ kcal/mol}$ is calculated from the estimated $\Delta H_{298}^\circ = 55 \pm 5 \text{ kcal/mol}$ for $\text{ZrBr}_2(c) \rightarrow \text{ZrBr}_2(g)$, using $\Delta H_{298}^\circ(\text{ZrBr}_2, g) = -41.7 \text{ kcal/mol}$ (1). The estimated ΔH_{298}° is obtained as an average of the heats of sublimation at 298°K for CrBr_2 , MnBr_2 , CoBr_2 , NiBr_2 , SbBr_2 given by Brewer, Somayajulu and Brackett (2) and TiBr_2 and FeBr_2 listed in JANAF tables (3).

Heat Capacity and Entropy

The heat capacities of $\text{ZrBr}_2(c)$ are estimated from $\text{TiBr}_2(c)$ (3), based on the assumption $\text{Cp}(\text{ZrBr}_2) = \text{Cp}(\text{TiBr}_2) + 3/2 R \ln(\text{at. wt. of Zr}/(\text{at. wt. of Ti}))$. The entropy, S_{298}° - 27.7 eu, is estimated in a similar manner based on $\text{TiCl}_2(c)$ (4) and $\text{TiBr}_2(c)$ (3).

Melting Data

The heat of fusion is roughly estimated, so that the entropy of vaporization is about 20 eu. The melting point was estimated by Brewer (5).

References

1. JANAF $\text{ZrBr}_2(g)$ table dated June 30, 1970.
2. L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).
3. JANAF $\text{TiBr}_2(c)$ table dated June 30, 1968 and $\text{FeBr}_2(c)$ table dated Sept. 30, 1966.
4. JANAF $\text{TiCl}_2(c)$ table dated Dec. 31, 1968.
5. L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill Ed., McGraw-Hill Book Company, New York, 1949.

T, °K	C_p°	$S^\circ - (C_p^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
100						
200						
298	20.727	27.700	.000	-96.700	-91.334	66.950
300	20.732	27.858	.034	-96.706	-91.300	66.912
400	20.806	28.550	2.250	-96.706	-91.300	66.882
500	21.240	30.547	6.240	-102.901	-88.299	66.844
600	21.554	32.451	11.815	-107.326	-80.675	66.808
700	21.828	34.179	19.550	-101.756	-77.054	66.772
800	22.102	35.727	29.547	-101.188	-73.563	66.736
900	22.376	37.197	41.822	-100.622	-70.144	66.700
1000	22.650	38.595	56.395	-100.062	-66.747	66.664
1100	22.924	39.979	73.261	-99.502	-63.487	66.628
1200	23.198	41.350	92.407	-98.935	-60.186	66.592
1300	23.472	42.712	113.840	-98.368	-56.914	66.556
1400	23.746	44.063	137.561	-97.801	-53.700	66.520
1500	24.020	45.413	163.576	-97.234	-50.540	66.484

Mar. 31, 1962; June 30, 1970



GFW = 251.038

(LIQUID)

ZIRCONIUM DIBROMIDE (ZrBr₂)

ΔH_f° _{298.15} = [-81.920] kcal/mol

ΔH_m° = [15.0 ± 10] kcal/mol

ΔH_v° = [31.5] kcal/mol

$S_{298.15}^\circ$ = [43.983] gibbs/mol

T_m = [900]*K

T_b = [1555.1]*K

Zirconium Dibromide (ZrBr₂)

(Liquid)

GFW = 251.038

T, °K	C _p ^o	S ^o - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0						
100	21.750	43.983	0.000	- 81.420	- 81.308	59.600
200	21.750	44.117	0.040	- 81.423	- 81.304	59.230
300	21.750	44.251	0.080	- 81.426	- 81.300	58.860
400	21.750	44.385	0.120	- 81.429	- 81.296	58.490
500	21.750	44.519	0.160	- 81.432	- 81.292	58.120
600	21.750	44.653	0.200	- 81.435	- 81.288	57.750
700	21.750	44.787	0.240	- 81.438	- 81.284	57.380
800	21.750	44.921	0.280	- 81.441	- 81.280	57.010
900	21.750	45.055	0.320	- 81.444	- 81.276	56.640
1000	21.750	45.189	0.360	- 81.447	- 81.272	56.270
1100	21.750	45.323	0.400	- 81.450	- 81.268	55.900
1200	21.750	45.457	0.440	- 81.453	- 81.264	55.530
1300	21.750	45.591	0.480	- 81.456	- 81.260	55.160
1400	21.750	45.725	0.520	- 81.459	- 81.256	54.790
1500	21.750	45.859	0.560	- 81.462	- 81.252	54.420
1600	21.750	45.993	0.600	- 81.465	- 81.248	54.050
1700	21.750	46.127	0.640	- 81.468	- 81.244	53.680
1800	21.750	46.261	0.680	- 81.471	- 81.240	53.310
1900	21.750	46.395	0.720	- 81.474	- 81.236	52.940
2000	21.750	46.529	0.760	- 81.477	- 81.232	52.570

Heat of Formation

The ΔH_f° (ZrBr₂, l) is calculated from ΔH_f° (ZrBr₂, c) by adding ΔH_m° and the difference between $H_{900}^\circ - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

See ZrBr₂(c) table for details.

Vaporization Data

T_b is the temperature at which the Gibbs energy change approaches zero for the process ZrBr₂(l) + ZrBr₂(g). The difference between ΔH_f° for ZrBr₂(l) and ZrBr₂(g) at T_b is ΔH_v° .



ZIRCONIUM DIBROMIDE (ZrBr₂)

(IDEAL GAS)

GFW = 251.038

Point Group [D_{2h}] $\Delta H_f^\circ = [-38.2 \pm 10] \text{ kcal/mol}$ $S_{298.15}^\circ = [75.7 \pm 3] \text{ gibbs/mol}$ $\Delta H_f^\circ_{298.15} = [-41.7 \pm 10] \text{ kcal/mol}$

Ground State Quantum Weight = [3]

Zirconium Dibromide (ZrBr₂)

GFW = 251.038

T, °K	Cp°	S°	-(G°-H°)/T	H°-H° ₂₉₈	kcal/mol	ΔG°	Log Kp
0	.000	INFINITE	INFINITE	-3.720	34.240	INFINITE	INFINITE
100	12.473	40.000	12.473	-3.720	34.240	34.240	16.241
200	14.073	49.970	17.000	-3.720	34.240	34.240	16.241
298	14.504	51.210	17.000	-3.720	34.240	34.240	16.241
300	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
400	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
500	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
600	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
700	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
800	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
900	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
1000	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
1100	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
1200	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
1300	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
1400	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
1500	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
1600	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
1700	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
1800	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
1900	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
2000	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
2100	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
2200	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
2300	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
2400	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
2500	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
2600	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
2700	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
2800	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
2900	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
3000	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
3100	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
3200	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
3300	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
3400	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
3500	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
3600	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
3700	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
3800	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
3900	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
4000	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
4100	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
4200	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
4300	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
4400	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
4500	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
4600	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
4700	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
4800	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
4900	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
5000	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
5100	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
5200	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
5300	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
5400	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
5500	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
5600	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
5700	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
5800	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
5900	14.509	51.210	17.000	-3.720	34.240	34.240	16.241
6000	14.509	51.210	17.000	-3.720	34.240	34.240	16.241

Mar. 31, 1962; June 30, 1970

Electronic Levels and Quantum Weights

 $\epsilon_i, \text{ cm}^{-1}$ g_i

0

[7000]

[17000]

[22000]

[15]

Vibrational Frequencies and Degeneracies

 $\omega_e, \text{ cm}^{-1}$

[160] (1)

[84] (2)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

[265] (1)

Bond Distance: Zr-Br = [2.47] Å
Bond Angle: Br-Zr-Br = [180°]
Rotational Constant: B₀ = [0.01729] cm⁻¹
σ = [2]

Heat of Formation

The heat of formation, $\Delta H_f^\circ(\text{ZrBr}_2, g) = -41.7 \text{ kcal/mol}$, is derived from the estimated $\Delta H_f^\circ(\text{Zr-Br}_2) = 243.5 \pm 10 \text{ kcal/mol}$ for $\text{ZrBr}_2(g) + \text{Zr}(g) + 2\text{Br}(g)$. The value of ΔH_f° is twice the average bond dissociation energy, $D_{298}^\circ(\text{Zr-Br}_2) = 121.75 \text{ kcal/mol}$, which is calculated from the relation $D_{298}^\circ(\text{Zr-Br}_2) = D_{298}^\circ(\text{Zr-Br}) + D_{298}^\circ(\text{Ti-Br})$. The average bond dissociation energies, $D_{298}^\circ(\text{Zr-Br}) = 102.2 \text{ kcal/mol}$, $D_{298}^\circ(\text{Ti-Br}) = 87.9 \text{ kcal/mol}$ and $D_{298}^\circ(\text{Ti-Br}_2) = 104.6 \text{ kcal/mol}$, are all calculated from JANAF $\Delta H_f^\circ_{298}$ for $\text{ZrBr}_4(g)$, $\text{TiBr}_4(g)$, $\text{TiBr}_3(g)$, $\text{TiBr}_2(g)$, $\text{TiBr}(g)$ and $\text{Br}(g)$.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the transition metal dihalides are generally linear ($\bar{A}$, $\bar{B}$, $\bar{C}$, $\bar{D}$, $\bar{E}$) even though a few fluorides are bent ($\bar{G}$). The bond distance is assumed to be the same as that in $\text{ZrBr}_4(g)$ which was estimated as 2.47 Å by Godnev et al. ($\bar{Z}$). The moment of inertia is $161.8979 \times 10^{-39} \text{ g cm}^2$.

The vibrational frequencies are calculated from a valence force field model. The stretching force constant is estimated to be 1.2 millidyne/Å and the bending force constant 0.06 millidyne/Å . These values are derived from force constants of transition metal dihalides listed by Brewer, Somayajulu and Brackett ($\bar{B}$). The electronic levels and quantum weights are estimated to be the same as those of gaseous TiCl_2 ($\bar{Z}$).

References

1. R. A. Berg and O. Sinanoglu, J. Chem. Phys. **32**, 1082 (1960).
2. J. T. Houghen, G. E. Leroi and T. C. James, J. Chem. Phys. **34**, 1670 (1961).
3. A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. **40**, 3471 (1964).
4. M. E. Jacox and D. E. Milligan, J. Chem. Phys. **51**, 4143 (1969).
5. K. R. Thompson and K. D. Carlson, J. Chem. Phys. **49**, 4379 (1968).
6. J. W. Haas, R. H. Hauge and J. L. Margrave, J. Chem. Phys. **51**, 2648 (1969).
7. I. N. Godnev, A. M. Alekandrova and I. V. Rigina, Optics and Spectroscopy **2**, 172 (1959).
8. L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963).
9. JANAF $\text{TiCl}_2(g)$ table dated Dec. 31, 1968.

Phosphoryl Bromide (POBr₃)
(Ideal Gas) Mol. Wt. = 286.723

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	-4.744	-87.056	-87.056	INFINITE
100	14.159	66.247	103.348	-3.710	-87.472	-89.990	100.555
200	19.200	77.635	87.881	-2.009	-88.185	-92.136	100.676
298	21.478	83.978	83.978	0.000	-88.185	-92.136	68.485
300	21.508	84.111	83.979	0.040	-88.185	-92.136	68.063
400	22.770	92.487	86.839	2.259	-93.025	-93.434	49.684
500	23.567	97.660	88.502	4.579	-104.055	-91.305	38.517
600	24.105	102.007	90.401	6.964	-103.996	-88.125	30.944
700	24.480	105.753	92.332	9.394	-103.921	-84.958	25.539
800	24.751	109.040	94.220	11.856	-103.852	-81.803	22.938
900	24.951	111.968	96.032	14.362	-103.782	-78.655	19.172
1000	25.102	114.605	97.760	16.845	-103.712	-75.507	15.166
1100	25.218	117.003	99.402	19.361	-103.641	-72.359	13.713
1200	25.309	119.203	100.961	21.888	-103.570	-69.211	11.674
1300	25.382	121.230	102.443	24.422	-103.500	-66.063	9.953
1400	25.441	123.113	103.853	26.964	-103.430	-62.915	8.481
1500	25.489	124.870	105.196	29.510	-103.360	-59.767	7.209
1600	25.529	126.516	106.478	32.061	-103.290	-56.619	6.098
1700	25.563	128.065	107.703	34.616	-103.220	-53.471	5.121
1800	25.591	129.527	108.875	37.174	-103.150	-50.323	4.254
1900	25.615	130.911	109.999	39.734	-103.080	-47.175	3.481
2000	25.636	132.226	111.077	42.296	-103.010	-44.027	2.787
2100	25.654	133.477	112.114	44.851	-102.940	-40.879	2.160
2200	25.670	134.671	113.113	47.407	-102.870	-37.731	1.591
2300	25.683	135.812	114.075	49.965	-102.800	-34.583	1.073
2400	25.695	136.905	115.004	52.524	-102.730	-31.435	0.600
2500	25.706	137.955	115.901	55.083	-102.660	-28.287	0.165
2600	25.716	138.963	116.769	57.642	-102.590	-25.139	0.000
2700	25.724	139.934	117.609	60.201	-102.520	-22.000	0.000
2800	25.732	140.869	118.423	62.760	-102.450	-18.861	0.000
2900	25.739	141.772	119.213	65.319	-102.380	-15.722	0.000
3000	25.745	142.645	119.979	67.878	-102.310	-12.583	0.000
3100	25.750	143.489	120.724	70.437	-102.240	-9.444	0.000
3200	25.756	144.307	121.448	73.000	-102.170	-6.305	0.000
3300	25.760	145.100	122.153	75.573	-102.100	-3.166	0.000
3400	25.764	145.869	122.839	78.150	-102.030	0.000	0.000
3500	25.768	146.615	123.508	80.730	-101.960	2.861	0.000
3600	25.772	147.341	124.160	83.313	-101.890	5.722	0.000
3700	25.775	148.048	124.796	85.899	-101.820	8.583	0.000
3800	25.778	148.735	125.417	88.488	-101.750	11.444	0.000
3900	25.781	149.405	126.024	91.080	-101.680	14.305	0.000
4000	25.784	150.057	126.616	93.674	-101.610	17.166	0.000
4100	25.786	150.694	127.196	96.269	-101.540	20.027	0.000
4200	25.788	151.316	127.763	98.864	-101.470	22.888	0.000
4300	25.790	151.922	128.318	101.460	-101.400	25.749	0.000
4400	25.792	152.515	128.861	104.056	-101.330	28.610	0.000
4500	25.794	153.095	129.393	106.651	-101.260	31.471	0.000
4600	25.796	153.662	129.914	109.246	-101.190	34.332	0.000
4700	25.798	154.217	130.426	111.841	-101.120	37.193	0.000
4800	25.799	154.760	130.927	114.436	-101.050	40.054	0.000
4900	25.801	155.292	131.419	117.031	-100.980	42.915	0.000
5000	25.802	155.813	131.901	119.626	-100.910	45.776	0.000
5100	25.803	156.324	132.375	122.221	-100.840	48.637	0.000
5200	25.804	156.825	132.841	124.816	-100.770	51.498	0.000
5300	25.805	157.317	133.298	127.409	-100.700	54.359	0.000
5400	25.806	157.799	133.747	130.000	-100.630	57.220	0.000
5500	25.807	158.273	134.189	132.591	-100.560	60.081	0.000
5600	25.808	158.738	134.623	135.182	-100.490	62.942	0.000
5700	25.809	159.194	135.050	137.773	-100.420	65.803	0.000
5800	25.810	159.643	135.470	140.364	-100.350	68.664	0.000
5900	25.811	160.084	135.884	142.955	-100.280	71.525	0.000
6000	25.812	160.518	136.291	145.546	-100.210	74.386	0.000

Mar. 31, 1963; Dec. 31, 1965

(IDEAL GAS)

PHOSPHORYL BROMIDE (POBr₃)

Point Group C_{3v}
S_{298.15} = 85.978 cal. deg.⁻¹ mole⁻¹
Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
118 (2)	340 (1)
175 (1)	488 (2)
267 (2)	1261 (1)

Bond Distances: P-O = 1.41 ± 0.07 Å P-Br = 2.06 ± 0.03 Å

Bond Angle: Br-P-Br = 108° ± 3°

Product of the Moments of Inertia: I_AI_BI_C = 2.2602 × 10⁻¹¹² g.³ cm.⁶

Heat of Formation.

The ΔH_f⁰ 298.15 of POBr₃(g) was calculated from the heat of formation of the crystal and the heat of sublimation. The heat of sublimation was obtained by combining the ΔH_f⁰ and an estimated ΔH_{sub}⁰. The heat of formation of the crystal was derived from the heat observed for the reaction: POBr₃(c) + (n+3)H₂O(l) → [H₃PO₄·3HBr] in nH₂O(l). The data used in these calculations may be summarized as follows:

Data	Source
ΔH _f ⁰ 298.15 (water solutions) H ₃ PO ₄	Obtained graphically from W. S. Holmes, Trans. Faraday Soc. 59, 1916 (1962).
ΔH _f ⁰ 298.15 (water solutions) HBr	Obtained graphically from "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Stds. Circular 500.
ΔH _f ⁰ 298.15 (liquid) H ₂ O = -58.3174 kcal. mole ⁻¹	"Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500.
ΔH _f ⁰ 298.15 (crystal) POBr ₃ = -109.1 kcal. mole ⁻¹	Recalculated from heats observed by T. Charnley and H. A. Skinner, J. Chem. Soc. 450 (1953).
ΔH _f ⁰ 298.15 = [3.7] kcal. mole ⁻¹	Estimated from comparison with POCl ₃ .
ΔH _f ⁰ 298.15 = [12.1] kcal. mole ⁻¹	Estimated from the ΔH _f ⁰ at T _m (10.6 kcal. mole ⁻¹ at 464.9°K). ΔH _f ⁰ was calculated from a least squares treatment of the v.p. data of M. Van Driel, Rec. Trav. Chim. 61, 748 (1942).

Heat Capacity and Entropy.

The molecular constants used were calculated from electron diffraction measurements by J. H. Searles and L. O. Brockway, J. Am. Chem. Soc. 85, 1941 (1944). The calculated moments are I_A = I_B = 8.69174 × 10⁻⁸⁶ g.² cm.² and I_C = 1.474471 × 10⁻⁵⁷ g.² cm.²

From the Raman spectra of POBr₃ the vibrational frequencies were measured and assigned by H. Garding and M. van Driel, Rec. Trav. Chim. 61, 419 (1942). The Raman spectra was studied and the vibrational frequencies were listed by M. L. Delvaule and P. Francois, Compt. Rend. 220, 817 (1945). The frequencies may also be found in Compt. Rend. 222, 550 (1946) and J. Chim. Phys. 45, 87 (1948) by Delvaule and Francois.

Br₃OP

MOL. WT. = 286.723

Br₃OP

Phosphorus Tribromide (PBr₃)
(Ideal Gas) Mol. Wt. = 270.723

T. °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	+∞	∞	∞	∞	-25.293	-25.293	INFINITE
100	13.090	65.896	8.214	3.232	-25.474	-29.884	65.308
200	16.674	76.227	8.482	1.721	-25.938	-34.190	37.359
298	18.173	83.206	+∞	+∞	-30.700	-37.611	27.568
300	18.191	83.206	+∞	+∞	-30.725	-37.653	27.439
400	18.863	88.655	8.929	1.890	-41.761	-37.697	20.596
500	19.206	92.905	8.514	3.796	-41.751	-36.684	16.034
600	19.402	96.426	8.681	5.727	-41.753	-35.671	12.992
800	19.523	103.677	8.404	6.674	-41.779	-34.656	10.820
900	19.569	104.332	8.147	11.593	-62.669	-38.043	9.732
1000	19.699	106.425	92.863	13.561	-61.890	-33.160	7.247
1100	19.729	108.304	94.183	15.533	-61.713	-30.297	6.019
1200	19.775	110.022	11.507	61.436	-41.536	-27.499	4.999
1300	19.775	111.422	11.507	61.436	-41.536	-27.499	4.999
1400	19.793	113.069	97.740	21.461	-61.588	-21.794	3.402
1500	19.795	114.434	97.868	23.440	-61.017	-18.968	2.766
1600	19.804	115.712	99.825	25.420	-60.847	-16.190	2.211
1800	19.816	120.795	21.400	60.860	-60.860	-13.402	1.723
1900	19.824	119.117	102.610	31.364	-60.347	-7.958	1.604
2000	19.829	120.134	103.461	33.347	-60.186	-5.104	1.558
2100	19.833	121.102	104.278	35.330	-60.024	-2.353	1.245
2200	19.839	122.066	105.821	37.297	-59.708	-0.297	1.000
2300	19.842	123.751	106.550	41.281	-59.453	5.854	+533
2400	19.844	124.561	107.254	43.265	-59.498	8.578	+750
2600	19.847	125.393	107.935	45.250	-59.247	11.293	+949
2700	19.848	126.088	108.556	47.236	-59.233	14.707	+1304
2800	19.850	126.810	109.231	49.220	-58.949	16.707	+1463
2900	19.852	127.556	109.850	51.205	-58.401	19.407	+1610
3000	19.853	128.180	110.450	53.190	-58.456	22.101	+1748
3100	19.854	128.831	111.022	55.175	-58.414	24.793	+1907
3200	19.855	130.072	112.149	57.166	-58.233	27.476	+2117
3300	19.856	130.672	112.789	59.154	-58.233	30.151	+2252
3400	19.857	131.265	112.465	61.132	-58.095	32.831	+2457
3500	19.858	131.240	113.207	63.118	-57.959	35.506	+2657
3600	19.859	131.900	113.715	65.104	-57.826	38.171	+2817
3700	19.860	132.474	114.244	67.090	-57.662	40.836	+2952
3800	19.860	132.873	114.666	69.076	-57.462	43.501	+3073
3900	19.861	133.389	115.168	71.062	-57.434	46.161	+3150
4000	19.862	133.892	115.630	73.048	-57.407	48.808	+3237
4100	19.862	134.383	116.082	75.034	-57.182	51.459	+3287
4200	19.863	134.854	116.554	77.007	-57.038	54.115	+3335
4300	19.863	135.329	116.955	78.971	-56.751	56.771	+3425
4400	19.863	135.795	117.378	80.993	-56.418	59.402	+3468
4500	19.864	136.232	117.792	82.979	-56.701	62.040	+3509
4600	19.864	136.668	118.198	84.964	-56.484	64.675	+3548
4700	19.865	137.095	118.595	86.939	-56.259	67.302	+3586
4800	19.865	137.514	118.985	88.939	-56.033	69.942	+3623
4900	19.865	137.923	119.367	90.925	-55.747	72.577	+3658
5000	19.866	138.325	119.742	92.912	-55.138	75.206	+3692
5100	19.866	138.718	120.111	94.898	-55.033	77.826	+3733
5200	19.866	139.104	120.472	96.885	-54.824	80.437	+3773
5300	19.866	139.482	120.827	98.871	-54.624	83.075	+3815
5400	19.867	139.854	121.176	100.858	-55.723	85.689	+3858
5500	19.867	140.218	121.519	102.845	-55.422	88.315	+3909
5600	19.867	140.576	121.854	104.831	-55.226	90.925	+3954
5700	19.867	140.928	122.188	106.818	-55.250	93.536	+4000
5800	19.867	141.273	122.514	108.805	-55.335	96.157	+4047
5900	19.868	141.613	122.835	110.792	-55.243	98.766	+4094
6000	19.868	141.947	123.150	112.778	-55.153	101.370	+4141

Dec. 31, 1963

PHOSPHORUS TRIBROMIDE (PBr₃)
(IDEAL GAS)

Point Group C_{3v}
S°_{298.15} = 83.206 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]
ΔH_f⁰ = -25.3 ± 1.5 kcal. mole⁻¹
ΔF_f⁰ = -30.7 ± 1.5 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
392 (1)	392.2 (2)
161.3 (1)	115.7 (2)

Bond Distance: P-Br = 2.20 ± 0.03 Å

Bond Angle: Br-P-Br = 106° ± 3°

Product of the Moments of Inertia: I_AI_BI_C = 1.1897 X 10⁻¹¹ g. cm.⁶

Heat of Formation.

The heat of formation of PBr₃ gas from white (α) phosphorus, -34.9 kcal. mole⁻¹, was obtained by T. Charnley and H. A. Skinner, J. Chem. Soc. 450 (1953). This was changed from white (α) to the red (V) phosphorus reference state to give the value used in this table (-30.7 kcal. mole⁻¹). To obtain their value (-34.9 kcal. mole⁻¹), Charnley and Skinner measured the heat of formation of the liquid, and combined it and their estimate of the liquid enthalpy with the heat of vaporization (9.5 kcal. mole⁻¹) calculated by M. Van Driel and H. Oardings, Rec. Trav. Chem. 50, 943 (1941). For the liquid heat of formation Charnley and Skinner observed the ΔH_f⁰ = -67.2 ± 0.6 kcal. mole⁻¹ for PBr₃(l) + (n+3)H₂O(l) → [H₃PO₃ + 3HBr] in nH₂O(l). Van Driel and Oardings measured the vapor pressure over PBr₃(l) and calculated the heat of vaporization with the aid of a modified Clapeyron equation. The uncertainties on the heats of formation are estimates.

Heat Capacity and Entropy.

Q. Williams and W. Oordy, Phys. Rev. 79, 225 (1950) have reported moments of inertia from the microwave spectrum of PBr₃. From this data D. H. Whiffen in "Tables of Interatomic Distances and Configuration in Molecules and Ions", Scientific Editor, L. E. Sutton, Special Publication No. 11, The Chemical Society (London) 1958, has calculated the selected molecular constants. From these constants the principal moments of inertia were calculated as I_A = I_B = 8.5214 X 10⁻³⁸ g. cm.² and I_C = 1.6363 X 10⁻³⁷ g. cm.²

M. Liatera and L. E. Sutton, Trans. Faraday Soc. 37, 393 (1941) have reported P-Br = 2.23 ± 0.04 Å and the angle P-Br-P = 100° ± 2°. S. M. Swingle has measured P-Br = 2.18 ± 0.03 Å and the angle P-Br-P = 101.5° ± 1.5°. The work of Swingle was reported in a private communication from L. Pauling and V. Schomaker, California Institute of Technology to P. W. Allen and L. E. Sutton, Acta. Cryst. 3, 48 (1950). Swingle's data as well as that of Liatera and Sutton was obtained by electron diffraction. The 106° angle was selected since 101.5° and 100° give imaginary force constants with the ranges allowed for the type A, 392 cm.⁻¹ frequency and the form of the potential function assumed by P. W. Davis and R. A. Oetjen, J. Molecular Spec. 2, 253 (1958).

The vibrational frequencies were measured and assigned in the infrared by Davis and Oetjen. Raman measurements and assignments by J. Cabannes and A. Rausset, Ann. Phys. (Paris) 19, 229 (1953) were also listed by M. L. Delaunay, Compt. Rend. 222, 1391 (1946) and Compt. Rend. 224, 389 (1947). The Raman assignments were as follows: type A, 380 cm.⁻¹ and 162 cm.⁻¹ and type E, 400 cm.⁻¹ and 116 cm.⁻¹.

Br₃P

Thiophosphoryl Bromide (PSBr₃)

(Ideal Gas) Mol. Wt. = 302.789

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	INFINITE	-	5.064	-	57.361	INFINITE
100	15.556	67.925	107.578	-	57.361	-	135.352
200	20.462	80.447	91.099	-	57.361	-	72.253
298	22.690	89.084	81.084	-	57.361	-	50.861
300	22.719	89.225	80.985	-	57.361	-	50.575
400	23.861	95.934	89.992	2.377	74.683	69.427	37.841
500	24.491	101.333	91.738	4.797	75.097	67.858	29.659
600	24.868	105.634	93.723	7.267	75.417	66.380	24.178
700	25.195	109.151	95.897	9.767	75.646	64.988	19.078
800	25.470	112.051	97.693	12.286	75.791	63.671	15.761
900	25.698	114.634	99.269	14.819	75.851	62.426	13.115
1000	25.877	116.913	100.651	17.362	75.828	61.251	10.957
1100	25.999	118.844	101.842	19.912	75.721	60.145	9.151
1200	26.064	120.416	102.877	22.464	75.536	59.097	7.650
1300	26.074	121.616	103.664	25.027	75.271	58.100	6.356
1400	26.034	122.315	104.208	27.590	74.936	57.153	5.239
1500	25.958	122.685	104.582	30.155	74.741	56.256	4.264
1600	25.848	122.743	104.890	32.723	74.497	55.404	3.422
1700	25.705	122.593	105.123	35.293	74.114	54.593	2.686
1800	25.538	122.170	105.284	37.864	73.591	53.821	2.047
1900	25.350	121.500	105.364	40.437	72.928	53.088	1.494
2000	25.140	120.601	105.376	43.010	72.133	52.393	0.937
2100	24.906	119.483	105.320	45.585	71.206	51.736	0.380
2200	24.649	118.163	105.193	48.160	70.146	51.114	-0.173
2300	24.370	116.660	104.993	50.733	68.953	50.526	-0.716
2400	24.070	114.993	104.723	53.303	67.628	50.000	-1.247
2500	23.747	113.083	104.393	55.869	66.168	49.536	-1.764
2600	23.400	110.940	103.913	58.427	64.573	49.133	-2.267
2700	23.030	108.583	103.283	60.975	62.843	48.791	-2.756
2800	22.640	106.033	102.513	63.513	60.973	48.500	-3.232
2900	22.230	103.303	101.603	66.040	58.953	48.256	-3.697
3000	21.800	100.500	100.553	68.557	56.883	48.056	-4.151
3100	21.350	97.623	99.363	71.063	54.663	47.891	-4.594
3200	20.880	94.673	98.033	73.563	52.293	47.661	-5.026
3300	20.390	91.643	96.563	76.053	49.773	47.361	-5.447
3400	19.880	88.533	94.953	78.523	47.113	46.991	-5.856
3500	19.350	85.343	93.203	80.973	44.313	46.551	-6.254
3600	18.800	82.073	91.323	83.403	41.373	46.051	-6.641
3700	18.230	78.723	89.313	85.813	38.293	45.491	-7.016
3800	17.640	75.293	87.163	88.193	35.073	44.871	-7.379
3900	17.030	71.783	84.883	90.543	31.713	44.191	-7.730
4000	16.400	68.203	82.453	92.863	28.213	43.451	-8.069
4100	15.750	64.553	79.883	95.153	24.573	42.651	-8.397
4200	15.080	60.843	77.173	97.413	20.803	41.791	-8.714
4300	14.390	57.073	74.323	99.643	16.913	40.871	-9.019
4400	13.680	53.243	71.343	101.843	12.903	40.001	-9.312
4500	12.950	49.353	68.233	104.013	8.873	39.171	-9.594
4600	12.200	45.403	65.003	106.153	4.723	38.281	-9.865
4700	11.430	41.393	61.643	108.263	0.453	37.331	-10.126
4800	10.640	37.323	58.153	110.343	-3.923	36.331	-10.377
4900	9.830	33.193	54.533	112.393	-8.153	35.281	-10.618
5000	9.000	29.003	50.883	114.413	-12.343	34.181	-10.849
5100	8.150	24.743	47.193	116.403	-16.493	33.031	-11.070
5200	7.280	20.513	43.453	118.363	-20.603	31.831	-11.281
5300	6.390	16.313	39.663	120.293	-24.673	30.581	-11.482
5400	5.480	12.143	35.823	122.193	-28.703	29.281	-11.674
5500	4.550	8.003	31.933	124.063	-32.693	27.931	-11.857
5600	3.600	3.913	27.963	125.893	-36.643	26.531	-12.032
5700	2.630	-0.213	23.933	127.683	-40.553	25.081	-12.199
5800	1.640	-4.343	19.843	129.433	-44.423	23.581	-12.358
5900	0.630	-8.473	15.693	131.143	-48.253	22.031	-12.509
6000	-0.400	-12.603	11.483	132.813	-52.043	20.431	-12.652

March 31, 1963

Br₃PS

THIOPHOSPHORYL BROMIDE (PSBr₃)

MOL. WT. = 302.789

(IDEAL GAS)

Point Group C_{3v}
 $\Delta H_f^0 = [-57] \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = 89.084 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 \text{ 298.15} = [-63] \text{ kcal. mole}^{-1}$
 Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	
299 (1)	
438 (2)	
718 (1)	
115 (2)	
165 (1)	
179 (2)	

Bond Distance: P-Br = $2.13 \pm 0.03 \text{ \AA}$ P-S = $1.89 \pm 0.06 \text{ \AA}$
 Bond Angle: Br-P-Br = $106^\circ \pm 3^\circ$ $\sigma = 3$
 Product of the Moments of Inertia: $I_A I_B I_C = 1.8780 \times 10^{-111} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The $\Delta H_f^0 \text{ 298.15}$ of PSBr₃(g) was calculated from the $\Delta H_f^0 \text{ 298.15}$ of POBr₃(g) and estimated strengths for P-S and P-O bonds.

The difference in the P-S and P-O bond strengths was assumed to be the same for POBr₃ - PSF₃ and POBr₃ - PSBr₃. For the P-S bond strength in PSF₃, C. B. Henderson and R. S. Scheffer, "Survey of Thermochemical Data," January 1960, Atlantic Research Corp., Alexandria, Virginia, estimated 91 kcal., from a consideration of unpublished data. The P-O bond was estimated to be 115 kcal. by E. Neale and L. T. D. Williams, J. Chem. Soc. 2485 (1955) and E. Neale, L. T. D. Williams, and V. T. Moores, J. Chem. Soc., 422 (1956).

The $\Delta H_f^0 \text{ 298.15}$ of POBr₃(g), [-93] kcal. mole⁻¹, was taken from the March 31, 1963, JANAP Table. The $\Delta H_f^0 \text{ 298.15}$ of O(g) and S(g) were taken from June 30, 1952, and March 31, 1961, JANAP Tables.

Heat Capacity and Entropy.

The molecular constants were determined from electron diffraction data by J. H. Secriast and L. O. Brockway, J. Am. Chem. Soc. 66, 1941 (1944). The principal moments of inertia calculated from these constants were $I_A = 1.105941 \times 10^{-37} \text{ g. cm.}^2$, and $I_C = 1.535429 \times 10^{-37} \text{ g. cm.}^2$.

The vibrational frequencies obtained from the Raman spectra of PSBr₃ were reported by M. L. Delvaux and P. Francois, Compt. Rend. 224, 1422 (1947).

Br₃PS

(Crystal)

GFW = 287.627

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log K ^e
0	1.600	INFINITE		5.460	-127.050	-127.050	INFINITE
100	16.596	37.103	63.609	2.307	-127.517	-126.494	136.226
200	23.596	37.403	62.110	1.000	-127.517	-125.618	92.060
298	24.308	42.171	42.171		-131.500	-125.580	91.405
300	24.325	42.321	42.321	0.045	-131.516	-125.580	91.405
400	25.591	45.424	43.134	2.516	-142.022	-121.415	66.336
500	27.416	55.287	44.992	5.148	-141.361	-116.337	50.851
600	29.597	60.511	47.150	8.017	-140.490	-111.410	40.561
700	32.794	65.350	46.408	11.159	-139.373	-106.649	33.597
800	35.200	69.000	51.688	14.570	-136.017	-102.084	27.893
900	36.300	74.110	53.949	16.145	-136.585	-97.489	23.715
1000	37.446	77.995	56.162	21.633	-134.850	-91.659	20.115
1100	38.500	81.614	58.313	25.631	-133.294	-89.350	17.752
1200	39.463	85.006	60.397	29.530	-132.502	-85.392	15.552
1300	40.333	88.199	62.414	33.520	-130.583	-81.543	13.709
1400	41.113	91.217	64.365	37.594	-128.586	-77.586	12.152
1500	41.600	94.076	66.251	41.740	-126.539	-74.279	10.824

Dec. 31, 1961; June 30, 1964; June 30, 1968

TITANIUM TRIBROMIDE (TiBr₃)

(CRYSTAL)

GFW = 287.627

$\Delta H_f^\circ = -127.0 \pm 2.0$ kcal/mol
 $\Delta H_f^\circ = -127.050$
 $\Delta H_f^\circ = -131.5 \pm 2.0$ kcal/mol
 $\Delta H_f^\circ = 0$ kcal/mol
 $\Delta H_s^\circ = 33.165$ kcal/mol

$S_{298.15}^\circ = 42.2 \pm 0.8$ gibbs/mol

$T_t = 179.9^\circ\text{K}$

$T_s = 1067.2^\circ\text{K}$

Heat of Formation

The heat of formation of TiBr₃(c) is based on the vapor pressure data reported by Hall and Blocher (1) for the process 1/2Hg₂Br₂(c) + TiBr₃(c) = TiBr₄(g) + Hg(l) over the temperature range 430 to 546°K. Second and third law analyses of these data give values for the heat of reaction of 24.2 ± 0.3 and 24.4 kcal/mol, respectively, for seventy three points, with ten points rejected due to failure of a statistical test. The third law drift in the data is calculated as 0.6 ± 0.6 eu. The third law value of 24.4 kcal/mol is combined with the JANAF heats of formation of TiBr₄(g) and Hg₂Br₂(c) to obtain the adopted heat of formation.

Heat Capacity and Entropy

The heat capacity and entropy of TiBr₃(c) have been measured over the temperature range 51° to 800°K by King et al. (2). Heat capacities above 800°K are estimated from graphical extrapolation. The value of S_{298}° is derived from these data, based on $S_{51}^\circ = 8.60$ eu. The value of S_{51}° is estimated from a Debye-Einstein extrapolation of the measured heat capacities, the equation being $C_p = D(70.0/T) + E(120/T) + 2E(306/T)$. It is assumed that all electronic entropy is contained within the measured and extrapolated heat capacities.

Transition Data

A second order transition at 179.9°K was observed by King et al. (2). The heat capacity at this temperature is in excess of 56.1 gibbs/mol. King et al. measured the value of $H_{160}^\circ - H_{160}^\circ$ as 0.773 kcal/mol.

Heat of Sublimation

The heat of sublimation is calculated from the heats of formation of TiBr₃(c) and TiBr₃(g) at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta G_r = 0$ for the process TiBr₃(c) = TiBr₃(g).

References

1. E. H. Hall and J. M. Blocher, Jr., J. Electrochem. Soc. 105, 40 (1958).
2. E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI5799, 1961.

Titanium Tribromide (TiBr₃)

(Ideal Gas)

GFW = 287.627

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈ ^o)/T	H ₂₉₈ ^o - H ₂₉₈ ^o /T	kcal/mol ΔH _f ^o	ΔG ^o	Log K _p
0	1.000	INFINITE	4.331	83.991	83.991	INFINITE
100	13.163	48.146	3.713	84.788	83.219	7.046
200	17.526	61.160	1.778	84.788	83.219	10.845
298	18.561	65.777	1.000	89.600	86.719	17.897
300	18.585	65.695	0.935	89.625	86.742	17.891
400	19.462	61.493	1.983	100.655	96.875	52.930
500	20.271	55.974	3.992	100.617	95.936	41.934
600	20.962	50.689	6.030	100.577	95.004	34.605
700	20.547	42.851	9.136	100.551	94.078	29.372
800	20.579	35.597	12.925	100.549	93.154	25.448
900	20.567	28.021	16.470	100.573	92.227	22.396
1000	20.585	20.191	19.936	100.629	91.297	19.953
1100	20.579	12.152	27.322	100.712	90.360	17.953
1200	20.571	4.942	34.634	101.761	89.376	16.278
1300	20.562	1.589	41.987	101.776	88.343	14.852
1400	20.553	117.112	101.053	101.809	87.309	13.430
1500	20.544	118.530	102.171	101.861	86.273	12.370
1600	20.535	119.855	103.235	101.933	85.230	11.442
1700	20.526	121.100	104.250	102.028	84.183	10.622
1800	20.518	122.273	105.219	102.147	83.132	10.094
1900	20.509	123.382	106.146	102.291	82.070	9.440
2000	20.501	124.434	107.034	102.459	81.009	8.835
2100	20.494	125.434	107.887	102.649	79.941	8.278
2200	20.487	126.387	108.706	102.856	78.827	7.771
2300	20.480	127.298	109.495	103.046	77.692	7.307
2400	20.474	128.169	110.255	103.212	76.569	6.882
2500	20.468	128.995	110.989	103.361	75.477	6.489
2600	20.463	129.780	111.697	103.497	74.421	6.127
2700	20.458	130.520	112.382	103.612	73.400	5.790
2800	20.453	131.224	113.045	103.707	72.413	5.477
2900	20.449	131.891	113.688	103.784	71.460	5.185
3000	20.445	132.525	114.312	103.843	70.541	4.912
3100	20.441	133.125	114.917	103.892	69.659	4.656
3200	20.437	133.694	115.505	103.927	68.809	4.416
3300	20.433	134.233	116.076	103.950	67.994	4.190
3400	20.429	134.743	116.633	103.961	67.213	3.977
3500	20.425	135.225	117.174	103.961	66.472	3.776
3600	20.421	135.680	117.702	103.952	65.768	3.570
3700	20.417	136.110	118.217	103.931	65.099	3.372
3800	20.413	136.564	118.719	103.898	64.465	3.183
3900	20.409	136.994	119.209	103.853	63.863	2.999
4000	20.405	137.411	119.687	103.800	63.294	2.823
4100	20.401	137.815	120.155	103.739	62.764	2.650
4200	20.397	138.206	120.612	103.668	62.278	2.480
4300	20.392	138.586	121.060	103.588	61.824	2.322
4400	20.388	138.955	121.497	103.498	61.401	2.175
4500	20.383	139.313	121.926	103.398	61.009	2.030
4600	20.379	139.661	122.346	103.288	60.646	1.890
4700	20.374	140.000	122.757	103.168	60.312	1.750
4800	20.370	140.328	123.160	103.038	60.009	1.610
4900	20.365	140.648	123.556	102.900	59.734	1.470
5000	20.360	140.961	123.944	102.756	59.487	1.330
5100	20.355	141.268	124.325	102.608	59.264	1.190
5200	20.350	141.568	124.698	102.456	59.064	1.050
5300	20.346	141.864	125.065	102.300	58.887	0.910
5400	20.341	142.156	125.426	102.140	58.734	0.770
5500	20.336	142.444	125.782	101.976	58.594	0.630
5600	20.331	142.728	126.134	101.808	58.466	0.490
5700	20.326	143.008	126.482	101.636	58.350	0.350
5800	20.321	143.284	126.826	101.460	58.246	0.210
5900	20.316	143.556	127.156	101.280	58.152	0.070
6000	20.311	143.824	127.482	101.096	58.068	-0.070

June 30, 1964; June 30, 1968

Br₃TiTITANIUM TRIBROMIDE (TiBr₃)

(IDEAL GAS)

GFW = 287.627

Point Group C_{3v}ΔH_f^o = -84.0 ± 2.5 kcal/molS_{298.15}^o = (85.8 ± 1.2) gibbs/molΔH_f^o = -89.6 ± 2.5 kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights			
ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	[2]	[4000]	[2]
[600]	[2]	[10000]	[2]
[1500]	[2]		

Vibrational Frequencies and Degeneracies			
ω_i , cm ⁻¹	ω_i , cm ⁻¹	ω_i , cm ⁻¹	
[360] (1)	[427] (2)		
[162] (1)	[103] (2)		

Bond Distance: Ti-Br = [2.4] Å

Bond Angle: Br-Ti-Br = [100]°

Product of the Moments of Inertia: I_AI_BI_C = 11.70 × 10⁻¹¹ g³ cm⁶

σ = 3

Heat of Formation

The heat of formation of TiBr₃(g) is calculated from the heat of sublimation of TiBr₃(c). A tentative equation for the vapor pressure of TiBr₃(c) was reported by Hall and Blocher (1). Second and third law analyses of the equation over the temperature range 700° to 900°K give values of ΔH_f^o of 45.2 and 41.9 kcal/mol, respectively, with a third law drift of -4.2 eu. The chosen value of ΔH_f^o is based on the third law ΔH_f^o298.

Heat Capacity and Entropy

The interatomic distance is estimated from those of TiCl₄, TiCl₃ and TiBr₄. The pyramidal bond angle is estimated by assuming that TiBr₃(g) is similar to the group V trihalides. The principal moments of inertia are I_A = 9.76 × 10⁻³⁶ g cm² and I_C = 1.78 cm². The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti³⁺ (2).

References

1. E. H. Hall and J. M. Blocher, J. Phys. Chem. **53**, 1525 (1959).
2. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Br₃Ti

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	II ^o -II ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	INFINITE	5.347	-147.242	-147.242	-147.242	INFINITE	INFINITE
100	17.787	17.852	61.092	-4.324	-147.433	-146.950	321.144	321.144
200	22.283	31.007	43.257	-2.270	-147.658	-146.380	159.940	159.940
298	23.777	41.122	0.000	-152.000	-145.213	-145.213	106.430	106.430
300	23.796	41.260	41.122	-0.044	-152.016	-145.170	106.751	106.751
400	24.500	44.220	12.474	-12.514	-145.110	-145.110	106.477	106.477
500	24.800	53.733	43.868	4.932	-162.110	-135.273	59.125	59.125
600	25.000	58.274	45.002	7.423	-161.664	-129.066	47.331	47.331
700	25.100	62.136	47.952	9.920	-161.222	-124.606	38.030	38.030
800	25.150	65.435	50.839	12.448	-160.759	-119.508	29.546	29.546
900	25.200	68.465	53.635	14.969	-160.276	-114.150	21.825	21.825
1000	25.350	71.137	53.635	17.502	-159.027	-109.285	23.883	23.883
1100	25.370	73.554	55.338	20.038	-159.514	-104.242	20.710	20.710
1200	25.390	75.763	56.949	22.576	-160.069	-99.187	18.064	18.064
1300	25.420	77.670	58.426	25.114	-160.560	-94.150	15.254	15.254
1400	25.430	79.379	59.782	27.648	-161.000	-89.135	12.254	12.254
1500	25.430	81.634	61.300	30.200	-161.487	-84.109	10.809	10.809
1600	25.440	83.075	62.610	32.744	-161.982	-79.135	9.537	9.537
1700	25.450	84.618	63.860	35.288	-162.482	-74.188	8.409	8.409
1800	25.460	85.943	65.057	37.832	-162.982	-69.263	7.409	7.409
1900	25.470	87.443	66.197	40.376	-163.482	-64.373	6.499	6.499
2000	25.480	88.756	67.292	42.928	-163.982	-59.473	5.649	5.649

Mar. 31, 1962; June 30, 1964

ZIRCONIUM TRIBROMIDE (ZrBr₃)

(CRYSTAL)

MOL. WT. = 330.968

$\Delta F_f^o = [-147] \text{ kcal. mole}^{-1}$
 $\Delta F_f^o \text{ 298.15} = [-152] \text{ kcal. mole}^{-1}$
 $\Delta F_g^o \text{ 298.15} = [49] \text{ kcal. mole}^{-1}$

$S^o \text{ 298.15} = [41.12] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$
 $T_g = [1100]^{\circ}\text{K.}$

Heat of Formation.

E. M. Larsen and J. J. Leddy, J. Am. Chem. Soc. 78, 5983 (1956), studied the reaction $\text{Zr(c)} + 3\text{ZrBr}_4(\text{g}) = 4\text{ZrBr}_3(\text{c})$ in the temperature range 473 to 973°K. and pressure range 5 to 15 atm. They present a plot of the fractional reaction, for a series of temperatures, as a function of the reaction time; however, they express doubt concerning the attainment of thermodynamic equilibrium.

The free energy function change for this reaction was calculated at 100° intervals from 500 to 1100°K. At each temperature, the equilibrium constant was assumed to be 1, and ΔF_f^o 298 accordingly calculated. These values and the heat of formation of $\text{ZrBr}_4(\text{g})$ [see ZrBr₄ table] were used to compute a series of values for the standard heat of formation of $\text{ZrBr}_3(\text{c})$. The following table gives representative values at four temperatures.

T(°K.)	K _p	ΔF _f ^o 298	ΔF _f ^o 298.15 [ZrBr ₃ (c)]
500	1	-70.26 kcal. mole ⁻¹	-132.8 kcal. mole ⁻¹
700	1	-96.48 kcal. mole ⁻¹	-139.3 kcal. mole ⁻¹
900	1	-121.75 kcal. mole ⁻¹	-145.6 kcal. mole ⁻¹
1100	1	-146.28 kcal. mole ⁻¹	-151.8 kcal. mole ⁻¹

If one assumes an initial pressure of from 5 to 10 atm. for ZrBr_4 and stoichiometric amounts of reactants, then, on the basis of zirconium, the reaction must proceed to the extent of 80 to 90% for the pressure of ZrBr_4 to attain a value of 1 atm. and hence an equilibrium constant of 1. The data of Larsen and Leddy indicate about 82% reaction at 973°K. It was assumed that around 1100°K. the equilibrium constant attains a value of 1 giving -152 kcal. mole⁻¹ for the heat of formation of $\text{ZrBr}_3(\text{c})$ at 298.15°K. The limits of error were taken to be ±16 kcal. mole⁻¹ which corresponds to a ±500° temperature spread in the above table.

A second law calculation of their data was carried out but the results are of doubtful value in view of the uncertainty in the attainment of equilibrium at the lower temperatures.

Heat Capacity and Entropy.

The heat capacity was estimated in the same manner as for $\text{ZrBr}_4(\text{c})$ [see ZrBr₄(c) table]. The values for Q_p and Q_g were taken to be the same as those estimated for $\text{ZrBr}_4(\text{c})$. The internal contribution was obtained from the estimated ZrBr_3 vibrational frequencies and the anharmonicity factor " θ " was taken to be 2.5×10^{-3} . The specific heat above 300°K. was obtained by graphical extrapolation.

It was assumed, in the above estimation, that the crystalline lattice is made up of ZrBr_3 molecules. However, E. Holze [see R. P. Rolsten, "Iodide Metals and Metal Iodides", John Wiley & Sons, Inc., New York, 1961, page 46] concluded that crystalline ZrI_3 was composed of a chain lattice of $(\text{Zr}_2\text{I}_6)_n$ units. A chain lattice of $(\text{Zr}_2\text{Br}_6)_n$ units is probably a better representation of the solid state structure of ZrBr_3 . Until more quantitative data become available, however, it is felt that the above analysis gives a fair approximation to the heat capacity of ZrBr_3 .

Temperature of Disproportionation.

As detailed in the "Heat of Formation" section, this was assumed to be 1100 ± 500°K.

Liquid Phase.

It is assumed that the liquid phase is thermodynamically unstable under ordinary conditions.

Sublimation Data.

The heat of sublimation at 298.15°K. was obtained from the difference in the heats of formation of the gas and solid at 298.15°K. The sublimation point was obtained from the free energy crossover between gas and solid.

Mar. 31, 1962; June 30, 1964



Zirconium Tribromide (ZrBr₃)

(Ideal Gas) Mol. Wt. = 330.968

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞.000	INFINITE	4.613	- 97.508	- 97.508	INFINITE
100	14.892	69.838	4.618	- 97.616	- 97.616	223.637
200	18.063	81.371	4.626	- 98.214	- 98.214	116.732
298	18.968	86.787	4.635	- 103.400	- 110.424	80.939
300	18.998	88.905	4.635	- 103.425	- 110.469	80.473
400	19.365	94.427	4.638	- 114.100	- 110.681	60.470
500	19.543	98.770	4.642	- 114.149	- 109.821	48.001
600	19.642	102.342	4.647	- 114.225	- 108.949	39.489
700	19.702	105.375	4.652	- 114.322	- 108.063	33.737
800	19.742	108.009	4.657	- 114.432	- 107.162	29.274
900	19.769	110.336	4.662	- 114.548	- 106.245	25.799
1000	19.789	112.420	4.665	- 114.674	- 105.314	23.015
1100	19.803	114.296	4.667	- 114.816	- 104.378	20.736
1200	19.812	115.916	4.669	- 114.968	- 103.435	18.200
1300	19.818	117.316	4.670	- 115.129	- 102.487	15.805
1400	19.823	118.544	4.671	- 115.296	- 101.535	13.595
1500	19.825	119.644	4.672	- 115.468	- 100.578	11.540
1600	19.826	120.644	4.673	- 115.644	- 99.616	9.529
1700	19.827	121.574	4.674	- 115.824	- 98.649	7.554
1800	19.828	122.464	4.675	- 116.008	- 97.677	5.619
1900	19.829	123.324	4.676	- 116.196	- 96.700	3.729
2000	19.830	124.164	4.677	- 116.388	- 95.718	1.889
2100	19.831	124.984	4.678	- 116.584	- 94.731	0.104
2200	19.832	125.784	4.679	- 116.784	- 93.739	10.340
2300	19.833	126.564	4.680	- 116.988	- 92.742	8.729
2400	19.834	127.324	4.681	- 117.196	- 91.740	7.173
2500	19.835	128.064	4.682	- 117.408	- 90.733	5.673
2600	19.836	128.784	4.683	- 117.624	- 89.721	4.229
2700	19.837	129.484	4.684	- 117.844	- 88.704	2.849
2800	19.838	130.164	4.685	- 118.068	- 87.682	1.529
2900	19.839	130.824	4.686	- 118.296	- 86.655	0.269
3000	19.840	131.464	4.687	- 118.528	- 85.623	5.589
3100	19.841	132.084	4.688	- 118.764	- 84.586	4.959
3200	19.842	132.684	4.689	- 119.004	- 83.544	4.329
3300	19.843	133.264	4.690	- 119.248	- 82.497	3.699
3400	19.844	133.824	4.691	- 119.496	- 81.445	3.069
3500	19.845	134.364	4.692	- 119.748	- 80.388	2.439
3600	19.846	134.884	4.693	- 120.004	- 79.326	1.809
3700	19.847	135.384	4.694	- 120.264	- 78.259	1.179
3800	19.848	135.864	4.695	- 120.528	- 77.187	0.549
3900	19.849	136.324	4.696	- 120.796	- 76.110	0.000
4000	19.850	136.764	4.697	- 121.068	- 75.028	5.589
4100	19.851	137.184	4.698	- 121.344	- 73.941	4.959
4200	19.852	137.584	4.699	- 121.624	- 72.849	4.329
4300	19.853	137.964	4.700	- 121.908	- 71.752	3.699
4400	19.854	138.324	4.701	- 122.196	- 70.650	3.069
4500	19.855	138.664	4.702	- 122.488	- 69.543	2.439
4600	19.856	139.004	4.703	- 122.784	- 68.431	1.809
4700	19.857	139.324	4.704	- 123.084	- 67.314	1.179
4800	19.858	139.624	4.705	- 123.388	- 66.192	0.549
4900	19.859	139.904	4.706	- 123.696	- 65.065	0.000
5000	19.860	140.164	4.707	- 124.008	- 63.933	5.589
5100	19.861	140.404	4.708	- 124.324	- 62.796	4.959
5200	19.862	140.624	4.709	- 124.644	- 61.654	4.329
5300	19.863	140.824	4.710	- 124.968	- 60.507	3.699
5400	19.864	141.004	4.711	- 125.296	- 59.355	3.069
5500	19.865	141.164	4.712	- 125.628	- 58.198	2.439
5600	19.866	141.304	4.713	- 125.964	- 57.036	1.809
5700	19.867	141.424	4.714	- 126.304	- 55.869	1.179
5800	19.868	141.524	4.715	- 126.648	- 54.697	0.549
5900	19.869	141.604	4.716	- 126.996	- 53.520	0.000
6000	19.870	141.664	4.717	- 127.348	- 52.338	5.589
6100	19.871	141.704	4.718	- 127.704	- 51.151	4.959
6200	19.872	141.724	4.719	- 128.064	- 49.959	4.329
6300	19.873	141.724	4.720	- 128.428	- 48.762	3.699
6400	19.874	141.704	4.721	- 128.796	- 47.560	3.069
6500	19.875	141.664	4.722	- 129.168	- 46.353	2.439
6600	19.876	141.604	4.723	- 129.544	- 45.141	1.809
6700	19.877	141.524	4.724	- 129.924	- 43.924	1.179
6800	19.878	141.424	4.725	- 130.308	- 42.702	0.549
6900	19.879	141.304	4.726	- 130.696	- 41.475	0.000
7000	19.880	141.164	4.727	- 131.088	- 40.242	5.589
7100	19.881	141.004	4.728	- 131.484	- 39.004	4.959
7200	19.882	140.824	4.729	- 131.884	- 37.761	4.329
7300	19.883	140.624	4.730	- 132.288	- 36.514	3.699
7400	19.884	140.404	4.731	- 132.696	- 35.262	3.069
7500	19.885	140.164	4.732	- 133.108	- 34.005	2.439
7600	19.886	139.904	4.733	- 133.524	- 32.742	1.809
7700	19.887	139.624	4.734	- 133.944	- 31.475	1.179
7800	19.888	139.324	4.735	- 134.368	- 30.202	0.549
7900	19.889	139.004	4.736	- 134.796	- 28.925	0.000
8000	19.890	138.664	4.737	- 135.228	- 27.642	5.589
8100	19.891	138.304	4.738	- 135.664	- 26.355	4.959
8200	19.892	137.924	4.739	- 136.104	- 25.062	4.329
8300	19.893	137.524	4.740	- 136.548	- 23.765	3.699
8400	19.894	137.104	4.741	- 136.996	- 22.462	3.069
8500	19.895	136.664	4.742	- 137.448	- 21.155	2.439
8600	19.896	136.204	4.743	- 137.904	- 19.842	1.809
8700	19.897	135.724	4.744	- 138.364	- 18.525	1.179
8800	19.898	135.224	4.745	- 138.828	- 17.202	0.549
8900	19.899	134.704	4.746	- 139.296	- 15.875	0.000
9000	19.900	134.164	4.747	- 139.768	- 14.542	5.589
9100	19.901	133.604	4.748	- 140.244	- 13.205	4.959
9200	19.902	133.024	4.749	- 140.724	- 11.862	4.329
9300	19.903	132.424	4.750	- 141.208	- 10.515	3.699
9400	19.904	131.804	4.751	- 141.696	- 9.162	3.069
9500	19.905	131.164	4.752	- 142.188	- 7.805	2.439
9600	19.906	130.504	4.753	- 142.684	- 6.442	1.809
9700	19.907	129.824	4.754	- 143.184	- 5.075	1.179
9800	19.908	129.124	4.755	- 143.688	- 3.702	0.549
9900	19.909	128.404	4.756	- 144.196	- 2.325	0.000
10000	19.910	127.664	4.757	- 144.708	- 0.942	5.589

ZIRCONIUM TRIBROMIDE (ZrBr₃) (IDEAL GAS) MOL. WT. = 330.968

Point Group = [C_{3v}]

S_{298.15}° = [88.75] cal. mole⁻¹ deg.⁻¹

Ground State Quantum Weight = [2]

ΔH_f° 0 = [-98] kcal. mole⁻¹

ΔH_f° 298.15 = [-103] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	(255) (1)	(120) (1)	(273) (2)	(95) (2)
----------------------	-----------	-----------	-----------	----------

Bond Distances: Zr-Br = [2.39] Å

Bond Angle: Br-Zr-Br = [98°]

Product of the Moments of Inertia: I_AI_BI_C = [1.757 X 10⁻¹¹¹] gm.³ cm.⁶

G° = [3]

Heat of Formation

The heats of formation, from the gaseous atoms, of the gaseous zirconium tetrahalides were computed from data issued in these tables. The zirconium-halide bond energy, taken as 1/4 of this heat of formation, was found to be linear with internuclear separation. From gaseous titanium tri- and tetrachloride, it was found that the bond energy of the trichloride was around 7 kcal. mole⁻¹ greater than that for titanium tetrachloride. This amount was added to the bond energy of zirconium tetrachloride to get that of zirconium trichloride which, when used with its estimated internuclear distance, was found to lie almost exactly on the bond energy versus internuclear distance curve for the tetrahalides. The bond energy for each of the gaseous trihalides of zirconium was determined from this curve and their estimated bond distances.

For zirconium tribromide, the heat of formation from the gaseous atoms was -329 kcal. mole⁻¹ and from the elements in their standard state, -103 kcal. mole⁻¹.

Heat Capacity and Entropy

The measured internuclear distances for the tribromides of P, As, and Sb were plotted as a function of the atomic weight of these atoms and a smooth curve was drawn through the points. The internuclear distance for ZrBr₃ was taken from this plot. The bond angle was assumed to be intermediate between the bond angles of AsBr₃ and SbBr₃; it was taken to be 98°. The individual moments of inertia are I_A = I_B = 101.408 X 10⁻³⁹ gm. cm.², I_C = 172.669 gm. cm.².

The measured vibrational frequencies for the tribromides of phosphorus, arsenic, and antimony were plotted as a function of internuclear distance. Smooth curves through these points were obtained for ω₁, ω₂, and ω₄; these curves and the estimated ZrBr₃ bond distance were used to obtain correlation values of ω₁, ω₂, and ω₄ for ZrBr₃. Force constants, assuming a valence force field and a Br-Zr-Br angle of 98°, were derived from the above values for ω₁ and ω₂. These force constants were then used to derive values for ω₃ and ω₄. By a process of successive approximation, a set of force constants was obtained which gave frequencies in good agreement with the three correlation values. The three correlation frequencies and the derived frequency were used in this table.



T, °K	C _p ^o	S ^o	-(G ^o -H ^o ₂₉₈)/T	ΔH ^o	ΔG ^o	Log K _p
0	0.000	INFINITE	INFINITE	- 7.937	- 54.569	INFINITE
100	27.616	90.000	150.521	- 54.569	- 60.540	12.978
200	31.236	110.967	123.304	- 54.569	- 60.500	12.538
298	31.236	123.304	123.304	0.000	- 60.500	12.538
300	31.240	123.497	123.304	0.058	- 60.530	12.524
400	31.479	132.522	124.533	3.195	- 75.125	12.481
500	31.593	139.560	126.860	6.350	- 75.086	11.902
600	31.659	145.326	129.472	9.512	- 75.160	11.170
700	31.709	150.210	132.084	12.681	- 75.355	10.208
800	31.759	154.447	134.630	15.854	- 75.710	9.062
900	31.817	158.191	137.063	19.033	- 76.279	7.756
1000	31.886	161.547	139.329	22.218	- 77.208	6.4894
1100	31.970	164.590	141.489	25.411	- 78.569	5.345
1200	32.063	167.376	143.532	28.612	- 79.500	4.2093
1300	32.164	169.946	145.466	31.824	- 79.744	3.6471
1400	32.270	172.333	147.301	35.045	- 80.013	3.1963
1500	32.377	174.563	149.045	38.278	- 80.302	2.8284
1600	32.482	176.656	150.706	41.521	- 80.615	2.5173
1700	32.584	178.629	152.291	44.774	- 81.532	2.2466
1800	32.681	180.494	153.807	48.037	- 82.073	2.0122
1900	32.770	182.263	155.256	51.310	- 82.778	1.8003
2000	32.859	183.946	156.651	54.591	- 83.637	1.6074
2100	32.942	185.551	157.989	57.880	- 84.618	1.4301
2200	32.985	187.084	159.277	61.175	- 85.710	1.2669
2300	33.039	188.551	160.518	64.476	- 86.930	1.1169
2400	33.094	189.964	161.716	67.791	- 88.280	1.0000
2500	33.121	191.310	162.873	71.093	- 89.763	0.9000
2600	33.149	192.609	163.991	74.407	- 91.289	0.8147
2700	33.171	193.861	165.075	77.723	- 92.866	0.7447
2800	33.185	195.068	166.124	81.041	- 94.494	0.6887
2900	33.197	196.236	167.142	84.361	- 96.173	0.6447
3000	33.207	197.368	168.131	87.679	- 97.899	0.6107
3100	33.216	198.446	169.092	90.999	- 99.627	0.5847
3200	33.219	199.500	170.026	94.318	- 101.357	0.5647
3300	33.218	200.521	170.934	97.637	- 103.087	0.5497
3400	33.215	201.511	171.814	100.956	- 104.817	0.5397
3500	33.212	202.473	172.681	104.276	- 106.546	0.5337
3600	33.213	203.406	173.522	107.584	- 108.274	0.5307
3700	33.215	204.314	174.342	110.897	- 110.004	0.5297
3800	33.209	205.197	175.142	114.207	- 111.734	0.5297
3900	33.204	206.056	175.916	117.517	- 113.464	0.5297
4000	33.204	206.893	176.668	120.822	- 115.194	0.5297
4100	33.204	207.704	177.434	124.125	- 116.924	0.5297
4200	33.200	208.504	178.165	127.426	- 118.654	0.5297
4300	33.195	209.291	178.879	130.725	- 120.384	0.5297
4400	33.189	210.064	179.574	134.024	- 122.114	0.5297
4500	32.924	210.779	180.244	137.315	- 123.844	0.5297
4600	32.899	211.502	180.895	140.606	- 125.574	0.5297
4700	32.874	212.204	181.503	143.895	- 127.304	0.5297
4800	32.849	212.901	182.074	147.181	- 129.034	0.5297
4900	32.824	213.594	182.611	150.466	- 130.764	0.5297
5000	32.801	214.241	183.192	153.746	- 132.494	0.5297
5100	32.777	214.890	183.711	157.025	- 134.224	0.5297
5200	32.753	215.527	184.269	160.304	- 135.954	0.5297
5300	32.730	216.150	184.767	163.576	- 137.684	0.5297
5400	32.706	216.764	185.214	166.849	- 139.414	0.5297
5500	32.686	217.369	185.641	170.117	- 141.144	0.5297
5600	32.665	217.951	186.049	173.389	- 142.874	0.5297
5700	32.644	218.529	186.537	176.650	- 144.604	0.5297
5800	32.623	219.096	187.007	179.914	- 146.334	0.5297
5900	32.602	219.654	187.454	183.175	- 148.064	0.5297
6000	32.584	220.201	187.884	186.436	- 149.794	0.5297

Sept. 30, 1966

IRON DIBROMIDE, DIMERIC (Fe₂Br₄)
(IDEAL GAS)
GFW = 431.330
Point Group [D_{2h}]
S_{298.15} = [123.3] gibbs/mol
ΔH₀^o = [-54.6 ± 2] kcal/mol
ΔH_{298.15}^o = [-60.5 ± 2] kcal/mol

Electronic Levels and Quantum Weights

ε ₁ , cm ⁻¹	g ₁
0	[5]
[4450]	[5]
[6900]	[5]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
[110] (1)	[75] (1)	[95] (2)
[70] (1)	[100] (1)	[24] (2)
[110] (1)	[115] (1)	[190] (2)

Bond Distance: Fe-Br = [2.24] Å

Bond Angles: Fe-Br₂-bridge - Fe = [90]^o Br₂-bridge - Fe-Br₂-bridge = [90]^o

Br-Fe-Br₂-bridge = [135]^o σ = [4]

Product of the Moments of Inertia: I_AI_BI_C = [1.4498 x 10⁻¹¹⁰] g³ cm⁶

Heat of Formation

The chemical equilibria, 622-665°K, for the reaction Fe₂Br₄(g) = 2 FeBr₂(g) were studied by R. P. Porter and R. C. Schoonmaker, J. Phys. Chem. 63, 626 (1959), using a mass spectrometer. Based on the reported partial pressures for the two species, the enthalpy change (ΔH_{298.15}^o) for the reaction was evaluated by both the second and third law methods to be 40.36 ± 2.0 and 40.75 ± 0.2 kcal/mol, respectively. Using the third law ΔH^o value and ΔH_{298.15}^o (FeBr₂,g) = -9.9 ± 0.5 kcal/mol, the heat of formation (ΔH_{298.15}^o) for Fe₂Br₄(g) was calculated as -60.5 ± 2.0 kcal/mol and was adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be planar. The two Fe atoms are at the two opposite corners of a square. The other two corners of the square are occupied by two Br atoms. The two remaining Br atoms are situated outside the square on a straight line joining the two Fe atoms. The Fe-Br bond distance was estimated to be the same as that in the FeBr₂(g) molecule. The first six vibrational frequencies were estimated by comparison with those for FeBr₂(g) calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960). The last three degenerate frequencies were assigned arbitrarily in order to give good second and third law agreement for the heats of dissociation of dimer to monomer. The order of the frequencies listed above is arbitrary and not related to their species types.

The electronic levels and quantum weights were estimated by comparison with those for FeBr₂(g). The three principal moments of inertia are: I_A = 6.6576 x 10⁻³⁸, I_B = 4.3456 x 10⁻³⁷ and I_C = 5.0113 x 10⁻³⁷ g cm².

Lead Tetrabromide (PbBr₄)

(Ideal Gas) Mol. Wt. = 526.87

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞
100	20.684	76.241	-4.699	-36.827	-36.827	INFINITE
200	25.109	91.924	-10.516	-41.267	-41.267	90.184
298	25.008	101.750	-0.000	-45.192	-45.192	49.381
300	25.018	101.905	0.046	-45.000	-45.000	35.201
400	25.365	109.156	10.737	-48.048	-48.048	35.002
500	25.530	114.836	10.409	-46.341	-46.341	18.940
600	25.622	119.500	10.614	-44.032	-44.032	14.679
700	25.671	123.577	10.877	-41.267	-41.267	10.258
800	25.714	126.885	11.187	-38.891	-38.891	7.453
900	25.739	129.415	11.527	-36.695	-36.695	6.011
1000	25.757	132.028	11.874	-34.750	-34.750	4.033
1100	25.771	134.684	12.230	-32.426	-32.426	2.522
1200	25.781	137.377	12.597	-29.872	-29.872	1.164
1300	25.789	139.991	12.972	-27.139	-27.139	0.272
1400	25.795	142.532	13.352	-24.328	-24.328	0.000
1500	25.800	145.002	13.735	-21.485	-21.485	2.314
1600	25.804	147.412	14.121	-18.617	-18.617	4.033
1700	25.808	149.767	14.512	-15.736	-15.736	5.278
1800	25.811	152.067	14.907	-12.846	-12.846	6.030
1900	25.813	154.312	15.307	-9.950	-9.950	6.284
2000	25.815	156.506	15.712	-7.052	-7.052	6.516
2100	25.817	158.650	16.122	-4.152	-4.152	6.729
2200	25.818	160.754	16.537	-1.250	-1.250	6.925
2300	25.820	162.818	16.957	1.652	1.652	7.107
2400	25.821	164.842	17.382	4.552	4.552	7.274
2500	25.822	166.826	17.812	7.452	7.452	7.430
2600	25.823	168.770	18.247	10.352	10.352	7.576
2700	25.824	170.684	18.687	13.252	13.252	7.712
2800	25.825	172.568	19.132	16.152	16.152	7.840
2900	25.826	174.422	19.582	19.052	19.052	7.960
3000	25.826	176.246	20.037	21.952	21.952	8.072
3100	25.826	178.040	20.497	24.852	24.852	8.177
3200	25.827	179.804	20.962	27.752	27.752	8.277
3300	25.828	181.538	21.432	30.652	30.652	8.372
3400	25.828	183.242	21.907	33.552	33.552	8.462
3500	25.828	184.916	22.387	36.452	36.452	8.547
3600	25.829	186.560	22.872	39.352	39.352	8.627
3700	25.829	188.184	23.362	42.252	42.252	8.702
3800	25.829	189.788	23.857	45.152	45.152	8.772
3900	25.829	191.372	24.357	48.052	48.052	8.837
4000	25.830	192.936	24.862	50.952	50.952	8.897
4100	25.830	194.480	25.372	53.852	53.852	8.952
4200	25.830	196.004	25.887	56.752	56.752	9.002
4300	25.830	197.508	26.407	59.652	59.652	9.047
4400	25.831	198.992	26.932	62.552	62.552	9.087
4500	25.831	200.456	27.462	65.452	65.452	9.122
4600	25.831	201.900	27.997	68.352	68.352	9.152
4700	25.831	203.324	28.537	71.252	71.252	9.177
4800	25.831	204.728	29.082	74.152	74.152	9.202
4900	25.831	206.112	29.632	77.052	77.052	9.222
5000	25.831	207.476	30.187	79.952	79.952	9.242
5100	25.832	208.820	30.747	82.852	82.852	9.262
5200	25.832	210.144	31.312	85.752	85.752	9.282
5300	25.832	211.448	31.882	88.652	88.652	9.302
5400	25.832	212.732	32.457	91.552	91.552	9.322
5500	25.832	214.006	33.037	94.452	94.452	9.342
5600	25.832	215.260	33.622	97.352	97.352	9.362
5700	25.832	216.494	34.212	100.252	100.252	9.382
5800	25.832	217.708	34.807	103.152	103.152	9.402
5900	25.832	218.902	35.407	106.052	106.052	9.422
6000	25.832	220.076	36.012	108.952	108.952	9.442

Lead Tetrabromide (PbBr₄)

(Ideal Gas)

Mol. Wt. = 526.87

ΔH_f° 298.15 = [-44] kcal. mole⁻¹S° 298.15 = 101.8 cal. deg.⁻¹ mole⁻¹Point group T_d

Vibrational Levels and Multiplicities

ω, cm.⁻¹

207 (1)

59 (2)

231 (3)

73 (3)

Pb-Br distance = 2.54 Å

Br-Pb-Br angle = 109° 28'

I_A¹_B¹_C = 1.1920 X 10⁻¹¹⁰ g.³ cm.⁶

σ = 12

Heat of Formation. ΔH_f° 298.15 was estimated by comparison with the value of ΔH_f° 298.15 for PbBr₂(g).

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagarsen, Bull. Soc. Chim. Belg., 71, 119 (1962).

Titanium Tetrabromide (TiBr₄)
(Crystal)

GFW = 367.536

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	22.490	28.901	83.641	5.474	-141.655	-141.655	INFINITE
200	26.059	46.402	60.992	2.918	-141.774	-141.893	310.107
298	31.430	58.227	58.227	0.000	-142.018	-141.925	195.089
300	31.505	58.422	58.422	-0.058	-142.018	-141.139	103.488
400	31.974	67.612	59.795	1.255	-141.622	-136.030	102.820
500	31.974	74.746	61.845	6.450	-160.837	-129.749	56.713
600	31.974	80.566	64.496	9.848	-160.081	-123.603	45.072
700	31.974	85.700	66.721	14.603	-158.460	-111.462	30.505
800	31.974	90.724	69.721	19.240	-157.995	-105.827	25.698
900	31.974	93.540	72.152	22.437	-157.362	-100.064	21.869
1000	31.974	94.909	74.472	25.435	-156.757	-94.363	18.748
1100	31.974	95.956	76.652	28.330	-156.144	-88.755	15.954
1200	31.974	96.728	77.728	31.030	-155.528	-83.002	13.079
1300	31.974	97.268	78.640	33.227	-154.914	-77.379	12.079
1400	31.974	97.667	82.505	35.227	-154.300	-71.801	10.461
1500	31.974	97.873	84.257	36.424	-153.686	-66.273	9.461

Dec. 31, 1961; June 30, 1964; June 30, 1968

TITANIUM TETRABROMIDE (TiBr₄)

(CRYSTAL)

GFW = 367.536

ΔHf° = -141.7 ± 1.1 kcal/mol
ΔHf°_{298.15} = -147.7 ± 1.0 kcal/mol
ΔHm° = 3.08 kcal/mol

S°_{298.15} = 56.2 ± 1.6 kcal/mol
Tm = 311.4°K

Heat of Formation

The heat of formation, ΔHf°₂₉₈, of TiBr₄(c) has been determined calorimetrically by several investigators as follows.

Investigators	Reaction	ΔHf° _{298.15} kcal/mol
Nelson, Johnson and Prosen (1)	Ti(c) + 2Br ₂ (g) = TiBr ₄ (c)	-147.3 ± 1.1
Johnson, Gilliland and Prosen (2)	TiCl ₄ (l) + 2Br ₂ (l) = TiBr ₄ (c) + 2Cl ₂ (g)	-147.6 ± 1.3
Schlafer and Schmidtke (3)	Ti(c) + 2Br ₂ (l) = TiBr ₄ (c)	-147.7 ± 0.3
Gross, Hayman and Levi (4)	Ti(c) + 2Br ₂ (l) = TiBr ₄ (c)	-146.1 ± 0.3

The chosen value of ΔHf°₂₉₈ is the average of these determinations. The value from the work of Nelson et al. (1) is obtained from their heat of reaction and the JANAF value for the heat of vaporization of bromine. The value obtained from Johnson et al. (2) is a combination of their heat of reaction and the JANAF value for the heat of formation of TiCl₄(l).

Heat Capacity and Entropy

The heat capacity of TiBr₄(c) has been measured over the temperature range 51° to 298°K by King et al. (5). They reported a value of 42.74 eu for S°₂₉₈ - S°₅₁ based on their measurements. The value of S°₅₁ is estimated as 15.46 eu. King et al. (5) reported an estimate of 14.75 ± 1.60 for the same quantity. The former estimate is used so that the values of ΔHf°₂₉₈ obtained by both second and third law methods are in agreement. See TiBr₄(g) table for details. The value of H°₅₁ - H°₀ is estimated as 0.372 kcal/mol. This estimate is based on a Debye-Einstein extrapolation of the measured heat capacity with vibrational contributions removed.

Melting Data

The melting temperature and heat of melting were reported by King et al. (5).

References

1. R. A. Nelson, W. H. Johnson and E. J. Prosen, J. Res. Natl. Bur. Std. **62**, 67 (1959).
2. W. H. Johnson, A. Gilliland and E. J. Prosen, J. Res. Natl. Bur. Std. **63**, 161 (1959).
3. H. L. Schlafer and H. H. Schmidtke, Z. Physik. Chem. **11**, 297 (1959).
4. P. Gross, C. Hayman and D. L. Levi, Trans. Faraday Soc. **53**, 1601 (1957).
5. E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 1961.

Br₄Ti

Titanium Tetrabromide (TiBr₄)

(Liquid)

GFW = 367.536

T, °K	C _p ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$\frac{-(G^\circ - H^\circ_{298})/T}{H^\circ - H^\circ_{298}}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log K _p
0						
100						
200						
298	36.300	67.918	.000	-144.681	-141.051	103.393
300	36.300	68.142				
400	36.300	76.585	3.697	-154.691	-141.027	102.738
500	36.300	86.685	7.327	-158.159	-138.892	97.690
600	36.300	93.304	10.957	-156.991	-131.892	91.690
700	36.300	98.899	14.587	-155.753	-126.911	86.227
800	36.300	103.746	18.217	-154.595	-122.197	81.152
900	36.300	108.022	21.847	-153.467	-117.646	76.139
1000	36.300	111.847	25.477	-152.369	-113.234	71.497
1100	36.300	115.306	29.107	-151.303	-108.942	67.269
1200	36.300	118.465	32.737	-150.266	-104.757	63.413
1300	36.300	121.370	36.367	-150.194	-100.626	59.977
1400	36.300	124.060	39.997	-149.088	-96.540	56.230
1500	36.300	126.565	43.627	-147.999	-92.500	52.446
				-146.930	-88.617	48.911

TITANIUM TETRABROMIDE (TiBr₄)

(LIQUID)

GFW = 367.536

$$S_{298.15}^\circ = 67.918 \pm 1.6 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^\circ = -144.681 \pm 1.0 \text{ kcal/mol}$$

$$T_m = 311.4^\circ\text{K}$$

$$\Delta H_m^\circ = 3.08 \text{ kcal/mol}$$

$$T_b = 504.1^\circ\text{K}$$

$$\Delta H_v^\circ = 10.80 \text{ kcal/mol}$$

Heat of Formation

The heat of formation of TiBr₄(l) is calculated from the heat of melting, ΔH_m° , the heat of formation of TiBr₄(c), and the values of $H_{311.4}^\circ - H_{298.15}^\circ$ for both crystal and liquid.

Heat Capacity and Entropy

King et al. (1) reported the heat capacity of TiBr₄(l) between the melting point and normal boiling point. The entropy, S_{298}° , of TiBr₄(l) is calculated from $\Delta S_{311.4}^\circ$, the values of $S_{311.4}^\circ - S_{298.15}^\circ$ of both crystal and liquid and the value of $S_{298.15}^\circ$ of TiBr₄(c).

Melting Data

The melting temperature and heat of melting were reported by King et al. (1).

Vaporization Data

The boiling temperature, T_b , is taken as the point at which $K_p = 1$ for the reaction $\text{TiBr}_4(l) = \text{TiBr}_4(g)$. The heat of vaporization is calculated as the difference between ΔH_f° of the liquid and gas at the boiling temperature. The vapor pressure data are discussed in the table for TiBr₄(g).

Reference

1. E. G. King, W. W. Meller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5795, 1961.

Titanium Tetrabromide (TiBr₄)

(Ideal Gas)

GFW = 367.536

TITANIUM TETRABROMIDE (TiBr₄)

(IDEAL GAS)

Br₄Ti

GFW = 367.536

T, °K	Cp°	S° - (C° - H° ₂₉₈)/T	ΔH° _f	ΔG°	Log Kp
0	∞.000	INFINITE	- 5.713	- 124.343	INFINITE
100	18.359	71.735	- 4.367	- 128.870	281.644
200	22.469	85.929	- 2.205	- 135.165	133.008
298	24.070	93.246	∞.000	- 136.010	99.704
300	24.089	93.395	∞.045	- 131.532	99.108
400	24.793	102.434	96.201	- 134.538	73.508
500	25.148	108.008	98.025	- 136.636	57.539
600	25.350	112.611	100.081	- 138.755	46.499
700	25.475	116.531	102.160	- 140.942	39.303
800	25.557	119.938	104.174	- 143.025	33.609
900	25.614	122.952	106.096	- 145.000	28.181
1000	25.655	125.653	107.919	- 146.866	23.038
1100	25.686	128.089	109.448	- 148.691	18.240
1200	25.709	130.335	111.277	- 150.480	13.817
1300	25.727	132.394	112.823	- 152.227	9.853
1400	25.742	134.301	114.290	- 153.939	6.462
1500	25.753	136.078	115.684	- 155.620	4.069
1600	25.761	137.740	117.011	- 157.282	2.710
1700	25.771	139.302	118.277	- 158.930	1.778
1800	25.778	140.775	119.486	- 160.569	1.182
1900	25.783	142.169	120.644	- 162.200	0.847
2000	25.788	143.492	121.753	- 163.828	0.606
2100	25.792	144.750	122.819	- 165.456	0.415
2200	25.796	145.950	123.843	- 167.084	0.268
2300	25.799	147.097	124.829	- 168.712	0.157
2400	25.802	148.195	125.780	- 170.340	0.081
2500	25.804	149.248	126.698	- 171.968	0.047
2600	25.807	150.260	127.585	- 173.596	0.028
2700	25.808	151.234	128.443	- 175.224	0.018
2800	25.810	152.173	129.274	- 176.852	0.010
2900	25.812	153.079	130.079	- 178.480	0.005
3000	25.813	153.954	130.860	- 180.108	0.002
3100	25.814	154.800	131.619	- 181.736	0.001
3200	25.816	155.620	132.356	- 183.364	0.000
3300	25.817	156.414	133.073	- 184.992	0.000
3400	25.818	157.185	133.771	- 186.620	0.000
3500	25.818	157.933	134.451	- 188.248	0.000
3600	25.819	158.661	135.113	- 189.876	0.000
3700	25.820	159.368	135.759	- 191.504	0.000
3800	25.821	160.057	136.390	- 193.132	0.000
3900	25.821	160.727	137.005	- 194.760	0.000
4000	25.822	161.381	137.606	- 196.388	0.000
4100	25.822	162.019	138.194	- 198.016	0.000
4200	25.823	162.641	138.769	- 199.644	0.000
4300	25.823	163.249	139.331	- 201.272	0.000
4400	25.824	163.842	139.881	- 202.900	0.000
4500	25.824	164.423	140.420	- 204.528	0.000
4600	25.825	164.990	140.948	- 206.156	0.000
4700	25.825	165.546	141.466	- 207.784	0.000
4800	25.825	166.089	141.973	- 209.412	0.000
4900	25.826	166.622	142.471	- 211.040	0.000
5000	25.826	167.144	142.959	- 212.668	0.000
5100	25.826	167.655	143.438	- 214.296	0.000
5200	25.826	168.157	143.909	- 215.924	0.000
5300	25.827	168.648	144.371	- 217.552	0.000
5400	25.827	169.131	144.825	- 219.180	0.000
5500	25.827	169.605	145.271	- 220.808	0.000
5600	25.827	170.071	145.710	- 222.436	0.000
5700	25.828	170.528	146.141	- 224.064	0.000
5800	25.828	170.977	146.566	- 225.692	0.000
5900	25.828	171.418	146.983	- 227.320	0.000
6000	25.828	171.852	147.394	- 228.948	0.000

Dec. 31, 1961; June 30, 1964; June 30, 1968

Point Group T_dS°_{298.15} = 95.25 ± 1.0 gibbs/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
229.5 (1)	382 (3)
79 (2)	90.5 (3)

Bond Distance: Ti-Br = 2.31 Å

Bond Angle: Br-Ti-Br = 109° 28'

Product of the Moments of Inertia: I_AI_BI_C = 6.76 × 10⁻¹¹¹ g³ cm⁶

Heat of Formation

The heat of formation of TiBr₄(g) is calculated from those of TiBr₄(c) and TiBr₄(l) and the heats of reaction for the processes (A) TiBr₄(c) = TiBr₄(g) and (B) TiBr₄(l) = TiBr₄(g). Second and third law analyses of the vapor pressure data for these processes yield the following results. The first four investigations employed the spoon gauge method, the last investigation being a manometric determination.

Source	Reaction	No. Pts.	Range T°K	ΔH° ₂₉₈ , kcal/mol	Drift, kcal/mol
Boni, 1966 (1)	A	13	275 - 311	16.4 ± 0.2	16.19
Funaki et al., 1961 (2)	B	14	385 - 493	12.2 ± 0.3	12.92
Seki, 1941 (3)	A	12	286 - 306	15.4 ± 0.5	1.6 ± 0.3
Hall et al., 1958 (4)	B	69*	341 - 499	13.2 ± 0.1	13.14
Keavney & Smith, 1960 (5)	A	14	287 - 310	16.1 ± 0.3	16.14

* Four points rejected due to failure of a statistical test.

** Calculation based on third law ΔH°₂₉₈.

The adopted value of 131.5 kcal/mol is that obtained from the data of Hall et al. (4), whose third law drift was adjusted to zero by changing the entropy of the crystal within its uncertainty.

Heat Capacity and Entropy

The interatomic distance was reported by Lister and Sutton (6). The tetrahedral configuration is confirmed by spectroscopic studies (7,8). The individual moments of inertia are I_A = I_B = I_C = 1.89 × 10⁻³⁷ g cm².

The vibrational frequencies have been reported by Delvaux and Francois (7) and by Miller and Carlson (8). These values are based primarily on the Raman and infrared spectra of TiBr₄(l), the value of ν₃ being the only frequency measured for TiBr₄(g).

The electronic spectra of TiBr₄ in solution have been measured by Dijkgraaf (9). Di Sipio et al. (10) have reported the near ultraviolet spectra of TiBr₄(g). Both of these studies indicate that TiBr₄ has no low lying electronic levels which would contribute significantly to the entropy.

References

1. A. A. Boni, J. Electrochem. Soc. **113**, 1069 (1966).
2. K. Funaki, K. Uchimura and Y. Kuniya, Kogyo Kagaku Zasshi **64**, 1914 (1961).
3. S. Seki, J. Chem. Soc. Japan **62**, 789 (1941).
4. E. H. Hall, J. M. Blocher and I. E. Campbell, J. Electrochem. Soc. **105**, 271 (1958).
5. J. J. Keavney and M. O. Smith, J. Phys. Chem. **64**, 737 (1960).
6. M. W. Lister and L. E. Sutton, Trans. Faraday Soc. **37**, 393 (1941).
7. M. L. Delvaux and F. Francois, Compt. Rend. **220**, 173 (1945).
8. F. A. Miller and G. L. Carlson, Spectrochim. Acta **16**, 6 (1960).
9. C. Dijkgraaf, Spectrochim. Acta **21**, 769 (1965).
10. L. Di Sipio, G. DeMichelis, E. Tondello and L. Olcari, Chim. Ital. **96**, 1785 (1966).

Br₄Ti

Zirconium Tetrabromide (ZrBr₄)
(Crystal) Mol. Wt. = 410.884

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	0.000	INFINITE	0.731	175.296	175.296	INFINITE
100	22.377	24.895	5.391	175.504	175.504	32.540
200	28.629	31.157	10.000	175.615	175.615	190.860
298	29.629	33.702	15.000	175.680	175.680	128.909
300	29.656	33.667	15.055	175.682	175.682	128.087
400	30.900	38.638	3.100	175.692	175.692	91.413
500	31.800	42.615	6.228	175.692	175.692	70.085
600	32.400	45.909	9.408	175.692	175.692	55.084
700	32.800	48.638	12.609	175.692	175.692	44.791
800	33.100	50.972	15.836	175.692	175.692	36.249
900	33.350	52.881	18.085	175.692	175.692	32.403
1000	33.600	54.414	20.343	175.692	175.692	27.744
1100	33.820	55.622	22.605	175.692	175.692	23.988
1200	34.000	56.581	24.867	175.692	175.692	20.784
1300	34.150	57.312	27.132	175.692	175.692	18.111
1400	34.280	57.854	29.397	175.692	175.692	15.829
1500	34.390	58.248	31.664	175.692	175.692	13.856

Mar. 31, 1962; Mar. 31, 1964

ZIRCONIUM TETRABROMIDE (ZrBr₄)

(CRYSTAL)

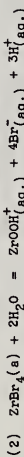
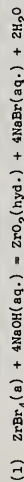
Br₄Zr

MOL. WT. = 410.884

S_{298.15} = [53.70] cal. deg.⁻¹ mole⁻¹
T_m = 723°K.
T_g = 630°K.
ΔH_f⁰ = -175.3 ± 0.8 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -181.6 ± 0.6 kcal. mole⁻¹
ΔH_g⁰ 298.15 = 28.0 ± 1.0 kcal. mole⁻¹

Heat of Formation.

A. G. Turnbull, J. Phys. Chem. 65, 1852 (1961), measured the heat effect accompanying the following reactions:



Turnbull also measured the chlorine analogue of the above reactions. He used the measured heat of formation of zirconium tetrachloride, reported by Gross, Hyman and Levi [see ZrCl₄ table], to calculate the heats of formation of ZrO₂(hyd.) and ZrO₂(aq.). The heat of formation of solid zirconium tetrabromide from reaction (1) was -182.2 ± 0.7 kcal. mole⁻¹ and from reaction (2) was -181.0 ± 0.6 kcal. mole⁻¹. An average of the two was taken to represent the heat of formation of the tetrabromide.

Heat Capacity and Entropy.

The heat capacity from 0 to 300°K. was calculated by means of the relationship $C_p = C_{vib}(e_D = 85°K.) + C_{tr}(e_D = 155°K.) + C_{vib} + a_2 C_{vib}$, where C_{vib} represents the hindered translational, C_{tr} the librational, and C_{vib} the internal vibrational contributions to the heat capacity of the solid. $C_v = C_{vib} + C_{tr} + C_{vib}$ represents the constant volume heat capacity to which $a_2 C_{vib}$, the anharmonic contribution, is added to convert to a heat capacity at constant pressure. The internal contribution, C_{vib} , was obtained from the estimated vibrational frequencies [see gas table]. The values for q_p and q_r were obtained from an elaborate correlation with the corresponding values for ZrCl₄ [see ZrCl₄ crystal table]. C_p was computed using a number of values for the constant term "a". The value, $a = 2.5 \times 10^{-3}$, was chosen from a consideration of the sublimation calculations [see below]. The heat capacity above 300°K. was obtained by a graphical extrapolation.

Melting Point.

This was reported by O. Rahlfs and M. Fischer, Z. anorg. allgem. Chem. 211, 349 (1933).

Sublimation Data.

Vapor pressure measurements have been reported by Rahlfs and Fischer (loc. cit.) and by H. L. Schlafer and H. Skoludek, Z. Elektrochem. 55, 367 (1952). The heat of sublimation results, for two values of "a", are given in the following table.

Reference	"a"	ΔH _g (298) [3rd Law]	ΔH _g (298) [2nd Law]
	A		B
Schlaf	3.0 X 10 ⁻³	27.43	28.82
Schlaf	2.5 X 10 ⁻³	27.73	28.68
Rahlfs	3.0 X 10 ⁻³	27.52	28.15
Rahlfs	2.5 X 10 ⁻³	27.85	27.99

All heat values are in kcal. mole⁻¹. Two sets of second law heat values are given; set "A" was obtained from the slope reported by the authors and set "B" from a least squares fit performed at The Dow Thermal Laboratory. Various high temperature extrapolations were carried out for a particular value of "a" but only insignificant changes in the heat of sublimation resulted. The data of Schlafer and Skoludek showed a considerable temperature dependent third law heat of sublimation at 298°K. when "a" was taken as 3.0 X 10⁻³, and a moderate temperature dependence when "a" was taken as 2.5 X 10⁻³. The data of Rahlfs and Fischer showed a very slight temperature dependence for a = 3.0 X 10⁻³ and no temperature dependence for a = 2.5 X 10⁻³.

In both sets of data there are large differences between 2nd and 3rd law values for a = 3.0 X 10⁻³, good 2nd and 3rd law agreement for the data of Rahlfs and Fischer and a = 2.5 X 10⁻³, and only fair agreement for the data of Schlafer and Skoludek and a = 2.5 X 10⁻³. Extrapolation of the data of Schlafer and Skoludek for a = 2.0 X 10⁻³ indicated a continuing temperature dependent third law heat of sublimation and disagreement between 2nd and 3rd law values. The heat of sublimation was taken as the average of the third law and two second law values calculated from the data of Rahlfs and Fischer using "a" = 2.5 X 10⁻³. The results of this analysis should not be considered conclusive since all of the data is estimated.

The sublimation point reported by Rahlfs and Fischer (loc. cit.) was 630°K., that calculated from the data of Schlafer and Skoludek was 624°K. and that obtained from the free energy crossover between solid and gas was 630°K. The sublimation point was taken as 630°K.

Since the sublimation point is lower than the melting point, the liquid phase is thermodynamically unstable under ordinary conditions.

Br₄Zr

Zirconium Tetrabromide (ZrBr₄)

(Ideal Gas) Mol. Wt. = 410.884

ZIRCONIUM TETRABROMIDE (ZrBr₄) (IDEAL GAS) MOL. WT. = 410.884Br₄ZrBr₄Zr

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	enthal. mole ⁻¹ deg ⁻¹	heat. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	-	-	5.962	- 164.527	- 164.527	INFINITE
100	19.371	74.781	110.095	-	4.515	- 151.194	- 151.194	330.422
200	23.211	84.622	101.942	-	4.352	- 155.505	- 155.505	164.920
298	24.511	84.173	94.174	+0.00	4.000	- 156.600	- 156.600	116.322
300	24.525	94.325	94.174	+0.45	-	- 153.632	- 158.727	115.627
400	25.066	106.464	100.143	2.528	-	- 168.264	- 157.419	86.006
500	25.332	112.080	101.990	5.050	-	- 168.179	- 154.718	67.624
600	25.482	116.722	104.071	7.591	-	- 168.118	- 152.032	55.375
700	25.573	120.638	106.166	10.144	-	- 168.076	- 149.356	46.629
800	25.634	124.077	108.196	12.705	-	- 168.045	- 146.684	40.070
900	25.675	127.099	110.132	15.270	-	- 168.021	- 144.015	34.970
1000	25.705	129.805	111.966	17.839	-	- 168.000	- 141.346	30.890
1100	25.728	132.256	113.701	20.411	-	- 168.008	- 138.682	27.552
1200	25.744	134.456	115.342	22.985	-	- 168.078	- 135.967	24.762
1300	25.758	136.457	116.896	25.560	-	- 168.987	- 133.215	22.394
1400	25.768	138.466	118.369	28.136	-	- 169.005	- 130.465	20.365
1500	25.777	140.244	119.764	30.713	-	- 169.032	- 127.712	18.607
1600	25.784	141.908	121.101	33.291	-	- 169.067	- 124.953	17.067
1700	25.789	143.472	122.371	35.870	-	- 169.111	- 122.193	15.708
1800	25.794	144.946	123.585	38.449	-	- 169.163	- 119.435	14.501
1900	25.798	146.340	124.746	41.029	-	- 169.223	- 116.668	13.410
2000	25.802	147.664	125.859	43.609	-	- 169.295	- 113.905	12.446
2100	25.805	148.923	126.928	46.189	-	- 169.373	- 111.133	11.565
2200	25.808	150.123	127.955	48.770	-	- 174.364	- 108.193	10.747
2300	25.810	151.271	128.944	51.351	-	- 174.467	- 105.181	9.994
2400	25.812	152.369	129.897	53.932	-	- 174.572	- 102.164	9.303
2500	25.814	153.423	130.813	56.513	-	- 174.679	- 99.146	8.667
2600	25.815	154.435	131.707	59.095	-	- 174.787	- 96.122	8.070
2700	25.817	155.410	132.566	61.676	-	- 174.898	- 93.097	7.535
2800	25.818	156.348	133.399	64.248	-	- 175.012	- 90.064	7.029
2900	25.819	157.254	134.206	66.840	-	- 175.126	- 87.026	6.558
3000	25.820	158.130	134.989	69.422	-	- 175.242	- 83.988	6.118
3100	25.821	158.976	135.749	72.004	-	- 175.262	- 80.944	5.706
3200	25.822	159.796	136.488	74.596	-	- 175.282	- 77.896	5.320
3300	25.822	160.591	137.207	77.168	-	- 175.306	- 74.846	4.957
3400	25.823	161.362	137.906	79.750	-	- 175.330	- 71.791	4.614
3500	25.824	162.110	138.587	82.333	-	- 175.357	- 68.730	4.291
3600	25.824	162.838	139.250	84.915	-	- 175.387	- 65.671	3.987
3700	25.825	163.545	139.897	87.498	-	- 175.416	- 62.605	3.698
3800	25.825	164.234	140.529	90.080	-	- 175.450	- 59.533	3.424
3900	25.826	164.905	141.145	92.663	-	- 175.485	- 56.456	3.164
4000	25.826	165.559	141.747	95.245	-	- 175.523	- 53.385	2.917
4100	25.827	166.196	142.336	97.828	-	- 175.562	- 50.306	2.681
4200	25.827	166.819	142.911	100.411	-	- 175.603	- 47.220	2.457
4300	25.827	167.426	143.473	102.993	-	- 175.647	- 44.130	2.243
4400	25.828	168.020	144.026	105.576	-	- 175.692	- 41.041	2.038
4500	25.828	168.601	144.565	108.159	-	- 175.739	- 37.949	1.843
4600	25.828	169.168	145.094	110.742	-	- 175.788	- 34.850	1.656
4700	25.828	169.724	145.612	113.324	-	- 175.840	- 31.745	1.476
4800	25.829	170.268	146.120	115.907	-	- 175.893	- 28.640	1.303
4900	25.829	170.800	146.618	118.490	-	- 175.947	- 25.535	1.137
5000	25.829	171.322	147.107	121.073	-	- 176.002	- 22.430	1.000
5100	25.829	171.833	147.597	123.656	-	- 176.058	- 19.325	0.862
5200	25.830	172.335	148.088	126.239	-	- 176.116	- 16.220	0.739
5300	25.830	172.827	148.571	128.822	-	- 176.175	- 13.115	0.617
5400	25.830	173.310	148.976	131.405	-	- 176.235	- 10.010	0.500
5500	25.830	173.784	149.402	133.988	-	- 176.296	- 6.905	0.383
5600	25.830	174.249	149.862	136.571	-	- 176.358	- 3.800	0.266
5700	25.830	174.706	150.353	139.154	-	- 176.421	- 0.695	0.150
5800	25.831	175.156	150.718	141.737	-	- 176.485	- 2.410	0.033
5900	25.831	175.597	151.136	144.320	-	- 176.550	- 4.125	0.000
6000	25.831	176.031	151.547	146.903	-	- 176.616	- 5.840	0.000

Mar. 31, 1962; Mar. 31, 1964

Point Group = [T_d]S°_{298.15} = [99.17] cal. deg⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH_f⁰ = [-146.5 ± 1.6] kcal. mole⁻¹ΔH_f⁰ 298.15 = -153.6 ± 1.6 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	[1217] (1)	[60] (2)	[322] (3)	[70] (3)

Bond Distance: Zr-Br = [2.45] Å

Bond Angle: Br-Zr-Br = [109° 29']

Product of the Moments of Inertia: I_AI_BI_C = [9.5782 × 10⁻¹¹¹] gm.³ cm.⁶O⁻ = [12]

Heat of Formation.

Calculated from the heats of formation and sublimation for the crystal at 298.15°K. (see crystal table for details).

Heat Capacity and Entropy.

The interatomic distance was obtained from an involved correlation of the interatomic distances and covalent radii of the tetrahalides of Pb, Si, Ti, Ge, and Sn. I. N. Odnev, A. M. Aleksandrovskaya, and I. V. Regins, Optics and Spectroscopy 7, 172 (1959), estimated the interatomic distance and report 2.47 Å as the Zr-Br distance. The bond angle was taken to be the tetrahedral angle. The three principal moments of inertia are: I_A = I_B = I_C = 2.1237 × 10⁻¹¹¹ gm. cm.².

The fundamental vibrational frequencies are all estimated. The product of ω₁ and ω₂ versus internuclear distance for these molecules gave nearly linear smooth curves. Values of ω₁ and ω₂ obtained from these plots were 216 cm.⁻¹ and 58 cm.⁻¹ respectively. These values for ω₁ and ω₂ were used in a valence force field calculation to derive values for ω₃ and ω₄. Central and valence force field calculations, using estimated force constants were carried out but the results proved to be inconsistent. Therefore, ω₁ was taken as the average of the two empirically derived values, ω₂ as its empirically derived value, and ω₃ and ω₄ as those derived from the empirical values and the valence force field calculation. Odnev, Aleksandrovskaya, and Regins (loc. cit.) estimated the vibrational frequencies; they obtained ω₁ = 224 cm.⁻¹, ω₂ = 65 cm.⁻¹, ω₃ = 309 cm.⁻¹, and ω₄ = 78 cm.⁻¹.

Tungsten Pentabromide (WBr₅)
(Crystal) GFW = 583.395

T, °K	C _p ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$\frac{-(G^\circ - H^\circ_{298})}{T}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log K _p
100						
200						
298	37.156	45.000	45.000	.000	- 74.500	- 64.433
300	37.200	45.230	45.001	.069	- 74.525	- 64.369
400	39.500	76.260	66.488	3.909	- 91.874	- 57.361
500	42.000	85.551	69.577	7.987	- 100.804	- 48.877
600	44.400	93.231	72.710	12.313	- 89.109	- 40.668
700	46.800	100.255	76.152	16.873	- 87.403	- 32.726
800	49.200	106.661	79.570	21.673	- 85.876	- 25.046
900	51.600	112.595	82.914	26.713	- 83.323	- 17.618
1000	54.000	118.155	86.163	31.493	- 80.947	- 10.440

TUNGSTEN PENTABROMIDE (WBr₅) (CRYSTAL)

GFW = 583.395

Br₅W

$\Delta H_f^\circ = \text{Unknown}$

$\Delta H_f^\circ_{298.15} = -74.5 \pm 3 \text{ kcal/mol}$

$\Delta H_m^\circ = 4.10 \text{ kcal/mol}$

$S^\circ_{298.15} = [65 \pm 5] \text{ gibbs/mol}$

$T_m = 559^\circ \pm 10^\circ \text{K}$

Heat of Formation

S. A. Shchukarev and G. A. Kokovin (1) have measured calorimetrically the heat of reaction $\Delta H_{298}^\circ = -187.475 \pm 0.9 \text{ kcal/mol}$ for $\text{WBr}_5(\text{c}) + 1/2\text{Br}_2(\text{l}) + 8\text{NaOH}(77.4\text{H}_2\text{O}) + \text{Na}_2\text{WO}_4(\text{c}) + 6\text{NaBr}(\text{c}) + \text{H}_2\text{O}(\text{l})$. This leads to $\Delta H_{298}^\circ(\text{WBr}_5, \text{c}) = -74.5 \pm 3 \text{ kcal/mol}$, using $\Delta H_{298}^\circ(\text{NaOH}(77.4\text{H}_2\text{O})) = -112.348 \text{ kcal/mol}$ (2), $\Delta H_{298}^\circ(\text{Na}_2\text{WO}_4, \text{c}) = -369.2 \text{ kcal/mol}$ (3), $\Delta H_{298}^\circ(\text{NaBr}, \text{c}) = -86.38 \text{ kcal/mol}$ (4) and $\Delta H_{298}^\circ(\text{H}_2\text{O}, \text{l}) = -68.315 \text{ kcal/mol}$ (5).

Heat Capacity and Entropy

$C_{p00} = 6.2 \text{ gibbs/g-atom}$ and $C_{p559} = 7.25 \text{ gibbs/g-atom}$ are estimated using the method described by O. Kubaschewski and E. L. Evans (6). Between 300°K and 559°K , which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, $S_{298}^\circ = 65 \text{ eu}$, is estimated from that of $\text{WCl}_5(\text{c})$ (7) and the entropy difference between bromides and chlorides. The latter is estimated to be 13 eu based on an extrapolation to pentavalent compounds of the entropy values of bromides and chlorides given by W. M. Latimer (8). Both WBr_5 and WCl_5 are paramagnetic with an effective moment of about 1.1 Bohr magnetons as indicated by B. N. Figgis and J. L. Lewis, "Progress in Inorg. Chem.," Vol. 6, page 121, Interscience Publishers, New York, 1964.

Melting Data

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin (8) have found the melting point, 559°K , by the thermographic method and 568°K by the tensimetric method. The value of 559°K is adopted in the tabulation.

The heat of melting is calculated from the difference between the heats of sublimation and vaporization at the melting point. The heats are both calculated from a second law analysis of the vapor pressure data reported by Shchukarev et al. (8), who gave the uncorrected heat of fusion, 5 kcal/mol . This value, when corrected for ΔC_p of vaporization and sublimation, is in good agreement with the value adopted in the tabulation.

References

1. S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. 9, 1309 (1964).
2. The value $\Delta H_{298}^\circ(\text{NaOH}(77.4\text{H}_2\text{O})) = -112.348 \text{ kcal/mol}$ is calculated from $\Delta H_{298}^\circ(\text{NaOH}(=\text{H}_2\text{O})) = -112.448 \text{ kcal/mol}$ and $\phi_L = 100 \text{ cal/mol}$ for $\text{NaOH}(=\text{H}_2\text{O}) + \text{NaOH}(77.4\text{H}_2\text{O})$. The former is obtained from JANAF $\text{NaOH}(\text{c})$ table (Mar. 31, 1966) and the latter is obtained from V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965.
3. JANAF $\text{Na}_2\text{WO}_4(\text{c})$ table (June 30, 1967).
4. JANAF $\text{NaBr}(\text{c})$ table (Sept. 30, 1964).
5. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
6. O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.
7. JANAF $\text{WCl}_5(\text{c})$ table (Dec. 31, 1966).
8. S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 4, 2185 (1959).
9. W. M. Latimer, J. Am. Chem. Soc. 73, 1480 (1951).

Br₅W

Tungsten Pentabromide (WBr₅)
(Liquid) GFW = 583.395

Br₅W

T, °K	C _p	$\frac{\text{gkcal/mole}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mole}}{\Delta H^\circ}$	ΔG°	Log K _p
0							
100							
200							
298	41.500	70.113	70.113	.000	- 71.236	- 62.693	45.955
300	43.500	70.382	70.114	.080	- 71.249	- 62.639	45.632
400	43.500	82.866	71.860	4.530	- 86.597	- 78.466	41.722
500	43.500	92.893	75.052	6.530	- 96.097	- 88.466	37.176
600	43.500	100.534	78.650	13.130	- 105.028	- 99.968	33.023
700	43.500	107.240	82.257	17.480	- 113.531	- 107.744	29.535
800	43.500	113.048	85.760	21.830	- 121.054	- 115.734	26.303
900	43.500	118.172	89.092	26.180	- 128.261	- 123.505	23.244
1000	43.500	122.755	92.224	30.350	- 134.943	- 130.230	20.293

TUNGSTEN PENTABROMIDE (WBr₅)
S_{298.15} = [70.113] gibbs/mol

T_m = 559° ± 10°K

T_b = 633.5°K

Heat of Formation

The heat of formation, ΔH_{f298}^o (WBr₅, l) = -71.236 kcal/mol, is calculated from that of WBr₅(c) by adding the heat of melting and the difference between H_{f559} - H_{f298} for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be a constant, 7.25 gibbs/g-atom.

The entropy, S₂₉₈ = 70.113 eu, is calculated in a manner analogous to that of the heat of formation.

Melting Data

See WBr₅(c) table (June 30, 1967) for details.

Vaporization Data

T_b is calculated as the temperatures at which the Gibbs energy of reaction WBr₅(l) → WBr₅(g) approaches zero. The differences between the heats of formation for liquid and gas at the boiling point is ΔH_v^o.

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 1, 2185 (1959), derived the boiling point 665°K and the heat of vaporization 14.5 ± 0.5 kcal/mol from vapor pressure data. Our second law values, corrected for ΔC_p, are T_b = 666°K and ΔH_v^o = 13.8 kcal/mol. The adopted values are significantly different because the second law value of ΔS_v is not adopted in the table.

(LIQUID)

GFW = 583.395

ΔH_{f298.15} = [-71.236] kcal/mol

ΔH_m^o = 4.10 kcal/mol

ΔH_v^o = 13.48 kcal/mol

Br₅W



Tungsten Pentabromide (WBr₅)
(Ideal Gas) GFW = 583.395

TUNGSTEN PENTABROMIDE (WBr₅)

(IDEAL GAS)

GFW = 583.395

$$\Delta H_f^\circ = -38.9 \pm 5 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = -47.6 \pm 5 \text{ kcal/mol}$$

$$S^\circ_{298.15} = [110.3] \text{ gibbs/mol}$$

Ground State Quantum Weight = [2]

Point Group [D_{3h}]

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
[300] (1)	[240] (2)
[250] (1)	[100] (2)
[235] (1)	[70] (2)
[90] (1)	[110] (2)

Bond Distance: W-Br = [2.40] Å

Bond Angles: Br*-W-Br* = [120°], Br*-W-Br** = [90°]

Br**=W-Br** = [180°]

*Equatorial **Axial

Product of the Moments of Inertia: $I_A I_B I_C = [1.640] \times 10^{-110} \text{ g cm}^6$

Heat of Formation

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 4, 2185 (1959), measured the vapor pressure of WBr₅(c, l) using a null manometer. Their results are given as below. The adopted heat of formation is -47.6 kcal/mol.

Reactions	No. of Exptl.	Temp. Range (°K)	ΔH _f ²⁹⁸ (kcal/mol)	Drift (kcal)
WBr ₅ (l) + WBr ₅ (g)	13	18.37	24.11	573.3-657.5
WBr ₅ (c) + WBr ₅ (g)	6	21.61	26.46	443.5-496.5

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of MoCl₅ determined by electron diffraction (1). The bond distance is estimated to be the same as that in WBr₅(g). The three principal moments of inertia are $I_A = I_B = 267.5 \times 10^{-39}$ and $I_C = 229.3 \times 10^{-39} \text{ g cm}^2$.

All vibrational frequencies are estimated from those of WCl₅(g) (2), using the average value of $\nu(\text{WBr}_5)/\nu(\text{WCl}_5) = 0.62$ for modes which are independent of the central atom and 0.68 for modes involving the central atom. These average values of 0.62 and 0.68 are obtained from the ratios of corresponding vibrational frequencies of ReX₅, SnX₅ and PtX₅ summarized by H. Siebert (3) and K. Nakamoto (4).

The electronic levels and quantum weights are estimated to be the same as those in WCl₅(g) (2).

References

1. R. V. G. Evans and M. W. Lister, Trans. Faraday Soc. 24, 1358 (1938).
2. JANAF WCl₅(g) table (Dec. 31, 1966).
3. H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie," Springer-Verlag, Berlin, 1966.
4. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, 1963.

Dec. 31, 1962; June 30, 1967



T, °K	C _p ^o	S ^o - (C ^o - H ²⁹⁸)/T	kcal/mol ΔH ^o	Log K _p
0	0.000	INFINITE	- 7.175	INFINITE
100	21.508	79.355	- 38.939	95.615
200	28.928	98.376	- 39.202	52.490
298	30.404	110.252	- 40.000	37.402
300	30.420	110.253	- 40.000	37.402
400	31.279	124.233	- 41.158	19.302
500	31.933	131.951	- 42.531	11.162
600	32.429	138.604	- 44.084	6.637
700	32.819	144.219	- 45.751	3.786
800	33.121	148.877	- 47.494	2.011
900	33.355	152.581	- 49.285	1.161
1000	33.529	155.330	- 51.109	0.629
1100	33.644	157.124	- 52.952	0.333
1200	33.710	158.888	- 54.811	0.161
1300	33.746	160.623	- 56.681	0.089
1400	33.759	162.333	- 58.559	0.051
1500	33.759	164.015	- 60.441	0.033
1600	33.746	165.668	- 62.325	0.021
1700	33.710	167.291	- 64.211	0.011
1800	33.644	168.883	- 66.095	0.006
1900	33.559	170.443	- 67.975	0.003
2000	33.444	171.971	- 69.849	0.001
2100	33.299	173.467	- 71.717	0.000
2200	33.124	174.930	- 73.578	0.000
2300	32.919	176.359	- 75.431	0.000
2400	32.684	177.753	- 77.275	0.000
2500	32.419	179.111	- 79.109	0.000
2600	32.124	180.433	- 80.933	0.000
2700	31.799	181.721	- 82.747	0.000
2800	31.444	182.975	- 84.551	0.000
2900	31.059	184.193	- 86.345	0.000
3000	30.644	185.375	- 88.119	0.000
3100	30.199	186.521	- 89.873	0.000
3200	29.724	187.633	- 91.607	0.000
3300	29.219	188.711	- 93.321	0.000
3400	28.684	189.755	- 95.015	0.000
3500	28.119	190.765	- 96.689	0.000
3600	27.524	191.741	- 98.343	0.000
3700	26.899	192.683	- 100.000	0.000
3800	26.244	193.591	- 101.657	0.000
3900	25.559	194.465	- 103.305	0.000
4000	24.844	195.305	- 104.945	0.000
4100	24.109	196.111	- 106.577	0.000
4200	23.344	196.883	- 108.191	0.000
4300	22.549	197.621	- 109.785	0.000
4400	21.724	198.325	- 111.359	0.000
4500	20.869	198.993	- 112.913	0.000
4600	20.000	199.625	- 114.447	0.000
4700	19.119	200.221	- 115.961	0.000
4800	18.214	200.783	- 117.455	0.000
4900	17.284	201.311	- 118.929	0.000
5000	16.329	201.805	- 120.383	0.000
5100	15.349	202.265	- 121.817	0.000
5200	14.344	202.691	- 123.231	0.000
5300	13.314	203.083	- 124.625	0.000
5400	12.259	203.441	- 126.000	0.000
5500	11.179	203.765	- 127.355	0.000
5600	10.074	204.055	- 128.691	0.000
5700	8.944	204.311	- 129.999	0.000
5800	7.789	204.533	- 131.289	0.000
5900	6.609	204.721	- 132.559	0.000
6000	5.404	204.875	- 133.809	0.000

T, °K	Cp°	gibbs/mol S°	-(C°-H° ₂₉₈)/T	II°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	43.352	75.000	75.000	4.000	- 82.000	- 69.490	50.930
300	43.400	75.268	75.001	4.080	- 82.030	- 69.411	50.566
400	46.000	88.110	76.734	4.550	- 107.869	- 60.855	33.250
500	48.600	98.654	80.093	9.280	- 101.389	- 50.520	22.082
600	51.200	107.411	83.941	19.250	- 97.724	- 40.703	18.753
700	54.800	117.632	87.984	25.030	- 95.535	- 31.380	5.841
800	56.400	123.186	91.898	30.600	- 93.101	- 12.252	2.975
900	59.000	129.979	95.756	36.830	- 90.425	- 3.408	
1000	61.600	136.330	99.499				

TUNGSTEN HEXABROMIDE (WBr₆)

(CRYSTAL)

GFW = 663.304

ΔHf° = Unknown

ΔHf°_{298.15} = -82.0 ± 3 kcal/mol

S°_{298.15} = [75 ± 5] gibbs/mol

ΔHm° = Unknown

Tm = 582°K

Heat of Formation

S. A. Shchukarev and G. A. Kokovin (1) have measured calorimetrically the heat of reaction ΔHr°₂₉₈ = -180.0 ± 0.8 kcal/mol for WBr₆(c) + 8NaOH(77.4H₂O) → Na₂WO₄(c) + 6NaBr(c) + 4H₂O(l). This leads to ΔHf°₂₉₈(WBr₆, c) = -82.0 ± 3 kcal/mol, using ΔHf°₂₉₈(NaOH·77.4H₂O) = -112.348 kcal/mol (2), ΔHf°₂₉₈(Na₂WO₄, c) = -369.2 kcal/mol (3), ΔHf°₂₉₈(NaBr, c) = -86.38 kcal/mol (4) and ΔHf°₂₉₈(H₂O, l) = -68.315 kcal/mol (5).

Heat Capacity and Entropy

Cp₃₀₀ = 6.2 gibbs/g-atom and Cp₅₈₂ = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. L. Evans (6). Between 300° and 582°K, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, S°₂₉₈(WBr₆, c) = 75 eu, is estimated by assuming S°₂₉₈(WBr₆) = S°₂₉₈(WCl₆) + 6[S°₂₉₈(Br⁻) - S°₂₉₈(Cl⁻)]. The value, S°₂₉₈(WCl₆, c) = 57 eu, is obtained from the JANAF WCl₆(a) table (Dec. 31, 1966); and the value, S°₂₉₈(Br⁻) - S°₂₉₈(Cl⁻) = 3 gibbs/mol, is obtained from the average entropy values for Br⁻ and Cl⁻ ions given by W. M. Latimer (7) and K. K. Kelley (8).

Melting Data

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin (9) have found the melting point, 582°K, under 50 atm pressure of Br₂(g) by the thermographic method. The heat of fusion is unknown.

References

1. S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. **9**, 1309 (1964).
2. This value, ΔHf°₂₉₈(NaOH·77.4H₂O) = -112.348 kcal/mol is calculated from ΔHf°₂₉₈(NaOH·H₂O) = 112.448 kcal/mol and ΔH°_f = 100 cal/mol for NaOH(-H₂O) → NaOH(77.4H₂O). The former is obtained from JANAF NaOH(c) table (Mar. 31, 1966) and the latter is obtained from V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.
3. JANAF Na₂WO₄(c) table (June 30, 1967).
4. JANAF NaBr(c) table (June 30, 1967).
5. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
6. O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.
7. W. M. Latimer, J. Am. Chem. Soc. **73**, 1480 (1951).
8. K. K. Kelley, private communication, June, 1950.
9. S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. **4**, 2185 (1959).

TUNGSTEN HEXABROMIDE (WBr_6)
 (IDEAL GAS)
 $\Delta H_f^\circ = [-47.7 \pm 10] \text{ kcal/mol}$
 $\Delta H_f^\circ = [-56.1 \pm 10] \text{ kcal/mol}$
 $S_{298.15}^\circ = [115.3 \pm 10] \text{ gibbs/mol}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies	
ω, cm^{-1}	ω, cm^{-1}
[250] (1)	[110] (3)
[200] (2)	[130] (3)
[250] (3)	[70] (3)

 $\sigma = [24]$
 Bond Distance: $\text{W-Br} = [2.40] \text{ \AA}$
 Bond Angle: $\text{Br-W-Br} = [90^\circ]$
 Product of the Moments of Inertia: $I_A I_B I_C = [2.857] \times 10^{-110} \text{ g}^3 \text{ cm}^6$

Heat of Formation

The heat of formation, $\Delta H_f^\circ(\text{WBr}_6, \text{g}) = -56.1 \text{ kcal/mol}$, is calculated from that of the crystal plus the estimated heat of sublimation $\Delta H_{\text{sub}}^\circ = 73.9 \text{ kcal/mol}$ for $\text{WBr}_6(\text{c}) + \text{WBr}_6(\text{g})$. The value of $\Delta H_{\text{sub}}^\circ$ is assumed to be the same as that for $\text{WCl}_6(\text{c}) + \text{WCl}_6(\text{g})$. See WCl_6 table (Dec. 31, 1966) for details.

Heat Capacity and Entropy

The molecular configuration is assumed to be an octahedron similar to those of $\text{WF}_6(\text{g})$, and $\text{WCl}_6(\text{g})$ determined by electron diffraction. The bond distance is estimated to be $2.40 \text{ \AA}$ by assuming $r_{\text{W-Br}} = r_{\text{W-Cl}} + (r_{\text{Na-Br}} - r_{\text{Na-Cl}})$. The bond distances, W-Cl , Na-Br and Na-Cl , are given in JANAF $\text{WCl}_6(\text{g})$ and $\text{NaBr}(\text{g})$ tables, as $2.26 \text{ \AA}$, $2.50 \text{ \AA}$ and $2.36 \text{ \AA}$, respectively. The three principal moments of inertia are: $I_A = I_B = I_C = 305.7 \times 10^{-39} \text{ g cm}^2$. All vibrational frequencies are estimated from those of $\text{WCl}_6(\text{g})$ (1), using the average value of $\nu(\text{WBr}_6)/\nu(\text{WCl}_6) = 0.62$ for modes which are independent of the central atom and 0.68 for modes involving the central atom. These average values of 0.62 and 0.68 are obtained from the ratios of corresponding vibrational frequencies of ReX_6 , SnX_6 and PtX_6 summarized by H. Siebert (2), and K. Nakamoto (3).

References

- J. C. Evans and G. Y.-S. Lo, The Dow Chemical Company, private communication, June 6, 1967, have obtained the six fundamental vibrational frequencies of WBr_6 , 312 , 367 , 165 , 206 and 97 cm^{-1} for $\text{WCl}_6(\text{g})$ by infrared spectrometry.
- H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie," Springer-Verlag, Berlin.
- K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons Inc., New York, 1968.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	.000	INFINITE	.252	.000	.000	.000
100	.1009	.720	.160	.000	.000	.000
200	1.202	.720	.160	.000	.000	.000
298	2.038	1.359	.000	.000	.000	.000
300	2.034	1.372	.004	.000	.000	.000
400	2.484	1.468	.000	.000	.000	.000
500	3.096	2.784	.569	.000	.000	.000
600	4.038	3.471	1.893	.000	.000	.000
700	4.840	4.126	2.166	.000	.000	.000
800	4.740	4.739	2.849	.000	.000	.000
900	4.611	5.111	3.111	.000	.000	.000
1000	5.149	5.844	3.824	.000	.000	.000
1100	5.304	6.300	3.347	.000	.000	.000
1200	5.430	6.809	3.573	.000	.000	.000
1300	5.527	7.248	3.839	.000	.000	.000
1400	5.605	7.651	4.165	.000	.000	.000
1500	5.669	8.030	4.558	.000	.000	.000
1600	5.721	8.417	6.122	.000	.000	.000
1700	5.765	8.787	6.696	.000	.000	.000
1800	5.803	9.096	7.275	.000	.000	.000
1900	5.836	9.341	7.861	.000	.000	.000
2000	5.865	9.711	8.442	.000	.000	.000
2100	5.891	9.968	9.029	.000	.000	.000
2200	5.914	10.272	9.620	.000	.000	.000
2300	5.936	10.736	10.212	.000	.000	.000
2400	5.957	11.241	10.804	.000	.000	.000
2500	5.974	11.782	11.403	.000	.000	.000
2600	5.992	11.287	6.631	12.002	.000	.000
2700	6.009	11.493	6.826	12.602	.000	.000
2800	6.026	11.702	7.077	13.207	.000	.000
2900	6.042	11.912	7.381	13.812	.000	.000
3000	6.057	12.159	7.735	14.412	.000	.000
3100	6.073	12.328	7.483	15.018	.000	.000
3200	6.088	12.521	7.638	15.626	.000	.000
3300	6.103	12.739	7.808	16.236	.000	.000
3400	6.119	12.981	8.000	16.848	.000	.000
3500	6.134	13.068	8.080	17.460	.000	.000
3600	6.150	13.281	8.221	18.074	.000	.000
3700	6.165	13.410	8.359	18.690	.000	.000
3800	6.181	13.557	8.500	19.307	.000	.000
3900	6.197	13.716	8.624	19.927	.000	.000
4000	6.213	13.893	8.756	20.546	.000	.000
4100	6.230	14.046	8.883	21.168	.000	.000
4200	6.247	14.197	9.008	21.792	.000	.000
4300	6.261	14.368	9.128	22.418	.000	.000
4400	6.281	14.488	9.250	23.045	.000	.000
4500	6.299	14.629	9.368	23.674	.000	.000
4600	6.317	14.768	9.484	24.305	.000	.000
4700	6.335	14.904	9.598	24.937	.000	.000
4800	6.353	15.034	9.708	25.568	.000	.000
4900	6.373	15.169	9.820	26.206	.000	.000
5000	6.392	15.298	9.928	26.846	.000	.000
5100	6.412	15.424	10.035	27.487	.000	.000
5200	6.432	15.549	10.140	28.129	.000	.000
5300	6.452	15.672	10.243	28.772	.000	.000
5400	6.473	15.793	10.345	29.419	.000	.000
5500	6.494	15.912	10.445	30.068	.000	.000
5600	6.516	16.029	10.543	30.718	.000	.000
5700	6.538	16.144	10.641	31.371	.000	.000
5800	6.560	16.258	10.738	32.026	.000	.000
5900	6.583	16.371	10.831	32.683	.000	.000
6000	6.606	16.481	10.924	33.342	.000	.000

March 31, 1961

 $\Delta H_f^{\circ} 298.15 = 0$ $\Delta S^{\circ} 298.15 = 1.359 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^{\circ} 298.15 = 170.89 \pm 0.5 \text{ kcal. mole}^{-1}$ Heat of Formation

Zero by definition.

Heat Capacity and Extrapolation

The low temperature C_p measurements of F. H. Keesom and N. Pearson (1° to 4°K. and 10° to 20°K.), Phys. Rev. 99, 1119 (1955), and of W. Dasorbo and G. E. Nichols (1° to 20°K.), The Phys. and Chem. of Solids 6, 352 (1956), were joined smoothly with the C_p measurements of W. Desorbo and W. W. Tyler (13° to 300°K.), J. Chem. Phys. 21, 1660 (1953). C_p values above 300°K were taken from National Bureau of Standards Report 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960. Heat capacity values above 1000°K were adjusted to give smooth results. Above 4000°K. the C_p values are estimated.

S_{15}° and H_{15}° were calculated to be 0.00265 cal. deg.⁻¹ mole⁻¹ and 0.03982 cal. mole⁻¹ respectively from smooth C_p values using Meddle's rule.

Carbon, Monatomic (C)

(Ideal Gas) At. Wt. = 12.011

CARBON, MONATOMIC (C) (IDEAL GAS) AT. WT. = 12.011

T, °K.	C _p ^o	S ^o	-(F ^o -H ₂₉₈ °)/T	H ^o -H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	5.000	-0.000	INFINITE	1.562	169,376	169,376	INFINITE
100	5.085	32.283	62.203	1,692	170,132	168,925	-344.756
200	4.997	39.217	39.217	1,889	170,557	163,547	-179.707
298	4.951	37.751	37.751	2,000	170,886	160,033	-117.302
300	4.951	37.752	37.751	2,009	170,891	159,965	-116.529
400	4.975	39.224	37.956	2,007	171,143	156,283	-85.385
500	4.973	40.334	38.325	1,004	171,321	152,946	-66.675
600	4.971	41.240	38.736	1,502	171,441	148,779	-54.190
700	4.970	42.070	39.531	2,496	171,531	144,206	-43.578
800	4.970	42.825	39.930	2,993	171,561	137,411	-33.366
900	4.969	43.499	40.280	3,490	171,552	133,616	-29.200
1000	4.969	44.233	40.629	3,986	171,525	129,824	-25.792
1100	4.969	45.003	41.242	4,480	171,436	125,249	-20.531
1200	4.971	45.803	41.841	4,976	171,276	119,869	-16.493
1300	4.972	46.624	42.424	5,471	171,039	114,692	-12.710
1400	4.975	47.464	43.000	5,975	170,727	108,727	-9.587
1500	4.976	48.316	43.576	6,473	170,331	101,168	-6.941
1600	4.980	49.176	44.146	6,969	170,000	92,126	-4.602
1700	4.986	50.046	44.711	7,460	169,563	81,641	-2.609
1800	4.993	50.922	45.272	7,956	169,024	69,768	-0.951
1900	5.001	51.803	45.822	8,447	168,386	56,549	0.266
2000	5.008	52.687	46.366	8,933	167,651	41,700	1.495
2100	5.015	53.574	46.904	9,414	166,811	25,217	2.466
2200	5.022	54.464	47.434	9,890	165,876	17,934	3.491
2300	5.028	55.356	47.956	10,361	164,846	9,451	4.491
2400	5.034	56.251	48.471	10,827	163,721	0	5.466
2500	5.039	57.149	48.980	11,289	162,501	-9,451	6.413
2600	5.044	58.051	49.483	11,746	161,186	-18,951	7.337
2700	5.048	58.956	49.971	12,199	159,776	-28,951	8.255
2800	5.052	59.864	50.454	12,647	158,281	-38,451	9.166
2900	5.055	60.774	50.931	13,090	156,701	-47,451	10.066
3000	5.058	61.684	51.404	13,527	155,036	-55,951	10.956
3100	5.061	62.594	51.871	13,959	153,286	-63,951	11.836
3200	5.063	63.504	52.334	14,386	151,451	-71,451	12.706
3300	5.065	64.414	52.791	14,809	149,531	-78,451	13.566
3400	5.067	65.324	53.244	15,227	147,531	-85,451	14.416
3500	5.069	66.234	53.691	15,640	145,451	-91,451	15.256
3600	5.071	67.144	54.134	16,049	143,281	-97,451	16.086
3700	5.073	68.054	54.571	16,454	141,031	-103,451	16.906
3800	5.075	68.964	55.004	16,854	138,701	-109,451	17.716
3900	5.077	69.874	55.431	17,249	136,301	-115,451	18.516
4000	5.079	70.784	55.854	17,639	133,831	-121,451	19.306
4100	5.081	71.694	56.271	18,024	131,281	-127,451	20.086
4200	5.083	72.604	56.684	18,404	128,651	-133,451	20.856
4300	5.085	73.514	57.091	18,779	125,951	-139,451	21.616
4400	5.087	74.424	57.494	19,149	123,181	-145,451	22.366
4500	5.089	75.334	57.891	19,514	120,331	-151,451	23.106
4600	5.091	76.244	58.284	19,874	117,401	-157,451	23.836
4700	5.093	77.154	58.671	20,229	114,391	-163,451	24.556
4800	5.095	78.064	59.054	20,579	111,301	-169,451	25.266
4900	5.097	78.974	59.431	20,924	108,131	-175,451	25.966
5000	5.099	79.884	59.804	21,264	104,881	-181,451	26.656
5100	5.101	80.794	60.171	21,600	101,551	-187,451	27.336
5200	5.103	81.704	60.534	21,931	98,141	-193,451	28.006
5300	5.105	82.614	60.891	22,257	94,651	-199,451	28.666
5400	5.107	83.524	61.244	22,579	91,081	-205,451	29.316
5500	5.109	84.434	61.591	22,896	87,431	-211,451	29.956
5600	5.111	85.344	61.934	23,209	83,701	-217,451	30.586
5700	5.113	86.254	62.271	23,517	79,891	-223,451	31.206
5800	5.115	87.164	62.604	23,820	75,991	-229,451	31.816
5900	5.117	88.074	62.931	24,119	72,001	-235,451	32.416
6000	5.119	88.984	63.254	24,414	67,931	-241,451	33.006

March 31, 1961

ΔH_f^o = 169.58 ± 0.45 kcal. mole⁻¹
 ΔH_f^o 298.15 = 170.89 ± 0.45 kcal. mole⁻¹
 Ground State Configuration 3P₀
 S_{298.15} = 37.76 ± 0.01 cal. deg.⁻¹ mole⁻¹

Electronic Levels and Multiplicities

E _i cm. ⁻¹	g _i	E _i cm. ⁻¹	g _i
0	1	60,360	9
16.4	3	61,982	3
43.5	5	64,090	15
10,194	5	70,000	34
21,649	1	75,000	99
33,735	5	85,000	401

Heat of Formation

The ΔH_f^o is given by the following cycle at 0°K.

(I) C(c) + 1/2 O ₂ (g) = CO(g)	-27.195 kcal. mole ⁻¹
(II) CO(g) = C(g) + O(g)	255.764
(III) O(g) = 1/2 O ₂ (g)	-58.989

For details concerning (I), (II), and (III) see the CO(g) and O₂(g) sheets. A definitive review of the heat of sublimation of carbon is given by L. Brewer and A. W. Searcy, Ann. Rev. Phys. Chem., 7, 259 (1956).

Heat Capacities and Entropies

The electronic energy levels are those listed by C. E. Moore, Nat. Bur. Standards (U. S.) Circ. 467, (1949). Levels above 50,000 cm.⁻¹ have been averaged.

Carbon Uninegative Ion (C⁻)

(Ideal Gas) At. Wt. = 12.0117

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _P
0								
100								
200								
298	4.968	36.156	36.156	•000	140.500	131.612	-	96.470
300	4.968	36.187	36.156	•009	140.496	131.557	-	95.835
400	4.968	37.016	36.351	•506	140.250	128.613	-	70.267
500	4.968	38.724	36.719	1.403	139.951	123.759	-	34.950
600	4.968	39.630	37.131	1.500	139.653	122.935	-	44.777
700	4.968	40.396	37.544	1.996	139.128	120.200	-	37.526
800	4.968	41.059	37.943	2.493	138.669	117.527	-	32.105
900	4.968	41.645	38.322	2.990	138.182	114.911	-	27.693
1000	4.968	42.168	38.681	3.487	137.676	112.353	-	24.554
1100	4.968	42.642	39.020	3.984	137.153	109.844	-	21.823
1200	4.968	43.074	39.340	4.481	136.617	107.386	-	19.557
1300	4.968	43.472	39.643	4.977	136.068	104.972	-	17.647
1400	4.968	43.840	39.930	5.474	135.512	102.602	-	16.016
1500	4.968	44.182	40.202	5.971	134.946	100.272	-	14.609
1600	4.968	44.503	40.461	6.468	134.378	97.978	-	13.383
1700	4.968	44.804	40.707	6.965	133.804	95.720	-	12.305
1800	4.968	45.088	40.943	7.461	133.225	93.498	-	11.352
1900	4.969	45.357	41.168	7.958	132.643	91.305	-	10.502
2000	4.969	45.612	41.384	8.455	132.058	89.144	-	9.741
2100	4.970	45.854	41.591	8.952	131.471	87.016	-	9.055
2200	4.971	46.085	41.790	9.449	130.880	84.911	-	8.435
2300	4.972	46.306	41.982	9.946	130.289	82.838	-	7.871
2400	4.973	46.516	42.166	10.443	129.694	80.795	-	7.366
2500	4.978	46.721	42.345	10.941	129.099	78.779	-	6.885
2600	4.982	46.917	42.517	11.439	128.501	76.756	-	6.452
2700	4.987	47.105	42.683	11.938	127.903	74.775	-	6.052
2800	4.993	47.286	42.844	12.437	127.304	72.821	-	5.684
2900	4.999	47.462	43.001	12.936	126.703	70.892	-	5.342
3000	5.010	47.631	43.152	13.437	126.102	68.973	-	5.024
3100	5.022	47.796	43.299	13.938	125.500	67.078	-	4.729
3200	5.035	47.955	43.442	14.441	124.898	65.202	-	4.453
3300	5.050	48.110	43.582	14.945	124.295	63.344	-	4.195
3400	5.066	48.261	43.717	15.451	123.694	61.505	-	3.954
3500	5.085	48.408	43.849	15.959	123.092	59.682	-	3.727
3600	5.107	48.552	43.978	16.468	122.490	57.881	-	3.514
3700	5.130	48.692	44.103	16.960	121.889	56.100	-	3.314
3800	5.155	48.829	44.226	17.494	121.289	54.330	-	3.125
3900	5.181	48.963	44.348	18.029	120.689	52.578	-	2.946
4000	5.213	49.095	44.463	18.551	120.094	50.838	-	2.776
4100	5.244	49.224	44.577	19.054	119.498	49.113	-	2.618
4200	5.278	49.351	44.689	19.560	118.903	47.402	-	2.466
4300	5.314	49.476	44.799	20.110	118.310	45.704	-	2.323
4400	5.351	49.601	44.906	20.661	117.718	44.023	-	2.187
4500	5.390	49.719	45.012	21.180	117.131	42.354	-	2.057
4600	5.431	49.838	45.116	21.721	116.544	40.699	-	1.934
4700	5.473	49.955	45.218	22.266	115.960	39.059	-	1.816
4800	5.517	50.071	45.318	22.816	115.378	37.430	-	1.704
4900	5.561	50.188	45.416	23.370	114.796	35.812	-	1.596
5000	5.607	50.298	45.512	23.928	114.223	34.203	-	1.493
5100	5.654	50.409	45.607	24.491	113.648	32.609	-	1.397
5200	5.702	50.520	45.701	25.059	113.077	31.021	-	1.304
5300	5.750	50.631	45.793	25.631	112.508	29.442	-	1.214
5400	5.801	50.739	45.881	26.204	111.936	27.872	-	1.126
5500	5.849	50.844	45.972	26.791	111.379	26.336	-	1.047
5600	5.899	50.949	46.060	27.379	110.821	24.805	-	•968
5700	5.949	51.054	46.147	27.971	110.263	23.264	-	•892
5800	6.000	51.158	46.235	28.569	109.709	21.756	-	•819
5900	6.051	51.261	46.321	29.171	109.157	20.267	-	•747
6000	6.100	51.363	46.400	29.779	108.609	18.779	-	•682

Sept. 30, 1965

CARBON UNINEGATIVE ION (C⁻) (IDEAL GAS)

AT. WT. = 12.0117

Ground State Configuration 4s²/2ΔH_f^o 0 = 140.8 ± 0.8 kcal. mole⁻¹S₂₉₈^o.15 = 36.156 cal. deg.⁻¹ mole⁻¹ΔH_f^o 298.15 = 140.5 ± 0.8 kcal. mole⁻¹

Electronic Levels and Quantum Weight

E ₁ , cm. ⁻¹	E ₁	E ₁ , cm. ⁻¹	E ₁
0	4	86223.2	4
19223.9	6	96751.7	4
19233.1	4	96788.2	4
28840.0	6	96864.2	6
83285.5	2	97770.1	2
83319.3	4	97805.8	4
83366.0	6	99653.0	10
86131.4	2		

Heat of Formation.

The heat of formation was calculated from the equation: C(g) + e⁻ → C⁻(g) with the JANAP auxiliary value for C(g); using an electron affinity = 1.25 e.v. (28.83 kcal/mole) obtained from M. Senan and L. M. Branscomb, Phys. Rev. 125, 1602 (1962). Other values for the electron affinity are: 1.17 e.v. reported by E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964); 1.12 e.v. reported by E. Clementi, A. D. McLean, D. L. Raimondi and M. Yoshimine, Phys. Rev. 133, A1274 (1964); and 1.24 e.v. reported by B. Edlen, J. Chem. Phys. 33, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, U. S. National Bureau of Standards Circular 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case nitrogen. The electronic levels above 1 X 10⁵ cm⁻¹ were omitted because their contribution is negligible below 5000°K. The H₂₉₈ value at 0°K. is -1.481 kcal/mole.

Aluminum Carbide (AIC)

(Ideal Gas) Mol. Wt. = 38.991

CAI

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	164.012	164.012	INFINITE
100	6.963	45.523	2.134	164.597	160.221	-350.146
200	7.710	50.430	4.439	164.799	151.308	-110.908
298	7.710	50.430	4.439	164.799	151.308	-110.908
300	7.718	53.428	5.014	164.799	151.224	-110.161
400	8.106	55.705	5.688	164.799	146.705	-80.152
500	8.366	57.544	6.281	164.799	142.207	-62.156
600	8.540	59.085	6.837	164.799	137.739	-50.169
700	8.660	60.411	7.364	164.799	133.308	-41.619
800	8.747	61.574	7.864	164.799	128.918	-35.217
900	8.813	62.608	8.337	164.799	124.567	-30.248
1000	8.864	63.559	8.789	164.799	120.344	-26.322
1100	8.906	64.386	9.219	164.799	116.240	-23.133
1200	8.940	65.161	9.628	164.799	112.249	-20.482
1300	8.970	65.879	10.014	164.799	108.361	-18.244
1400	8.996	66.545	10.379	164.799	104.574	-16.330
1500	9.019	67.166	10.726	164.799	100.881	-14.674
1600	9.040	67.749	11.056	164.799	97.279	-13.229
1700	9.059	68.298	11.371	164.799	93.759	-11.957
1800	9.077	68.816	11.674	164.799	90.319	-10.829
1900	9.093	69.307	11.964	164.799	86.959	-9.822
2000	9.109	69.774	12.241	164.799	83.674	-8.918
2100	9.125	70.219	12.506	164.799	80.464	-8.102
2200	9.139	70.644	12.761	164.799	77.329	-7.362
2300	9.153	71.050	13.006	164.799	74.269	-6.688
2400	9.167	71.440	13.241	164.799	71.284	-6.071
2500	9.180	71.815	13.466	164.799	68.374	-5.505
2600	9.194	72.175	13.681	164.799	65.539	-4.984
2700	9.209	72.522	13.886	164.799	62.779	-4.506
2800	9.219	72.857	14.081	164.799	60.094	-4.071
2900	9.232	73.181	14.266	164.799	57.484	-3.679
3000	9.244	73.494	14.441	164.799	54.949	-3.329
3100	9.256	73.797	14.606	164.799	52.489	-3.019
3200	9.268	74.091	14.761	164.799	50.104	-2.739
3300	9.280	74.377	14.906	164.799	47.794	-2.489
3400	9.292	74.654	15.041	164.799	45.469	-2.269
3500	9.303	74.924	15.166	164.799	43.129	-2.079
3600	9.315	75.186	15.281	164.799	40.774	-1.914
3700	9.327	75.441	15.386	164.799	38.404	-1.774
3800	9.338	75.691	15.481	164.799	36.019	-1.654
3900	9.350	75.933	15.566	164.799	33.619	-1.554
4000	9.361	76.170	15.641	164.799	31.204	-1.474
4100	9.372	76.401	15.706	164.799	28.774	-1.414
4200	9.384	76.627	15.761	164.799	26.329	-1.364
4300	9.395	76.848	15.806	164.799	23.869	-1.324
4400	9.406	77.064	15.841	164.799	21.394	-1.294
4500	9.417	77.275	15.866	164.799	18.904	-1.274
4600	9.429	77.483	15.891	164.799	16.399	-1.264
4700	9.440	77.685	15.916	164.799	13.879	-1.264
4800	9.451	77.884	15.941	164.799	11.344	-1.274
4900	9.462	78.079	15.966	164.799	8.794	-1.294
5000	9.473	78.271	15.991	164.799	6.229	-1.324
5100	9.484	78.458	16.016	164.799	3.649	-1.364
5200	9.495	78.643	16.041	164.799	1.059	-1.414
5300	9.506	78.824	16.066	164.799	-1.544	-1.474
5400	9.517	79.001	16.091	164.799	-4.114	-1.544
5500	9.528	79.176	16.116	164.799	-6.649	-1.624
5600	9.539	79.348	16.141	164.799	-9.149	-1.714
5700	9.550	79.517	16.166	164.799	-11.614	-1.814
5800	9.561	79.683	16.191	164.799	-14.044	-1.924
5900	9.572	79.847	16.216	164.799	-16.439	-2.044
6000	9.583	80.007	16.241	164.799	-18.799	-2.174

Dec. 31, 1960; June 30, 1965

ALUMINUM CARBIDE (AIC)

MOL. WT. = 38.991

(IDEAL GAS)

Ground State Configuration $2\uparrow\uparrow$ $\Delta H_f^0 = [164] \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = [53.4] \text{ cal. deg}^{-1} \text{ mole}^{-1}$ $\Delta H_f^0 298.15 = [164.8] \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$$\frac{\epsilon_i, \text{ cm}^{-1}}{0} \quad \frac{g_i}{4}$$

$$\omega_e x_e = [760] \text{ cm}^{-1}$$

$$B_e = [0.650] \text{ cm}^{-1}$$

$$\omega_e x_e = [5.0] \text{ cm}^{-1}$$

$$\alpha_e = [0.006] \text{ cm}^{-1}$$

$$r_e = [1.77] \text{ \AA}$$

$$B = 1$$

Heat of Formation.

ΔH_f^0 was calculated from D_0 , 83.0 kcal. mole⁻¹, estimated by J. S. Gordon, AstroSystems International, Livingston, N. J., private communication, June 6, 1963. $\Delta H_f^0 298.15$ was then calculated. P. Zeeman, Can. J. Phys. 32, 9 (1954) reported a $D_0 = 1.6 \pm 0.2 \text{ e.v.}$, 36.9 kcal. mole⁻¹, for a molecule that was apparently AlC(g) . However, H. Wooley, Nat'l Bur. Std. Report No. 6928, July 1, 1960, surmised that this D_0 and the reported molecular constants were for the $\text{Al}_2(\text{g})$ molecule. His judgment was accepted.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit.

CAI

{Ideal Gas} Mol. Wt. = 22.831

BORON CARBIDE (BC)

(IDEAL GAS)

MOL. WT. = 22.831

T, °K	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	-	2.080	196.464	196.464	INFINITE	
100	6.957	42.195	50.049	-1.385	197.139	192.948	-421.667	
200	6.972	47.020	50.466	-	197.682	188.532	-206.008	
298	7.009	48.822	49.822	-	198.000	183.966	-134.844	
300	7.102	49.865	49.822	-	198.004	183.970	-133.640	
400	7.359	51.942	50.103	0.13	198.144	179.145	-92.876	
500	7.642	53.615	50.644	1.486	198.155	174.392	-76.223	
600	7.895	55.031	51.260	2.263	198.080	169.645	-61.790	
700	8.102	56.265	51.889	3.000	197.959	164.912	-51.487	
800	8.276	57.389	52.430	3.715	197.799	160.180	-42.187	
900	8.408	58.339	52.900	4.475	197.519	155.452	-37.767	
1000	8.504	59.230	53.669	5.561	197.257	150.681	-32.973	
1100	8.569	60.044	54.212	6.416	196.966	146.237	-29.057	
1200	8.619	60.795	54.730	7.278	196.650	141.661	-25.700	
1300	8.666	61.500	55.216	8.147	196.324	137.064	-22.847	
1400	8.706	62.138	55.664	9.021	195.998	132.552	-20.691	
1500	8.809	62.744	56.144	9.900	195.589	128.036	-18.654	
1600	8.845	63.314	56.575	10.783	195.207	123.543	-16.874	
1700	8.907	63.851	56.987	11.669	194.815	119.076	-15.308	
1800	8.932	64.350	57.373	12.558	194.420	114.640	-13.942	
1900	8.932	64.842	57.763	13.440	194.003	110.211	-12.677	
2000	8.955	65.300	58.128	14.344	193.587	105.812	-11.562	
2100	8.976	65.738	58.480	15.241	193.165	101.435	-10.556	
2200	9.014	66.156	58.828	16.130	192.736	97.099	-9.612	
2300	9.031	66.556	59.160	17.017	192.300	92.799	-8.730	
2400	9.031	66.940	59.464	17.942	187.261	88.618	-8.069	
2500	9.047	67.309	59.771	18.846	186.819	84.516	-7.388	
2600	9.062	67.664	60.068	19.751	186.375	80.432	-6.761	
2700	9.090	68.000	60.356	20.652	185.928	76.317	-6.161	
2800	9.103	68.456	60.606	21.547	185.480	72.244	-5.584	
2900	9.116	68.965	61.169	22.437	185.045	68.282	-5.146	
3000	9.128	69.264	61.426	23.387	184.601	64.265	-4.682	
3100	9.151	69.635	61.615	24.299	184.157	60.263	-4.248	
3200	9.151	69.835	61.815	25.217	183.713	56.262	-3.843	
3300	9.163	70.109	62.155	26.130	183.269	52.254	-3.477	
3400	9.174	70.375	62.386	27.043	182.822	48.332	-3.107	
3500	9.184	70.633	62.612	27.957	182.376	44.383	-2.771	
3600	9.184	70.633	62.612	28.878	181.930	40.446	-2.455	
3700	9.205	71.035	62.837	29.797	181.483	36.514	-2.177	
3800	9.205	71.369	63.257	30.717	181.038	32.574	-1.909	
3900	9.225	71.603	63.463	31.638	180.598	28.712	-1.609	
4000	9.235	71.831	63.664	32.558	180.159	24.846	-1.362	
4100	9.235	71.831	63.664	33.483	179.713	20.980	-1.121	
4200	9.254	72.271	64.094	34.403	179.267	17.116	-0.886	
4300	9.264	72.484	64.244	35.322	178.822	13.254	-0.666	
4400	9.273	72.692	64.429	36.258	178.376	9.392	-0.467	
4500	9.283	72.896	64.611	37.184	177.930	5.530	-0.283	
4600	9.283	72.896	64.611	38.112	177.483	1.668	-0.124	
4700	9.301	73.292	64.984	39.071	177.038	-2.198	0.086	
4800	9.310	73.484	65.136	40.001	176.592	-6.340	0.310	
4900	9.319	73.672	65.305	41.833	176.146	-10.482	0.532	
5000	9.328	73.856	65.471	42.765	175.700	-14.633	0.757	
5100	9.346	74.216	65.794	43.692	175.254	-18.784	0.982	
5200	9.355	74.390	65.952	44.622	174.808	-22.935	1.207	
5300	9.364	74.562	66.107	45.548	174.362	-27.086	1.432	
5400	9.372	74.751	66.259	46.474	173.916	-31.237	1.657	
5500	9.372	74.751	66.259	47.400	173.470	-35.388	1.882	
5600	9.390	75.060	66.557	48.316	173.024	-39.539	2.107	
5700	9.398	75.221	66.703	49.243	172.578	-43.690	2.332	
5800	9.407	75.379	66.846	50.169	172.132	-47.841	2.557	
5900	9.407	75.379	66.846	51.196	171.686	-51.992	2.782	
6000	9.407	75.379	66.846	51.196	171.240	-56.143	3.007	

Dec. 31, 1962; June 30, 1963

$$\omega_e x_e = [1350] \text{ cm}^{-1}$$

$$\omega_e = [12.0] \text{ cm}^{-1}$$

$$P_e = [1.555] \text{ cm}^{-1}$$

$$d_e = [0.018] \text{ cm}^{-1}$$

$$\sigma = 1$$

Heat of Formation.

The heat of formation at 298.15°K. was calculated from $\Delta H_f^o = 105 \pm 10 \text{ kcal. mole}^{-1}$ for the reaction $\text{BC(g)} = \text{B(g)} + \text{C(g)}$ reported by G. Verhaegen, P. E. Stafford, M. Ackerman, and J. Drowart, *Nature*, **193**, 1280 (1962).

Heat Capacity and Entropy.

All spectroscopic constants were obtained from J. S. Gordon, Astroaystema, International, West Caldwell, New Jersey, private communication, November 2, 1962.

Tetraboron Monocarbide (B₄C)

(Crystal) Mol. Wt. = 55.25515

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	INFINITE	1.343	9.219	-	9.219	INFINITE
100	1.212	391	1.356	9.218	-	9.218	3.91
200	2.453	782	1.370	9.216	-	9.216	7.82
298	12.690	6.483	∞	9.296	-	9.151	10.039
300	12.820	6.562	6.483	9.296	-	9.151	6.666
400	18.250	11.047	7.058	9.258	-	9.105	4.974
500	21.460	15.486	8.104	9.234	-	9.071	3.965
600	23.510	19.591	9.848	9.257	-	9.036	3.291
700	24.780	23.315	11.511	9.329	-	8.994	2.808
800	25.730	26.687	13.200	9.441	-	8.939	2.442
900	26.527	29.764	14.872	9.579	-	8.871	2.154
1000	27.438	32.601	16.505	9.753	-	8.782	1.919
1100	28.044	35.239	18.090	9.903	-	8.681	1.725
1200	28.726	37.708	19.623	10.076	-	8.558	1.559
1300	29.376	40.033	21.104	10.256	-	8.427	1.417
1400	30.003	42.233	22.536	10.431	-	8.275	1.292
1500	30.614	44.324	23.919	10.608	-	8.121	1.185
1600	31.211	46.319	25.257	10.779	-	7.947	1.085
1700	31.799	48.229	26.553	10.942	-	7.767	.988
1800	32.379	50.063	27.808	11.092	-	7.577	.920
1900	32.953	51.829	29.026	11.220	-	7.378	.849
2000	33.522	53.534	30.209	11.317	-	7.171	.784
2100	34.087	55.183	31.359	11.383	-	6.959	.724
2200	34.649	56.782	32.479	11.417	-	6.749	.670
2300	35.207	58.334	33.569	11.417	-	6.536	.621
2400	35.764	59.844	34.633	11.383	-	6.321	.576
2500	36.318	61.316	35.671	11.317	-	6.099	.536
2600	36.871	62.751	36.685	11.220	-	5.871	.496
2700	37.423	64.153	37.676	11.092	-	5.636	.456
2800	37.973	65.524	38.637	10.942	-	5.395	.416
2900	38.523	66.866	39.567	10.779	-	5.149	.376
3000	39.071	68.181	40.468	10.608	-	4.899	.336
3100	39.618	69.471	41.340	10.431	-	4.644	.296
3200	40.165	70.738	42.196	10.256	-	4.384	.256
3300	40.711	71.982	43.036	10.076	-	4.119	.216
3400	41.257	73.205	43.859	9.890	-	3.850	.176
3500	41.802	74.409	44.659	9.699	-	3.576	.136

MOL. WT. = 55.25515

(CRYSTAL)

TETRABORON MONOCARBIDE (B₄C)

$$\Delta H_f^0 = -9.2 \pm 2.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = -9.3 \pm 2.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [25] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 6.483 \pm 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 2743 \pm 20^\circ \text{K.}$$

Heat of Formation.

The ΔH_f^0 298.15 was calculated from ΔH_f^0 298.15 = -683.3 ± 2.2 kcal. mole⁻¹ for the reaction B₄C(c) + 4O₂(g) → 2B₂O₃(amorph) + CO₂(g) measured by D. Smith, A. S. Dworkin and E. R. Van Artsdalen, J. Am. Chem. Soc. **71**, 2654-6 (1955) and the heat of formation for B₂O₃(amorph) (Dec. 31, 1964) and for CO₂(g) (March 31, 1961) in JANAF Tables.

Heat Capacity and Entropy.

The low temperature heat capacities, 54-294°K., were taken from K. K. Kelley, J. Am. Chem. Soc. **63**, 1137 (1941). Above 298°K., C_p was calculated using the equation C_p = 22.89 + 5.40 X 10⁻³T - 10.72 X 10⁻⁶T² obtained from the enthalpy data in the range 298 to 1726°K. reported by E. G. King, Ind. Eng. Chem. **41**, 1298 (1949). The values from the two sources join smoothly at 298°K. The S_{298.15} was calculated based on the low temperature heat capacities measured by K. K. Kelley, loc. cit., using S_{53.1} = 0.047 cal. deg.⁻¹ mole⁻¹.

Melting Data.

T_m was determined by Dolloff, WADD Tech. Rept. 60-143, 1960 and ΔH_m⁰ was estimated.

CB₄

CB₄

(Liquid) Mol. Wt. = 55.25515

MOL. WT. = 55.25515

(LIQUID)

TETRABORON MONOCARBIDE (B₄C)

$$\Delta H_f^\circ 298.15 = 16.592 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad \Delta H_f^\circ 298.15 = 16.1 \pm 2.5 \text{ kcal. mole}^{-1}$$

$$T_m = 2743 \pm 20^\circ \text{K.} \quad \Delta H_m^\circ = [25] \text{ kcal. mole}^{-1}$$

Heat of Formation.

The $\Delta H_f^\circ 298.15$ was obtained from $\Delta H_f^\circ 298.15(c)$ by adding ΔH_m° and the difference between H_m° and $H_{298.15}^\circ$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 1750°K. The heat capacity below 1750°K. was obtained from the heat capacity of the crystal. Above 1750°K. the heat capacity was assumed constant and estimated as 32.50 cal. deg.⁻¹ mole⁻¹ or 8.5 cal. deg.⁻¹ per g.-atom.

The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See B₄C(c) table.

Dec. 31, 1960; June 30, 1963; Dec. 31, 1965

CD 4

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° - (H° - H° ₂₉₈)/T cal. mole ⁻¹	H° - H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o	Log K _p
0					
100					
200					
298	12.545	16.592	0.000	15.226	- 11.161
300					
350	12.700	16.670	0.023	15.208	- 11.078
400	18.450	21.215	1.7173	12.200	- 7.740
500	21.400	25.669	3.618	18.154	- 5.794
600	23.250	29.742	5.855	18.143	- 4.470
700	24.580	33.430	8.244	18.048	- 3.529
800	25.500	36.485	10.741	17.877	- 2.864
900	26.530	39.485	13.371	17.740	- 2.384
1000	27.320	42.692	16.064	17.627	- 1.855
1100	28.040	45.330	18.932	17.456	- 1.506
1200	28.730	47.799	21.671	17.283	- 1.219
1300	29.400	50.140	24.384	17.114	- 0.956
1400	30.000	52.325	27.069	16.929	- 0.774
1500	30.610	54.416	30.576	16.751	- 0.597
1600	31.210	56.410	33.667	16.580	- 0.446
1700	31.800	58.320	36.603	16.417	- 0.313
1800	32.380	60.150	39.400	16.260	- 0.196
1900	32.500	61.919	39.135	16.136	- 0.093
2000	32.500	63.586	40.116	15.965	- 0.001
2100	32.500	65.172	41.462	15.768	- 0.082
2200	32.500	66.694	42.574	15.567	- 0.156
2300	32.500	68.151	43.500	15.360	- 0.226
2400	32.500	69.511	44.703	15.140	- 0.282
2500	32.500	70.838	45.722	14.900	- 0.298
2600	32.500	72.113	46.713	14.650	- 0.276
2700	32.500	73.329	47.676	14.390	- 0.233
2800	32.500	74.481	48.520	14.120	- 0.176
2900	32.500	75.662	49.527	13.840	- 0.100
3000	32.500	76.764	50.617	13.550	- 0.010
3100	32.500	77.829	51.284	13.250	- 0.082
3200	32.500	78.861	52.100	12.940	- 0.152
3300	32.500	79.855	52.955	12.620	- 0.226
3400	32.500	80.831	53.761	12.290	- 0.298
3500	32.500	81.773	54.548	11.950	- 0.366

Diberyllium Monocarbide Be_2C
(Crystal) Mol. Wt. = 30.037

T, °K.	C_p	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _P
0							
100							
200							
298	10.337	3.900	3.900	0.000	- 21.700	- 21.098	15.465
300	10.356	3.964	3.900	0.019	- 21.699	- 21.094	15.366
400	11.100	4.319	4.270	1.106	- 21.736	- 20.891	11.414
500	11.891	4.678	5.139	2.270	- 21.899	- 20.662	9.031
600	12.402	11.891	6.084	3.484	- 22.147	- 20.394	7.428
700	14.444	13.969	7.062	4.835	- 22.365	- 20.082	6.270
800	15.465	15.976	8.052	6.339	- 22.510	- 19.746	5.394
900	16.486	17.856	9.038	7.937	- 22.633	- 19.393	4.709
1000	17.507	19.646	10.010	9.636	- 22.720	- 19.028	4.136
1100	18.529	21.363	10.965	11.438	- 22.769	- 18.656	3.706
1200	19.550	23.019	11.901	13.342	- 22.779	- 18.281	3.329
1300	20.518	24.616	12.818	15.337	- 22.757	- 17.907	3.010
1400	20.860	26.142	13.715	17.398	- 22.724	- 17.535	2.737
1500	21.243	27.593	14.593	19.504	- 22.702	- 17.166	2.501
1600	21.517	28.976	15.449	21.643	- 28.211	- 16.641	2.273
1700	21.712	30.286	16.283	23.805	- 28.009	- 15.924	2.047
1800	21.833	31.531	17.096	25.983	- 27.806	- 15.219	1.848
1900	21.898	32.714	17.887	28.170	- 27.607	- 14.525	1.671
2000	21.922	33.838	18.657	30.361	- 27.417	- 13.842	1.513
2100	21.940	34.908	19.406	32.554	- 27.237	- 13.166	1.370
2200	21.961	35.929	20.134	34.749	- 27.069	- 12.502	1.242
2300	21.980	36.905	20.842	36.946	- 26.910	- 11.838	1.125
2400	21.995	37.843	21.531	39.145	- 26.762	- 11.186	1.019
2500	22.009	38.740	22.201	41.346	- 26.625	- 10.544	0.922
2600	22.049	39.604	22.854	43.550	- 26.496	- 9.900	0.832
2700	22.072	40.437	23.490	45.756	- 26.374	- 9.265	0.750
2800	22.094	41.240	24.109	47.965	- 168.320	- 6.418	0.501
2900	22.116	42.015	24.714	50.175	- 167.714	- 5.643	0.408
3000	22.137	42.765	25.303	52.388	- 167.110	- 5.106	0.372
3100	22.157	43.492	25.878	54.602	- 166.508	- 4.602	0.340
3200	22.177	44.195	26.439	56.819	- 165.907	- 4.130	0.308
3300	22.195	44.878	26.988	59.038	- 165.312	- 3.684	0.276
3400	22.213	45.541	27.524	61.258	- 164.723	- 3.254	0.244
3500	22.230	46.185	28.048	63.480	- 164.138	- 2.846	0.212

CBe_2

DIBERYLLIUM MONOCARBIDE (Be_2C) (CRYSTAL) MOL. WT. = 30.037

$\Delta F_f^\circ 0 = \text{Unknown}$
 $\Delta H_f^\circ 298.15 = 21.7 \pm 2.5 \text{ kcal. mole}^{-1}$
 $\Delta F_f^\circ = [16] \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [3.9 \pm 1.0] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = [2400]^\circ \text{K.}$

Heat of Formation.

The selected $\Delta H_f^\circ 298.15$ was calculated by the 3rd law method using vapor pressures reported by B. D. Pollock, J. Phys. Chem. 63, 587 (1959). Pressures for the reaction $\text{Be}_2\text{C}(c) \rightarrow 2\text{Be}(g) + \text{C}(\text{graphite})$ were measured by Pollock in the temperature range 1430-1669°K. by Knudsen technique. Vapor pressure data for this decomposition reaction have also been reported by J. Baboin, French Patents 1,193,790 (1959), J. Quirk, Reactor Handbook 3, 88 (1955) and P. Muratov and A. Novoselova, Dokl. Akad. Nauk SSSR 123, 334 (1959). The calculated $\Delta H_f^\circ 298.15$ values are summarized as follows:

Calc. Method	Number of Pressures	T, °K.	$\Delta H_f^\circ 298.15$ kcal. mole ⁻¹	$\Delta F_f^\circ 298.15$ kcal. mole ⁻¹	References
3rd law	14	1430-1669	89.117	-21.7	B. D. Pollock
2nd law	14	1430-1669	90.8	-25.1	Least squares fit of Pollock's v.p. to the equation: $\log P (\text{atm.}) = 6.946 - 19.593/T$
3rd law	6	1675-1953	71.411	+13.7	P. Muratov and A. Novoselova
3rd law	8	1900-2600	81.278	- 6.1	J. Quirk
3rd law	8	1800-2300	96.266	-36.0	J. Baboin

H. L. Schick, D. F. Anthrop, P. L. Hanst, R. E. Dreikorn, and M. B. Panish, "Thermodynamics of Certain Refractory Compounds, Part II", 1 March 1963 to 31 May 1963 have listed the measured vapor pressures. The vapor pressures reported by J. Baboin (loc. cit.) used in the 3rd law calculation were those listed by H. L. Schick, et al.

Heat Capacity and Entropy.

The heat capacity values, from 298.15 to 1200°K., were derived from the mean C_p data measured by J. J. Neely, E. Teeter, Jr., and J. B. Trice, J. Am. Ceramic Soc. 33, 363 (1950). Neely, et al., estimated an overall error of 15% in their mean heat capacity data. The powdered Be_2C material which was used analyzed 80 to 74% Be_2C . The impurities were mainly oxide and nitride of Be. No corrections were made for the effect of these impurities.

From 1200-2400°K. the C_p was extrapolated so as to approach the value, 22 cal. deg.⁻¹ mole⁻¹ calculated from O. H. Krikorian, "Estimation of High-Temperature Heat Capacities of Carbides," University of California, UCL 6785, February 6, 1962. The $S_{298.15}^\circ$, 3.9 cal. deg.⁻¹ mole⁻¹, was estimated by Krikorian (loc. cit.).

Melting Data.

H. L. Schick, et al., (loc. cit.) have summarized the available melting data i.e.: Y. Oishi and Y. Hamons, Osaka Kogyo Gijyuu Shikenjo Kiko 8, 89 (1957) have reported decomposition upon heating as low as 1873°K. L. Brewer, L. Bromley, P. Gilles, and N. Lofgren, "The Chemistry and Metallurgy of Miscellaneous Materials," in "Thermodynamics", McGraw-Hill, New York (1950) and I. S. Gev, AEC TR 3036 Transl. from Zh. Neorg. Khim. 1, 196 (1956) reported melting or dissociation between 2373° and 2423°K.

The melting point is assumed to be 2400°K. as estimated by T. B. Douglas and A. C. Victor, National Bureau of Standards Preliminary Report 6645, 1 January 1960 and H. L. Schick, et al. (loc. cit.). From the estimated melting point, 2400°K., and an estimated 2.5 cal. g. atom⁻¹ deg.⁻¹ for the entropy of melting, the heat of melting was calculated.

CBe_2

Diberyllium Monocarbide (Be₂C)

(Liquid) Mol. Wt. = 30.037

CBe₂DIBERYLLIUM MONOCARBIDE (Be₂C)

(LIQUID)

MOL. WT. = 30.037

T, K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100	10.337	11.345	11.345	0.000	3.798	5.416	3.970
200	10.356	11.409	11.345	0.019	3.797	5.426	3.952
300	11.380	11.529	11.764	1.106	3.867	5.967	3.260
400	11.891	17.123	12.584	2.270	3.997	6.483	2.634
500	12.402	19.336	13.529	3.484	4.245	6.959	2.535
600	16.444	21.414	14.507	4.835	4.463	7.392	2.308
700	15.465	23.421	15.497	6.339	4.608	7.800	2.131
800	15.486	25.301	16.483	7.937	4.731	8.192	1.989
900	17.507	27.091	17.455	9.636	4.818	8.571	1.873
1000	18.529	28.808	18.410	11.438	4.867	8.943	1.777
1200	19.550	30.464	19.346	13.342	4.877	9.313	1.696
1300	20.318	32.060	20.263	15.337	4.855	9.684	1.628
1400	20.860	33.587	21.160	17.398	4.822	10.056	1.570
1500	21.243	35.040	22.038	19.504	4.800	10.431	1.520
1600	22.000	36.421	22.894	21.643	10.309	10.651	1.455
1700	22.000	37.754	23.729	23.843	10.069	10.680	1.373
1800	22.000	39.012	24.544	26.043	9.844	10.722	1.302
1900	22.000	40.201	25.337	28.243	9.632	10.777	1.240
2000	22.000	41.330	26.108	30.443	9.433	10.843	1.185
2100	22.000	42.403	26.859	32.643	9.246	10.916	1.136
2200	22.000	43.427	27.589	34.843	9.073	11.002	1.093
2300	22.000	44.405	28.299	37.043	8.911	11.088	1.054
2400	22.000	45.341	28.990	39.243	8.762	11.186	1.019
2500	22.000	46.239	29.662	41.443	8.626	11.293	0.987
2600	22.000	47.102	30.316	43.643	8.501	11.400	0.958
2700	22.000	47.932	30.953	45.843	8.385	11.515	0.932
2800	22.000	48.732	31.574	48.043	8.274	11.636	0.906
2900	22.000	49.504	32.179	50.243	8.168	11.761	0.881
3000	22.000	50.250	32.769	52.443	8.066	11.890	0.856
3100	22.000	50.971	33.345	54.643	7.968	12.022	0.831
3200	22.000	51.670	33.906	56.843	7.874	12.157	0.806
3300	22.000	52.347	34.455	59.043	7.784	12.295	0.781
3400	22.000	53.004	34.991	61.243	7.697	12.436	0.756
3500	22.000	53.641	35.515	63.443	7.614	12.581	0.731

Dec. 31, 1950; Mar. 31, 1962; June 30, 1963

 $S_{298.15}^{\circ} = [11.345] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^{\circ} 298.15 = [3.798 \pm 10] \text{ kcal. mole}^{-1}$ $T_m = [2400]^{\circ}\text{K.}$ $\Delta H_m^{\circ} = [18] \text{ kcal. mole}^{-1}$

Heat of Formation.

The $\Delta H_f^{\circ} 298.15$ was calculated from the heat of formation of the crystal and the estimated heat of melting.

Heat Capacity and Entropy.

The heat capacity was assumed constant and equal to the heat capacity of the solid Be₂C at the estimated melting point.

Melting Data.

The National Bureau of Standards Report 6645, January, 1960, states that Be₂C seems to decompose easily only at temperatures above its reported melting point. For this reason they extended their Be₂C table into the liquid region. For detailed melting data see the Be₂C (c) table.CBe₂

Carbon Monobromide (CBr)
(Ideal Gas) GFW = 91.92015

CBr

T, °K	Cp°	S°	gibbs/mol -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 2.266	122.915	122.915	INFINITE
100	7.374	47.282	52.975	- 1.569	123.264	119.201	- 260.512
200	7.986	52.446	56.941	- .819	123.351	115.086	- 125.770
298	8.314	55.770	59.770	- .000	122.000	111.201	- 91.513
300	8.421	55.823	59.770	.016	121.995	111.135	- 90.961
400	8.976	58.344	58.112	.693	119.506	105.239	- 59.139
500	9.473	60.337	56.764	1.786	118.639	105.656	- 46.182
600	9.912	61.977	57.501	2.684	118.717	103.050	- 37.536
700	10.311	63.167	58.242	3.584	118.747	100.437	- 31.358
800	10.641	64.574	58.960	4.492	118.744	97.821	- 26.724
900	10.949	65.639	59.644	5.394	118.713	95.207	- 23.119
1000	11.256	66.593	60.292	6.301	118.662	92.589	- 20.237
1100	11.562	67.454	60.905	7.207	118.594	89.984	- 17.984
1200	11.869	68.245	61.484	8.114	118.513	87.394	- 15.917
1300	12.176	68.971	62.032	9.021	118.419	84.809	- 14.258
1400	12.483	69.644	62.552	9.929	118.317	82.229	- 12.836
1500	12.790	70.271	63.046	10.837	118.209	79.654	- 11.606
1600	13.098	70.858	63.516	11.747	118.093	77.084	- 10.530
1700	13.405	71.410	63.967	12.657	117.974	74.527	- 9.580
1800	13.712	71.930	64.393	13.564	117.850	71.976	- 8.739
1900	14.019	72.423	64.803	14.480	117.724	69.432	- 7.986
2000	14.326	72.891	65.195	15.392	117.595	66.893	- 7.310
2100	14.633	73.337	65.573	16.305	117.464	64.361	- 6.698
2200	14.940	73.762	65.935	17.220	117.329	61.836	- 6.133
2300	15.247	74.169	66.284	18.135	117.194	59.316	- 5.613
2400	15.554	74.559	66.621	19.050	117.055	56.800	- 5.173
2500	15.861	74.933	66.846	19.967	116.917	54.284	- 4.746
2600	16.168	75.293	67.060	20.885	116.775	51.769	- 4.354
2700	16.475	75.640	67.269	21.803	116.630	49.262	- 3.990
2800	16.782	75.974	67.459	22.722	116.483	46.763	- 3.653
2900	17.089	76.297	67.644	23.642	116.344	44.267	- 3.340
3000	17.396	76.609	67.821	24.563	116.199	41.786	- 3.048
3100	17.703	76.911	68.000	25.485	116.051	39.322	- 2.775
3200	18.010	77.206	68.175	26.408	115.901	36.861	- 2.520
3300	18.317	77.488	68.346	27.332	115.753	34.401	- 2.280
3400	18.624	77.764	68.504	28.256	115.602	31.940	- 2.054
3500	18.931	78.033	68.659	29.182	115.450	29.489	- 1.842
3600	19.238	78.294	68.810	30.108	115.298	27.044	- 1.643
3700	19.545	78.548	68.957	31.035	115.146	24.601	- 1.453
3800	19.852	78.795	69.100	31.963	114.997	22.155	- 1.274
3900	20.159	79.036	69.239	32.892	114.830	19.716	- 1.105
4000	20.466	79.272	70.816	33.822	114.672	17.276	- .944
4100	20.773	79.502	71.025	34.753	114.513	14.830	- .791
4200	21.080	79.726	71.235	35.685	114.352	12.386	- .645
4300	21.387	79.946	71.430	36.618	114.190	9.946	- .508
4400	21.694	80.160	71.626	37.551	114.027	7.509	- .376
4500	22.001	80.370	71.818	38.486	113.863	5.073	- .250
4600	22.308	80.574	72.006	39.422	113.697	2.636	- .130
4700	22.615	80.778	72.191	40.359	113.531	.199	- .015
4800	22.922	80.975	72.372	41.296	113.362	- 2.261	- .095
4900	23.229	81.169	72.549	42.235	113.193	- 4.716	- .200
5000	23.536	81.359	72.724	43.175	113.022	- 7.171	- .301
5100	23.843	81.545	72.895	44.114	112.853	- 9.626	- .398
5200	24.150	81.728	73.063	45.053	112.686	- 12.081	- .491
5300	24.457	81.908	73.228	46.002	112.501	- 14.536	- .580
5400	24.764	82.084	73.390	46.947	112.325	- 16.991	- .666
5500	25.071	82.258	73.550	47.892	112.146	- 19.446	- .748
5600	25.378	82.428	73.707	48.840	111.968	- 21.901	- .828
5700	25.685	82.596	73.861	49.788	111.786	- 24.356	- .905
5800	25.992	82.761	74.014	50.738	111.605	- 26.811	- .978
5900	26.299	82.924	74.163	51.689	111.421	- 29.266	- 1.049
6000	26.606	83.084	74.311	52.641	111.237	- 31.721	- 1.118

June 30, 1967

CARBON MONOBROMIDE (CBr)

Ground State Configuration 2π

$$S_{298.15}^{\circ} = [55.8] \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} = 123 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

(IDEAL GAS)

Electronic Levels and Quantum Weights

$$S_{298.15}^{\circ} = [55.8] \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} = 123 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

CARBON MONOBROMIDE (CBr)

Ground State Configuration 2π

$$S_{298.15}^{\circ} = [55.8] \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} = 123 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

CARBON MONOBROMIDE (CBr)

Ground State Configuration 2π

$$S_{298.15}^{\circ} = [55.8] \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} = 123 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = 122 \pm 15 \text{ kcal/mol}$$

BROMOTRIFLUOROMETHANE (CBrF₃)

(IDEAL GAS)

GFW = 148.91535

Bromotrifluoromethane (CBrF₃)

GFW = 148.91535

(Ideal Gas)

Point Group C_{3v} $\Delta H_f^\circ = -152.2 \pm 0.7$ kcal/mol $S_{298.15}^\circ = 71.155 \pm 0.12$ gibbs/mol $\Delta H_f^\circ = -155.1 \pm 0.7$ kcal/mol

Ground State Quantum Weight = 1

T, °K	C _p ^a	S ^b	-G°-H° ²⁹⁸ /T	H°-H° ²⁹⁸	kcal/mol ΔH°	Log Kp
0	9.308	0.000	INFINITE	2.458	-152.211	INFINITE
100	17.362	57.362	173.621	2.433	-151.746	331.635
200	13.485	65.167	76.453	1.482	-153.340	164.432
298	16.570	71.155	71.155	.000	-155.100	109.087
300	16.620	71.268	71.156	.031	-155.111	108.386
400	18.946	76.375	71.637	1.815	-158.887	79.717
500	20.627	80.794	73.197	3.798	-158.635	62.360
600	21.624	84.667	74.793	5.924	-158.779	50.791
700	22.682	88.099	76.453	8.152	-158.700	42.530
800	23.700	90.944	78.173	10.408	-158.505	36.156
900	24.683	93.194	79.713	12.686	-158.226	31.526
1000	24.121	96.467	81.264	15.203	-158.368	27.679
1100	24.392	98.779	82.732	17.629	-158.274	24.533
1200	24.695	100.911	84.178	20.080	-158.156	21.913
1300	24.930	102.884	85.599	22.557	-157.999	19.629
1400	24.913	104.729	86.986	25.031	-157.823	17.601
1500	25.028	106.452	88.333	27.531	-157.615	16.158
1600	25.119	108.070	89.626	30.038	-157.705	14.721
1700	25.186	109.537	90.850	32.574	-157.585	13.454
1800	25.238	110.905	92.024	35.140	-157.456	12.340
1900	25.320	112.405	92.612	37.606	-157.364	11.323
2000	25.369	113.705	93.634	40.141	-157.282	10.416
2100	25.411	114.943	94.620	42.680	-157.182	9.600
2200	25.448	116.126	95.573	45.223	-157.067	8.857
2300	25.480	117.266	96.491	47.774	-156.941	8.179
2400	25.508	118.363	97.377	50.319	-156.806	7.557
2500	25.533	119.385	98.237	52.871	-156.621	6.986
2600	25.555	120.387	99.070	55.425	-156.740	6.459
2700	25.573	121.361	99.879	57.980	-156.561	5.971
2800	25.593	122.322	100.661	60.530	-156.381	5.521
2900	25.609	123.181	101.422	63.100	-156.316	5.087
3000	25.624	124.049	102.162	65.662	-156.451	4.704
3100	25.637	124.890	102.881	68.225	-156.388	4.336
3200	25.649	125.693	103.584	70.785	-156.370	3.992
3300	25.660	126.464	104.264	73.321	-156.227	3.684
3400	25.670	127.259	104.929	75.821	-156.227	3.407
3500	25.679	128.004	105.578	78.489	-156.184	3.177
3600	25.687	128.727	106.211	81.057	-156.142	2.806
3700	25.694	129.411	106.826	83.566	-156.076	2.459
3800	25.702	130.074	107.433	86.067	-156.076	2.144
3900	25.709	130.784	108.023	88.767	-156.050	2.077
4000	25.715	131.435	108.600	91.338	-156.028	1.858
4100	25.720	132.070	109.165	93.909	-156.012	1.651
4200	25.725	132.683	109.718	96.459	-156.000	1.452
4300	25.730	133.295	110.259	99.055	-155.992	1.264
4400	25.735	133.887	110.790	101.628	-155.992	1.083
4500	25.739	134.465	111.309	104.202	-155.994	.911
4600	25.743	135.031	111.819	106.776	-156.002	.787
4700	25.747	135.581	112.319	109.340	-156.016	.684
4800	25.751	136.127	112.800	111.925	-156.036	.598
4900	25.754	136.658	113.290	114.500	-156.058	.529
5000	25.757	137.178	113.763	117.076	-156.087	.453
5100	25.760	137.688	114.297	119.652	-156.123	.400
5200	25.763	138.188	114.803	122.204	-156.160	.358
5300	25.765	138.679	115.311	124.804	-156.207	.323
5400	25.768	139.161	115.812	127.381	-156.259	.297
5500	25.770	139.634	116.005	129.958	-156.315	.270
5600	25.772	140.098	116.431	132.535	-156.377	.248
5700	25.775	140.558	116.850	135.112	-156.445	.228
5800	25.777	141.002	117.263	137.690	-156.518	.209
5900	25.778	141.443	117.669	140.268	-156.597	.189
6000	25.780	141.876	118.069	142.846	-156.681	.168

June 30, 1969

Vibrational Frequencies and Degeneracies

 $\frac{\omega_e}{\text{cm}^{-1}}$ $\frac{\omega_e}{\text{cm}^{-1}}$

Bond Distance: C-F = 1.328 Å C-Br = 1.909 Å

Bond Angle: F-C-F = 108.6 ± 1° F-C-Br = 110.33°

Product of the Moments of Inertia: $I_{ABC} = 2.3403 \times 10^{-113}$ g cm⁶ σ = 3

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₃X (X = H, Cl, Br, I, CF₃) and C₂F₄. Details of the input data and the adjustment are given in (1). Coomber and Whittle (2, 3, 4) have determined equilibrium data for CClF₃(g) + BrCl(g) = CBrF₃(g) + Cl₂(g) and for CF₃X(g) + Br₂(g) = CF₃Br(g) + BrX(g) where X = H, Cl, and CF₃. Equilibrium data for CF₃I(g) + BrI(g) = CBrF₃(g) + I₂(g) were obtained by Lord et al. (5). These data link CBrF₃ with C₂F₆, CHF₃, CClF₃ and CF₃I.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction studies by Sharbaugh et al. (6), Bowen (7), and Anderson (8) and from microwave data by Sheridan and Gordy (9). The adopted parameters are an average of those reported by (6, 7). Infrared spectra of the gas were observed by several investigators (10, 11, 12) and Raman spectra of the liquid were obtained by Edgell and May (12). The vibrational assignments of (11, 12) are in close agreement. These assignments are adopted but preference is given to frequencies observed for the gas. The value for ν₆ is taken as 300 cm⁻¹ which is between the values of 305 and 297 ± 3 cm⁻¹ derived from Raman spectra and IR (combination and overtone) spectra, respectively.

The thermodynamic functions of this table are essentially the same as those calculated by (11). Uncertainty in the entropy is estimated to vary from 0.12 to 0.5 gibbs/mol over the range from 300 to 1000°K. Uncertainty in ν₆ and neglect of anharmonicity are the major sources of error. Discussions of the magnitude of anharmonic effects appear on the tables for CClF₃(g) and CF₄(g). The principal moments of inertia are I_A = 14.68 × 10⁻³⁹ and I_B = I_C = 39.93 × 10⁻³⁹ g cm².

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFRL Contract Nr. F74611-67-C-0009, Dow Chemical Co., July, 1969.
2. J. W. Coomber and E. Whittle, Trans. Faraday Soc. **63**, 608 (1967).
3. J. W. Coomber and E. Whittle, Trans. Faraday Soc. **63**, 1394 (1967).
4. J. W. Coomber and E. Whittle, Trans. Faraday Soc. **63**, 2656 (1967).
5. A. Lord, C. A. Goy and H. O. Pritchard, J. Phys. Chem. **71**, 2705 (1967).
6. A. H. Sharbaugh, B. S. Pritchard and T. C. Madison, Phys. Rev. **171**, 302 (1950).
7. H. J. M. Bowen, Trans. Faraday Soc. **50**, 444 (1954).
8. R. E. Anderson, Dissertation Abstracts **19**, 50 (1959).
9. J. Sheridan and M. Gordy, J. Chem. Phys. **20**, 591 (1952).
10. E. K. Plyler and N. Acquista, J. Res. Nat. Bur. Stand. **48**, 92 (1952).
11. P. R. McGee, F. F. Cleveland, A. G. Weister and C. E. Decker, J. Chem. Phys. **21**, 242 (1953).
12. W. F. Edgell and C. E. May, J. Chem. Phys. **22**, 1808 (1954).

Cyanogen Bromide (BrCN)

CYANOGEN BROMIDE (BrCN)

(IDEAL GAS)

GFW = 105.92685

Point Group $C_{\infty v}$ $\Delta H_f^\circ = 46.1 \pm 1.5$ kcal/mol $S_{298.15}^\circ = 59.33 \pm 0.01$ gibbs/mol $\Delta H_f^\circ_{298.15} = 44.5 \pm 1.5$ kcal/mol

Ground State Quantum Weight = 1

 $\Delta H_f^\circ_{298.15} = 44.5 \pm 1.5$ kcal/mol

GFW = 105.92685

(Ideal Gas)

T, K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	7.000	48.000	INFINITE	2.647	46.071	46.071	INFINITE
100	7.000	48.000	48.000	2.647	46.071	46.071	INFINITE
200	9.970	50.336	48.000	1.047	45.965	41.483	25.331
298	11.263	59.334	59.334	0.000	44.500	39.462	26.926
300	11.280	59.404	59.334	0.021	44.494	39.431	26.725
400	11.983	62.751	59.786	1.186	40.944	36.474	21.024
500	12.451	65.477	60.680	2.406	41.055	37.846	16.593
600	12.826	67.781	61.659	3.673	41.141	37.198	13.549
700	13.150	69.783	62.680	4.972	41.205	36.536	11.407
800	13.433	71.537	63.681	6.301	41.256	35.865	9.798
900	13.680	73.154	64.646	7.657	41.294	35.188	8.545
1000	13.895	74.667	65.571	9.036	41.332	34.504	7.592
1100	14.081	75.940	66.454	10.435	41.363	33.823	6.720
1200	14.244	77.173	67.296	11.852	41.392	33.137	6.035
1300	14.386	78.316	68.100	13.283	41.416	32.448	5.455
1400	14.511	79.369	68.869	14.728	41.442	31.758	4.956
1500	14.621	80.394	69.604	16.185	41.466	31.066	4.526
1600	14.720	81.341	70.308	17.652	41.491	30.371	4.146
1700	14.809	82.236	70.984	19.129	41.517	29.675	3.815
1800	14.890	83.085	71.633	20.614	41.543	28.977	3.518
1900	14.965	83.892	72.257	22.106	41.571	28.281	3.253
2000	15.033	84.661	72.856	23.606	41.600	27.579	3.014
2100	15.096	85.396	73.438	25.113	41.631	26.878	2.797
2200	15.155	86.100	73.997	26.625	41.662	26.173	2.600
2300	15.211	86.775	74.538	28.144	41.695	25.470	2.420
2400	15.263	87.423	75.062	29.667	41.729	24.764	2.255
2500	15.313	88.047	75.569	31.196	41.765	24.056	2.103
2600	15.361	88.649	76.060	32.730	41.801	23.347	1.942
2700	15.406	89.230	76.538	34.266	41.840	22.635	1.832
2800	15.450	89.791	77.001	35.811	41.880	21.924	1.711
2900	15.492	90.334	77.451	37.358	41.920	21.211	1.599
3000	15.533	90.859	77.890	38.910	41.962	20.494	1.493
3100	15.573	91.369	78.316	40.465	42.005	19.780	1.395
3200	15.612	91.864	78.732	42.024	42.050	19.063	1.302
3300	15.650	92.345	79.137	43.587	42.094	18.341	1.215
3400	15.687	92.813	79.533	45.154	42.141	17.623	1.133
3500	15.723	93.268	79.918	46.725	42.187	16.898	1.055
3600	15.758	93.712	80.296	48.299	42.235	16.175	0.942
3700	15.793	94.144	80.664	49.876	42.284	15.451	0.815
3800	15.828	94.566	81.024	51.457	42.333	14.728	0.687
3900	15.861	94.977	81.377	53.042	42.384	14.002	0.548
4000	15.895	95.379	81.722	54.629	42.435	13.272	0.475
4100	15.928	95.772	82.060	56.221	42.487	12.540	0.366
4200	15.961	96.156	82.391	57.815	42.539	11.812	0.265
4300	15.993	96.532	82.715	59.413	42.591	11.080	0.180
4400	16.025	96.900	83.034	61.014	42.645	10.345	0.104
4500	16.057	97.261	83.346	62.618	42.698	9.604	0.047
4600	16.088	97.614	83.652	64.225	42.753	8.876	0.022
4700	16.119	97.960	83.953	65.835	42.808	8.139	0.015
4800	16.150	98.300	84.248	67.449	42.861	7.401	0.007
4900	16.181	98.633	84.538	69.065	42.917	6.660	0.002
5000	16.212	98.961	84.824	70.685	42.973	5.922	0.000
5100	16.242	99.282	85.104	72.304	43.027	5.172	0.000
5200	16.273	99.598	85.380	73.934	43.083	4.433	0.000
5300	16.303	99.908	85.651	75.562	43.139	3.691	0.000
5400	16.333	100.213	85.918	77.194	43.195	2.946	0.000
5500	16.363	100.513	86.180	78.829	43.249	2.204	0.000
5600	16.392	100.808	86.439	80.467	43.305	1.459	0.000
5700	16.422	101.098	86.694	82.107	43.360	0.705	0.000
5800	16.452	101.384	86.944	83.751	43.415	0.043	0.000
5900	16.481	101.666	87.192	85.394	43.470	-0.700	0.000
6000	16.510	101.943	87.435	87.047	43.524	-1.546	0.000

Vibrational Frequencies and Degeneracies

 ω, cm^{-1}

575 (1)

342.5 (2)

2200 (1)

C-N = 1.158 Å

Bond Distance: C-Br = 1.789 Å

Bond Angle: Br-C-N = 180°

Rotational Constants: $B_0 = 0.13705$ $D_0 = 2.929 \times 10^{-6}$ cm^{-1} $\sigma = 1$ Spectroscopic constants used in calculating corrections to rigid-rotator-harmonic oscillator approximation (cm^{-1}). $x_{11} = [-3.0]$ $x_{12} = [-4.0]$ $x_{22} = -0.86$ $x_{23} = -6.19$ $x_{33} = [-5.0]$ $x_{13} = [-3.0]$ $g_{22} = 1.14$

Heat of Formation

The heat of formation is calculated from $\Delta H_f^\circ(\text{BrCN}, \text{c}) = 33.58$ kcal/mol (1) and $\Delta H_f^\circ = 10.92 \pm 0.1$ kcal/mol.

This latter is obtained from an analysis of the vapor pressure data of Lord and Woolf (2) and Baxter et al. (3).

The heat of formation of the crystal is calculated from $\Delta H_f^\circ = -56.0$ kcal/mol obtained by Lord and Woolf (2)for the reaction $\text{BrCN(c)} + 2\text{NaOH(56 H}_2\text{O)} = \text{NaCNO(2800 H}_2\text{O)} + \text{NaBr(2800 H}_2\text{O)} + \text{H}_2\text{O(l)}$.The auxiliary data used were $\Delta H_f^\circ(\text{NaOH-56 H}_2\text{O)} = -112.26$ kcal/mol (1, 4), $\Delta H_f^\circ(\text{NaCNO-2800 H}_2\text{O)} = -92.25$ kcal/mol (1, 4) and $\Delta H_f^\circ(\text{NaBr-2800 H}_2\text{O)} = -70.54$ kcal/mol (1, 4). The uncertainty in the final value reflects the uncertainty in $\Delta H_f^\circ(\text{NaCNO-2800 H}_2\text{O})$ which was determined by Lord and Woolf (2) to be -93.6 kcal/mol in excess $\text{NaOH-56 H}_2\text{O}$.

Heat Capacity and Entropy

J. S. Gordon (5) used the constants given above to calculate the adopted table, using the method of Pennington and

Kobe (6) for anharmonicity, vibration rotation interaction, and centrifugal stretching corrections.

The bond lengths and angle were reported by Tyler and Sheridan (7).

References

1. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
2. G. Lord and A. A. Woolf, J. Chem. Soc. (London), 2546 (1954).
3. G. P. Baxter, T. K. Bezenburger and C. H. Wilson, J. Amer. Chem. Soc. 82, 1366 (1920).
4. V. B. Parker, U. S. Natl. Bur. Std. NBS-2, 1965.
5. J. S. Gordon, J. Chem. Eng. Data, 11, 553 (1966).
6. R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954).
7. J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 59, 2661 (1963).

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _f
0	∞	∞	∞	∞	∞	∞
100	19.456	77.319	8.248	19.097	19.097	INFINITE
200	21.793	85.563	8.563	18.166	11.205	1.244
298	21.826	85.698	8.563	12.000	8.590	6.297
300	21.826	85.698	8.563	11.970	8.570	6.243
400	23.204	92.183	8.438	2.268	10.421	5.694
500	24.012	97.456	8.613	4.662	13.618	5.952
600	24.510	101.681	9.064	7.050	16.759	6.104
700	24.834	105.685	9.203	9.559	19.855	6.199
800	25.054	109.017	9.394	12.003	22.915	6.260
900	25.210	111.977	9.571	14.567	25.946	6.300
1000	25.334	114.659	9.745	17.094	28.953	6.327
1100	25.409	117.057	9.921	19.631	31.935	6.345
1200	25.475	119.271	10.091	22.176	34.902	6.356
1300	25.527	121.312	10.292	24.726	37.852	6.363
1400	25.569	123.206	10.519	27.281	40.787	6.367
1500	25.602	124.971	10.768	29.639	43.707	6.368
1600	25.630	126.624	10.974	32.401	46.616	6.367
1700	25.653	128.179	10.761	34.965	49.516	6.365
1800	25.672	129.646	10.8795	37.531	52.403	6.362
1900	25.687	131.027	10.927	40.098	55.267	6.359
2000	25.703	132.352	11.017	42.669	58.135	6.355
2100	25.715	133.606	11.204	45.240	61.020	6.350
2200	25.725	134.803	11.370	47.812	63.874	6.345
2300	25.735	135.947	11.504	50.385	66.727	6.340
2400	25.743	137.046	11.618	52.958	69.572	6.335
2500	25.750	138.093	11.880	55.534	72.408	6.330
2600	25.756	139.103	11.6754	58.109	75.241	6.324
2700	25.762	140.075	11.759	60.685	78.063	6.318
2800	25.767	141.012	11.8419	63.261	80.888	6.313
2900	25.771	141.900	11.9285	65.838	83.706	6.308
3000	25.776	142.760	12.017	68.415	86.516	6.302
3100	25.779	143.636	120.735	70.993	89.330	6.297
3200	25.783	144.454	121.463	73.571	92.135	6.292
3300	25.786	145.247	122.172	76.150	94.930	6.287
3400	25.789	146.016	122.862	78.729	97.730	6.282
3500	25.791	146.765	123.534	81.307	100.525	6.277
3600	25.793	147.491	124.190	83.887	103.315	6.272
3700	25.796	148.198	124.829	86.466	106.105	6.267
3800	25.798	148.886	125.453	89.046	108.894	6.263
3900	25.801	149.556	126.063	91.626	111.682	6.258
4000	25.801	150.210	126.658	94.206	114.456	6.253
4100	25.803	150.847	127.240	96.786	117.234	6.249
4200	25.804	151.468	127.810	99.366	120.015	6.245
4300	25.806	152.076	128.367	101.947	122.792	6.241
4400	25.807	152.671	128.911	104.527	125.566	6.237
4500	25.808	153.249	129.447	107.108	128.334	6.232
4600	25.809	153.816	129.971	109.689	131.107	6.229
4700	25.810	154.371	130.484	112.270	133.880	6.225
4800	25.811	154.915	130.987	114.851	136.642	6.221
4900	25.812	155.446	131.482	117.432	139.411	6.218
5000	25.813	155.968	131.966	120.014	142.178	6.214
5100	25.814	156.479	132.441	122.595	144.932	6.210
5200	25.815	156.981	132.908	125.176	147.698	6.207
5300	25.815	157.472	133.367	127.758	150.467	6.204
5400	25.816	157.951	133.816	130.340	153.234	6.201
5500	25.817	158.429	134.261	132.921	155.992	6.198
5600	25.817	158.894	134.697	135.503	158.746	6.195
5700	25.818	159.351	135.126	138.085	161.507	6.192
5800	25.819	159.800	135.547	140.666	164.270	6.190
5900	25.819	160.241	135.967	143.247	167.032	6.187
6000	25.820	160.675	136.370	145.830	169.777	6.184

Dec. 31, 1963

Point Group T_d
ΔH_f^o = [19] kcal. mole⁻¹
ΔF_f^o 298.15 = [12] kcal. mole⁻¹
S_{298.15} = 85.563 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
267.2 (1)	670.7 (3)
122.5 (2)	102.5 (3)

Bond Distance: C-Br = 1.942 Å
Bond Angle: Br-C-Br = 109° 28'
Product of Moments of Inertia: I_AI_BI_C = 2.3756 X 10⁻¹¹¹ g.³ cm.⁶
σ = 12

Heat of Formation.

The heat of formation, ΔH_f^o 298.15, was calculated and reported by P. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards Circular 500, 1952.

Heat Capacity and Entropy.

The molecular constants, bond distance, and bond angle were determined by electron diffraction by C. Finbak, O. Haase, and B. Ottar, Arch. Math. Naturv B44, No. 13 (1941) and C. Finbak, O. Haase, and O. Olsson, Tidsskr. Kjemi Bergv. 3, 13 (1943). The constants reported by C. Finbak, et al., in 1943 were selected. These constants are listed in, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society (London), 1958. The principal moments of inertia calculated from these constants were I_A = I_B = I_C = 1.3343 X 10⁻³⁷ g. cm.²

The vibrational frequencies used were assigned by A. O. Meister, S. E. Rosser, and F. P. Cleveland, J. Chem. Phys. 18, 346 (1950). They measured the infrared and Raman spectrum, considered the previous literature, calculated force constants and made most probable value assignments for the frequencies. A more recent paper by B. Morzynska and J. P. Mathieu, Compt. Rend 255, 2820 (1963) made assignments from Raman and Infrared spectra which agreed with all of Meister, et al.'s assignments except ν₂ which they found was 126 cm.⁻¹ rather than 122 cm.⁻¹.

$$\text{GFN} = 47.46415$$

(IDEAL GAS)

CARBON MONOCHLORIDE (CCl)

Carbon Monochloride (CCl)

$$\text{GFN} = 47.46415$$

(Ideal Gas)

$$\Delta H_f^\circ = 119.1 \pm 5 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = 120 \pm 5 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 53.63 \pm 0.1 \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

State	$\epsilon_i, \text{cm}^{-1}$	g_i
$X^2\Pi$	0	2
4Σ	134.92	2
$A^2\Delta$	[20000]	4
$A^2\Delta$	36004	4

$$\omega_e = 876.4 \text{ cm}^{-1} \quad \sigma = 1$$

$$B_e = 0.69666 \text{ cm}^{-1} \quad \alpha_e = [0.0066] \text{ cm}^{-1}$$

$$r_e = 1.642 \text{ \AA}$$

Heat of Formation

The data of Miller and Palmer (1) provide a value of $D_0\text{-Cl} = 80 \pm 5 \text{ kcal/mol}$, which appears to be reasonably substantiated. They studied the chemiluminescence from flames of CHCl_3 and CCl_4 burning in potassium vapor. These flames exhibit C_2 Swan band radiation with major departures from vibrational and rotational equilibrium. The spectra are interpreted as due to the reaction $\text{C} + \text{CCl} + C_2^* + \text{Cl}$ where the carbon atom is either 3D ground state or 1D first excited state. The separation between the ground and first excited state of the carbon atom is matched closely by the difference in preferential population of the excited C_2 levels. The assumption is made that all the exothermicity of the reaction is retained as vibrational excitation of the C_2 , thus the populated levels are measures of the heat of reaction. In this manner we obtain a heat of reaction of $67 \pm 2.5 \text{ kcal}$ for the reaction $\text{C} + \text{CCl} + C_2 + \text{Cl}$ which, using JANAF auxiliary data, gives $\Delta H_f^\circ(\text{CCl}, g) = 124 \pm 2.5 \text{ kcal/mol}$; however, this represents the initial state of the CCl which in the flame is presumed to have about 4 kcal of vibrational energy at roughly 2000°K. Thus, we obtain $\Delta H_{298}^\circ(\text{CCl}, g) = 120 \pm 5 \text{ kcal/mol}$, which is adopted.

The heat of formation can also be estimated from the dissociation energy calculated from the linear Birge-Sponer extrapolation of the ground state vibrational constants. This yields $D_0 = 89 \text{ kcal}$ or $\Delta H_{298}^\circ = 111 \text{ kcal/mol}$. There are several indications that this dissociation energy is probably a maximum value, for example, Hildenbrand (3) has applied an ionic-covalent correction to the linear extrapolation which gives $D_0 = 72 \text{ kcal}$. We would expect this heat of formation to be a minimum value. A real minimum for the dissociation energy can be obtained from the knowledge that the first vibrational level of the $^2\Delta$ state is occupied and so the dissociation energy of this state must be greater than 850 cm^{-1} . This yields a minimum dissociation energy of the ground state of 76 kcal, assuming the dissociation products are $C(^3P)$ and $Cl(^2P)$, and $\Delta H_{298}^\circ(\text{CCl}, g) = 124 \text{ kcal/mol}$ which is the maximum value of the heat of formation.

Heat Capacity and Entropy

The rotational and electronic constants are those of Verma and Mulliken (2). The vibrational constants are those derived by Oucharenko et al. (3) from the data of Gordon and King (4). The anharmonicity constants listed by Verma and Mulliken are not used, since these are based only on the 0,0 and 0,1 transitions. The u_2 level is estimated by analogy with $\text{CF}(g)$. The value for a_e was obtained from the other constants assuming a Morse potential function.

References

1. W. J. Miller and R. S. Palmer, J. Chem. Phys. **40**, 3701 (1964).
2. R. D. Verma and H. S. Mulliken, J. Mol. Spectry. **5**, 419 (1961).
3. I. E. Oucharenko, Yu. Ya. Kuzyskov, and V. M. Tat'yevskii, Opt. Spectry. (Eng. Transl.) **18**, 294 (1965).
4. R. D. Gordon and G. W. King, Can. J. Phys. **39**, 252 (1961).
5. D. L. Hildenbrand, Douglas Advanced Research Laboratories, Huntington Beach, Calif., private communication, Dec. 30, 1969.

T, °K	C_p°	S°	$-(C_p^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-2.245	119.104	119.104	INFINITE
100	7.760	45.342	60.362	-1.502	119.485	117.229	256.204
200	7.484	50.612	54.330	-0.784	119.802	114.840	125.491
298	7.709	53.634	53.634	0.000	120.000	112.356	82.361
300	7.715	53.681	53.634	0.044	120.003	112.311	81.818
400	8.029	55.945	53.940	1.602	120.129	119.726	59.952
500	8.278	57.764	54.529	1.614	120.200	107.117	46.821
600	8.459	59.291	55.199	2.055	120.225	104.097	38.043
700	8.568	60.605	55.879	3.308	120.213	101.876	31.807
800	8.684	61.758	56.543	4.172	120.175	99.259	27.116
900	8.757	62.785	57.181	5.044	120.115	96.687	23.469
1000	8.814	63.711	57.768	5.923	120.041	94.043	20.553
1100	8.859	64.553	58.364	6.804	119.953	91.404	18.160
1200	8.897	65.326	58.918	7.684	119.855	88.800	15.884
1300	8.929	66.039	59.435	8.565	119.746	86.291	14.505
1400	8.957	66.702	59.931	9.480	119.633	83.712	13.068
1500	8.981	67.321	60.403	10.377	119.513	81.151	11.624
1600	9.003	67.901	60.854	11.274	119.388	78.594	10.173
1700	9.023	68.448	61.284	12.177	119.261	76.051	8.777
1800	9.041	68.964	61.697	13.080	119.129	73.512	8.926
1900	9.058	69.453	62.092	13.985	118.996	70.983	8.165
2000	9.074	69.918	62.472	14.892	118.860	68.459	7.481
2100	9.089	70.361	62.837	15.800	118.728	65.943	6.843
2200	9.103	70.784	63.190	16.710	118.594	63.431	6.200
2300	9.114	71.189	63.528	17.621	118.443	60.930	5.570
2400	9.131	71.578	63.855	18.533	118.300	58.432	5.321
2500	9.145	71.951	64.172	19.447	118.156	55.939	4.890
2600	9.159	72.310	64.478	20.362	118.010	53.458	4.493
2700	9.172	72.656	64.772	21.276	117.862	50.973	4.093
2800	9.186	72.989	65.062	22.197	117.714	48.500	3.766
2900	9.200	73.312	65.341	23.116	117.563	46.030	3.469
3000	9.215	73.624	65.612	24.037	117.410	43.565	3.174
3100	9.229	73.924	65.875	24.959	117.257	41.107	2.898
3200	9.245	74.220	66.131	25.883	117.102	38.653	2.608
3300	9.260	74.504	66.381	26.808	116.944	36.202	2.398
3400	9.277	74.781	66.624	27.735	116.787	33.760	2.170
3500	9.294	75.050	66.861	28.663	116.627	31.317	1.956
3600	9.311	75.312	67.092	29.594	116.467	28.883	1.753
3700	9.329	75.568	67.316	30.526	116.305	26.453	1.563
3800	9.348	75.817	67.538	31.459	116.142	24.028	1.382
3900	9.368	76.060	67.753	32.395	115.979	21.607	1.211
4000	9.388	76.297	67.964	33.333	115.815	19.190	1.048
4100	9.409	76.529	68.170	34.273	115.650	16.773	0.894
4200	9.431	76.756	68.372	35.215	115.484	14.364	0.748
4300	9.453	76.979	68.569	36.159	115.318	11.959	0.608
4400	9.476	77.196	68.763	37.106	115.152	9.556	0.475
4500	9.500	77.409	68.953	38.054	114.985	7.157	0.348
4600	9.524	77.618	69.139	39.006	114.819	4.764	0.226
4700	9.549	77.823	69.317	39.964	114.656	2.376	0.109
4800	9.574	78.025	69.501	40.915	114.486	0.012	0.001
4900	9.600	78.222	69.677	41.874	114.320	-2.395	-0.107
5000	9.626	78.417	69.850	42.835	114.155	-4.776	-0.209
5100	9.653	78.608	70.019	43.799	113.989	-7.156	-0.307
5200	9.680	78.795	70.184	44.764	113.824	-9.536	-0.405
5300	9.708	78.980	70.351	45.735	113.661	-11.916	-0.491
5400	9.736	79.162	70.512	46.708	113.498	-14.294	-0.577
5500	9.764	79.341	70.671	47.683	113.334	-16.672	-0.661
5600	9.793	79.517	70.827	48.661	113.173	-19.051	-0.741
5700	9.822	79.690	70.981	49.641	113.010	-21.435	-0.819
5800	9.851	79.861	71.133	50.625	112.849	-23.818	-0.893
5900	9.880	80.030	71.282	51.611	112.689	-26.206	-0.965
6000	9.909	80.196	71.429	52.601	112.529	-28.612	-1.035

(IDEAL GAS)

CHLOROTRIFLUOROMETHANE (CClF₃)

GFW = 104.45935

Chlorotrifluoromethane (CClF₃)
(Ideal Gas) GFW = 104.45935Point Group C_{3v} $\Delta H_f^\circ = -168.0 \pm 0.8$ kcal/mol $S_{298.15}^\circ = 68.174 \pm 0.1$ gibbs/mol $\Delta H_f^\circ = -168.0 \pm 0.8$ kcal/mol

Ground State Quantum Weight = 1

T, °K	Cp*	S*	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	3.294	-167.980	-167.980	INFINITE
100	8.799	55.209	60.045	2.484	-168.574	-165.712	362.164
200	12.679	62.465	69.536	1.414	-168.996	-177.753	177.753
298	15.986	68.174	77.000	0.000	-169.200	-159.510	116.924
300	16.040	68.273	78.174	0.30	-169.203	-159.450	116.159
400	18.531	73.247	88.335	1.765	-169.284	-156.184	66.836
500	20.320	77.586	97.161	3.712	-169.292	-152.907	44.336
600	21.490	81.400	105.724	5.811	-169.254	-149.633	34.504
700	22.159	84.759	113.580	8.000	-169.184	-146.364	27.097
800	23.159	87.859	120.830	10.303	-169.104	-143.114	21.397
900	23.450	90.617	127.567	12.645	-169.008	-139.871	17.575
1000	24.022	93.129	133.780	15.029	-168.904	-136.641	14.551
1100	24.309	95.432	139.472	17.446	-168.796	-133.420	12.008
1200	24.714	97.528	144.635	19.891	-168.684	-130.215	10.000
1300	24.714	99.528	149.283	22.351	-168.577	-127.005	8.591
1400	24.959	101.365	153.429	24.830	-168.467	-123.810	7.788
1500	24.959	103.085	157.070	27.322	-168.358	-120.623	7.308
1600	25.078	104.700	160.209	29.805	-168.252	-117.447	6.842
1700	25.231	106.223	162.837	32.287	-168.141	-114.271	6.391
1800	25.231	107.663	164.954	34.637	-168.043	-111.110	5.954
1900	25.291	109.029	166.598	36.854	-167.941	-107.947	5.534
2000	25.342	110.328	167.791	39.015	-167.842	-104.791	5.131
2100	25.387	111.565	168.522	41.124	-167.745	-101.642	4.748
2200	25.459	112.678	168.837	43.182	-167.648	-98.500	4.384
2300	25.459	113.678	168.837	45.182	-167.554	-95.354	4.041
2400	25.489	114.562	168.504	47.136	-167.479	-92.217	3.720
2500	25.516	116.003	168.504	50.084	-167.398	-89.085	3.414
2600	25.530	117.004	167.770	52.970	-167.321	-85.953	3.124
2700	25.579	117.869	166.282	55.767	-167.248	-82.821	2.851
2800	25.579	118.899	164.954	58.562	-167.178	-79.689	2.591
2900	25.596	119.797	162.663	61.261	-167.114	-76.553	2.341
3000	25.611	120.665	160.328	63.959	-167.056	-73.418	2.101
3100	25.625	121.505	157.976	66.657	-166.990	-70.283	1.871
3200	25.650	123.108	155.624	69.354	-166.924	-67.148	1.651
3300	25.650	123.873	153.271	72.051	-166.869	-64.013	1.441
3400	25.670	124.617	150.917	74.748	-166.817	-60.878	1.241
3500	25.670	124.617	148.564	77.445	-166.759	-57.743	1.051
3600	25.679	125.351	146.211	80.142	-166.700	-54.608	0.871
3700	25.687	126.044	143.858	82.839	-166.642	-51.473	0.701
3800	25.694	126.729	141.505	85.536	-166.584	-48.338	0.541
3900	25.701	127.397	139.152	88.233	-166.527	-45.203	0.391
4000	25.708	128.048	136.800	90.930	-166.470	-42.068	0.251
4100	25.714	128.683	134.447	93.627	-166.412	-38.933	0.121
4200	25.719	129.302	132.094	96.324	-166.354	-35.798	0.001
4300	25.725	129.908	129.741	99.021	-166.296	-32.663	-0.119
4400	25.729	130.499	127.388	101.718	-166.238	-29.528	-0.239
4500	25.734	131.077	125.035	104.415	-166.179	-26.393	-0.359
4600	25.738	131.643	122.682	107.112	-166.121	-23.258	-0.479
4700	25.742	132.196	120.329	109.809	-166.062	-20.123	-0.599
4800	25.746	132.738	117.976	112.506	-166.004	-16.988	-0.719
4900	25.749	133.269	115.623	115.203	-165.946	-13.853	-0.839
5000	25.753	133.790	113.270	117.900	-165.888	-10.718	-0.959
5100	25.756	134.300	110.917	120.597	-165.830	-7.583	-1.079
5200	25.759	134.800	108.564	123.294	-165.772	-4.448	-1.199
5300	25.762	135.290	106.211	125.991	-165.714	-1.313	-1.319
5400	25.764	135.772	103.858	128.688	-165.656	1.822	-1.439
5500	25.767	136.245	101.505	131.385	-165.598	4.987	-1.559
5600	25.769	136.709	99.152	134.082	-165.540	8.152	-1.679
5700	25.771	137.165	96.800	136.779	-165.482	11.317	-1.799
5800	25.773	137.611	94.447	139.476	-165.424	14.482	-1.919
5900	25.775	138.054	92.094	142.173	-165.366	17.647	-2.039
6000	25.777	138.487	89.741	144.870	-165.308	20.812	-2.159

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1969

Vibrational Frequencies and Dependences

ω_1 , cm ⁻¹	ω_2 , cm ⁻¹
1108 (1)	1217 (2)
782 (1)	560 (2)
474 (1)	350 (2)

Bond Distance: C-F = 1.328 Å C-Cl = 1.751 Å

Bond Angle: F-C-F = 108.6 ± 0.5° F-C-Cl = 110.33°

Product of the Moments of Inertia: $I_A I_B I_C = 9.4425 \times 10^{-114}$ g⁶ cm⁶

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₃X (X = H, Cl, Br, I, CF₃) and C₂F₄. Details of the input data and the adjustment are given in (1). Coomber and Whittle (2) have determined equilibrium data for CClF₃(g) + BrF₃(g) = CBrF₃(g) + ClF₃(g) where X = Cl and Br. Lord et al. (3) studied the analogous equilibria CF₃I(g) + ClI(g) = CClF₃(g) + I₂(g). These data link CClF₃ with CBrF₃ and CF₃I.

Other data which were omitted from the adjustment include those of Baibuz (4, 5), Mears (6), Kolesov (7), Kiribridge (8), and von Wartenberg (9). Baibuz (4, 5) derived $\Delta H_f^\circ = -166.2 \pm 2.2$ kcal/mol by applying the method of estimate in a spherical bomb to mixtures of H₂, O₂ and CClF₃. By comparison with similar data for CF₄ and CCl₄, we estimate the bias in Baibuz' value to be about +2 kcal/mol. Mears (6) gave a preliminary report of values of ΔH_f° for reactions involving HF, HCl and CCl₃F_n (n = 1, 2, 3, 4). We derive $\Delta H_f^\circ = -177$ and -173 kcal/mol from two different combinations of reactions; however, no detailed account of the data has been published. The other authors (7, 8, 9) measured ΔH_f° for reaction of CClF₃ with an alkali metal (Na or K) to form amorphous carbon and mixtures of the fluoride and chloride. Discrepancies of many kcal/mol exist in these studies, presumably due to inadequate characterization of the thermochemical reactions.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction studies by Bowen (10) and Bartell (11). Results from Bartell are adopted. These parameters are consistent with the microwave data of Coles (12). Principal moments of inertia are $I_A = 14.58 \times 10^{-39}$ and $I_B = I_C = 23.37 \times 10^{-39}$ g cm². Vibrational assignments are based on the work of Claassen (13) and the gas-phase Raman spectra observed by Holzer and Moser (14).

The largest uncertainty in Cp and S° probably results from the neglect of anharmonicity. Barbo (15) and Albright (16) have given estimates for the anharmonic contributions. These vary from 0.1 to 0.3 gibbs/mol in both Cp° and S° over the range from 300 to 1000°K, respectively. Somewhat larger contributions are possible based on the anharmonic functions calculated by McBride (17) for CF₄(g). We estimate the overall uncertainty in the entropy of this JANAF table to be 0.1 eu at 300°K and 0.4 eu at 1000°K. Cp° is consistent with Cv° measured at 300°K by the wire-ribbon method (18).

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFPL Contract Nr. F04611-67-C-0009, Dow Chemical Co., July, 1969.
2. J. W. Coomber and E. Whittle, Trans. Faraday Soc. 63, 2656 (1967).
3. A. Lord, C. A. Goy and H. O. Pritchard, J. Phys. Chem. 71, 2705 (1967).
4. V. F. Baibuz, Dokl. Akad. Nauk SSSR 140 (6), 1389 (1961); English translation, 786 (1961).
5. V. F. Baibuz and V. A. Medvedev, Tr. Gos. Inst. Prikl. Khim. No. 49, 84 (1962).
6. W. H. Mears and R. F. Stahl, I.U.P.A.C. Thermochemical Bulletin 2, 5 (1956).
7. V. P. Kolesov, I. D. Zenkov and S. M. Skuratov, Russ. J. Phys. Chem. (English Translation) 36 (9), 1120 (1962); 37 (3), 378 (1963).
8. F. W. Kiribridge and F. G. Davidson, Nature 174, 79 (1954).
9. H. von Wartenberg and J. Schiefer, Z. Anorg. Allg. Chem. 278, 326 (1955).
10. H. J. M. Bowen, Trans. Faraday Soc. 50, 444 (1954).
11. L. S. Bartell and L. O. Brockway, J. Chem. Phys. 23, 1860 (1955).
12. D. K. Coles and R. H. Hughes, Phys. Rev. 76, 858 (1949); recalculated by J. Sheridan and W. Gordy, J. Chem. Phys. 20, 591 (1952).
13. H. H. Claassen, J. Chem. Phys. 22, 50 (1954).
14. W. Holzer and H. Moser, J. Mol. Spectrosc. 20, 189 (1966).
15. W. Barbo, Kältetechnik 17, 219 (1965).
16. L. Albright, W. C. Callegar and K. K. Innes, J. Am. Chem. Soc. 76, 6017 (1954).
17. B. J. McBride, S. Heimal, J. G. Ehlers and S. Gordon, NASA SP-3001, 156 (1963).
18. W. N. Vanderkooi and T. DeVries, J. Phys. Chem. 60, 636 (1956).

(Ideal Gas) GFW = 61.47085

T, °K	Cp°	$\frac{\text{gibbs/mol}}{T}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	INFINITE	-2.554	32.801	32.801	INFINITE
100	7.468	46.584	65.084	-1.850	32.797	32.795	-70.646
200	10.870	52.389	57.389	-1.000	32.898	31.898	-34.704
300	12.820	56.459	58.459	-0.000	32.970	31.970	-22.950
400	14.638	59.526	59.526	+0.20	32.972	31.299	-22.801
500	16.164	61.644	60.760	1.146	32.972	30.723	-16.786
600	17.495	62.820	61.742	2.339	32.972	30.120	-13.166
700	18.627	64.083	62.715	3.581	32.969	29.500	-10.745
800	19.691	65.331	63.691	4.862	32.969	28.869	-9.013
900	20.700	66.561	64.641	6.177	32.969	28.232	-7.712
1000	21.657	67.771	65.571	7.521	32.969	27.589	-6.700
1100	22.567	68.961	66.481	8.890	32.969	26.943	-5.888
1200	23.433	70.133	67.343	10.270	32.969	26.294	-5.224
1300	24.260	71.288	68.168	11.660	32.969	25.643	-4.671
1400	25.052	72.428	68.952	13.050	32.969	24.992	-4.202
1500	25.812	73.555	69.695	14.440	32.969	24.341	-3.800
1600	26.544	74.671	70.401	15.820	32.969	23.686	-3.451
1700	27.252	75.777	71.077	17.190	32.969	23.028	-3.145
1800	27.932	76.875	71.725	18.540	32.969	22.371	-2.876
1900	28.588	77.958	72.348	19.870	32.969	21.712	-2.636
2000	29.225	79.028	72.948	21.180	32.969	21.056	-2.422
2100	29.848	80.085	73.525	22.470	32.969	20.393	-2.228
2200	30.458	81.130	74.078	23.740	32.969	19.732	-2.054
2300	31.058	82.163	74.608	25.000	32.969	19.066	-1.894
2400	31.648	83.185	75.115	26.240	32.969	18.405	-1.749
2500	32.228	84.198	75.598	27.460	32.969	17.739	-1.615
2600	32.798	85.203	76.063	28.670	32.969	17.070	-1.492
2700	33.358	86.198	76.510	29.860	32.969	16.401	-1.379
2800	33.908	87.183	76.938	31.030	32.969	15.731	-1.273
2900	34.448	88.158	77.348	32.180	32.969	15.062	-1.176
3000	34.978	89.123	77.743	33.310	32.969	14.390	-1.084
3100	35.498	90.078	78.123	34.420	32.969	13.716	-0.999
3200	36.008	91.023	78.488	35.510	32.969	13.043	-0.919
3300	36.508	91.958	78.838	36.580	32.969	12.365	-0.844
3400	37.000	92.883	79.173	37.630	32.969	11.687	-0.774
3500	37.483	93.798	79.493	38.660	32.969	11.012	-0.708
3600	37.958	94.703	79.798	39.670	32.969	10.331	-0.645
3700	38.423	95.598	80.088	40.660	32.969	9.652	-0.586
3800	38.878	96.483	80.363	41.630	32.969	8.971	-0.530
3900	39.323	97.358	80.623	42.580	32.969	8.294	-0.477
4000	39.758	98.223	80.868	43.510	32.969	7.614	-0.427
4100	40.183	99.078	81.103	44.420	32.969	6.937	-0.378
4200	40.598	99.923	81.328	45.310	32.969	6.261	-0.333
4300	41.003	100.758	81.543	46.180	32.969	5.587	-0.289
4400	41.398	101.583	81.748	47.030	32.969	4.872	-0.248
4500	41.783	102.398	81.943	47.860	32.969	4.188	-0.208
4600	42.158	103.203	82.128	48.670	32.969	3.497	-0.170
4700	42.523	103.998	82.303	49.460	32.969	2.811	-0.134
4800	42.878	104.783	82.468	50.230	32.969	2.121	-0.099
4900	43.223	105.558	82.623	50.980	32.969	1.433	-0.065
5000	43.558	106.323	82.768	51.710	32.969	0.740	-0.033
5100	43.883	107.078	82.903	52.420	32.969	0.054	-0.002
5200	44.198	107.823	83.028	53.110	32.969	-0.644	-0.028
5300	44.503	108.558	83.143	53.780	32.969	-1.332	-0.056
5400	44.798	109.283	83.248	54.430	32.969	-2.027	-0.084
5500	45.083	110.003	83.343	55.060	32.969	-2.717	-0.110
5600	45.358	110.718	83.428	55.670	32.969	-3.413	-0.136
5700	45.623	111.423	83.503	56.260	32.969	-4.113	-0.161
5800	45.878	112.118	83.568	56.830	32.969	-4.807	-0.184
5900	46.123	112.803	83.623	57.380	32.969	-5.505	-0.207
6000	46.358	113.478	83.668	57.910	32.969	-6.201	-0.230
6100	46.583	114.143	83.703	58.420	32.969	-6.896	-0.251

Dec. 31, 1980; June 30, 1981; June 30, 1986

CYANOGEN CHLORIDE (ClCN)

(IDEAL GAS)

OPW = 61.47085

Point Group C_{∞v} $\Delta H^\circ_f = 32.8 \text{ kcal/mol}$ $S^\circ_{298.15} = 56.459 \text{ gibbs/mol}$ $\Delta H^\circ_{298.15} = 32.97 \text{ kcal/mol}$

Round State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

 $\omega_j, \text{ cm}^{-1}$

714.52 (1)

378.3 (2)

2215.5 (1)

Bond Distances: Cl-C = 1.631 Å

C-N = 1.162 Å

Bond Angle: Cl-C-N = 180°

Rotational constants: B₀ = 0.19817 cm⁻¹D₀ = 5.503 X 10⁻⁸ cm⁻¹Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm⁻¹): $\alpha_1 = 8.25 \times 10^{-4}$ $\alpha_2 = -5.46 \times 10^{-4}$ $\alpha_3 = 1.06 \times 10^{-3}$ $x_{11} = [-4]$ $x_{22} = -0.85$ $x_{33} = [-7]$ $x_{12} = [-6.8]$ $x_{23} = -7.236$ $x_{13} = -2.8$ $\epsilon_{22} = 0.95$ $\epsilon_{23} = -2.8$

Heat of Formation:

The heat of formation was taken from D. D. Wagman, W. H. Evans, I. Helow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties" NBS Technical Note 270-1, Washington, 1965.

Heat Capacity and Entropy:

J. S. Gordon, AstroSystems International Inc., Fairfield, N. J., (private communication, Feb., 1966), has used the constants listed above to calculate C from 298.15 to 6000°K using the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The constants B₀ and D₀ were taken from C. A. Burrus and W. Gordy, Phys. Rev. 101, 599 (1956); ω_1 , α_1 , α_2 , α_3 , x_{11} , x_{22} , x_{13} and ϵ_{22} were obtained from W. J. Lafferty, D. R. Lide and R. A. Toth, J. Chem. Phys. 43, 2083 (1965); α_2 has been taken from C. H. Townes, A. N. Holden and P. R. Merritt, Phys. Rev. 74, 1113 (1948) and x_{11} , x_{33} and x_{12} were estimated by Gordon, loc. cit. The bond distances and bond angle were taken from Lafferty et al., loc. cit.

CCIN

Carbonyl Monochloride (COCl₂)

(Ideal Gas) Mol. Wt. = 63.46355

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f keal. mole ⁻¹	Log K _p
0	8.000	INFINITE	2.761	15.374	INFINITE
100	9.000	53.000	1.611	15.374	18.428
200	9.921	59.401	1.021	15.134	18.428
298	10.773	63.542	.000	15.000	13.467
300	10.784	63.609	.020	14.998	13.439
400	11.226	69.331	1.766	14.809	10.616
500	11.690	71.512	2.775	14.674	8.989
600	12.022	73.387	3.462	14.874	7.906
700	12.306	75.046	4.078	14.910	7.131
800	12.544	76.586	4.645	14.968	6.548
900	12.742	78.019	5.171	15.043	6.093
1000	12.906	79.367	5.659	15.126	5.727
1100	13.041	80.645	6.106	15.220	5.426
1200	13.152	81.873	6.523	15.320	5.173
1300	13.245	83.059	6.910	15.429	4.957
1400	13.323	84.204	7.267	15.540	4.771
1500	13.389	85.316	7.596	15.657	4.609
1600	13.445	86.392	7.901	15.778	4.466
1700	13.492	87.436	8.182	15.900	4.339
1800	13.533	88.450	8.440	16.028	4.225
1900	13.569	89.436	8.677	16.158	4.122
2000	13.600	90.397	8.894	16.292	4.028
2100	13.626	91.337	9.092	16.428	3.943
2200	13.650	92.250	9.273	16.570	3.865
2300	13.671	93.139	9.438	16.714	3.793
2400	13.689	94.007	9.588	16.862	3.727
2500	13.706	94.857	9.724	17.014	3.665
2600	13.720	95.690	9.847	17.171	3.608
2700	13.734	96.507	9.959	17.331	3.554
2800	13.746	97.307	10.061	17.495	3.504
2900	13.756	98.092	10.155	17.664	3.456
3000	13.766	98.862	10.242	17.838	3.412
3100	13.775	99.617	10.322	18.014	3.370
3200	13.783	100.358	10.397	18.197	3.330
3300	13.791	101.086	10.467	18.383	3.292
3400	13.797	101.802	10.532	18.574	3.256
3500	13.804	102.507	10.592	18.769	3.222
3600	13.809	103.202	10.648	18.968	3.189
3700	13.815	103.887	10.700	19.172	3.158
3800	13.819	104.562	10.748	19.379	3.128
3900	13.824	105.228	10.792	19.590	3.099
4000	13.828	105.885	10.832	19.806	3.071
4100	13.832	106.533	10.868	20.025	3.045
4200	13.836	107.173	10.900	20.248	3.019
4300	13.839	107.805	10.928	20.475	2.995
4400	13.842	108.429	10.953	20.704	2.971
4500	13.845	109.046	10.976	20.938	2.948
4600	13.848	109.656	10.996	21.174	2.926
4700	13.851	110.259	11.013	21.414	2.904
4800	13.853	110.856	11.028	21.657	2.883
4900	13.856	111.447	11.041	21.903	2.863
5000	13.858	112.032	11.052	22.151	2.843
5100	13.860	112.612	11.061	22.403	2.825
5200	13.861	113.187	11.068	22.657	2.806
5300	13.863	113.758	11.073	22.914	2.788
5400	13.865	114.324	11.077	23.174	2.770
5500	13.867	114.886	11.080	23.436	2.753
5600	13.868	115.444	11.082	23.701	2.736
5700	13.870	116.000	11.083	23.969	2.720
5800	13.871	116.552	11.084	24.239	2.704
5900	13.872	117.101	11.085	24.512	2.688
6000	13.874	117.646	11.086	24.787	2.673

Dec. 31, 1965

CARBONYL MONOCHLORIDE (COCl₂)

(IDEAL GAS)

MOL. WT. = 63.46355

Point Group C_{2v}

S_{298.15} = [64] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

(ω, cm.⁻¹)

570 (1)

281 (1)

1880 (1)

C-Cl = [1.75] Å

C-Cl-C = [120] °

Product of the Moments of Inertia: I_AI_BI_C = [1.27603 x 10⁻¹¹⁵] g.³ cm.⁶

Heat of Formation.

The enthalpy change (ΔH_f⁰) for the reaction COCl₂(g) = CO(g) + 2Cl(g) is calculated to be 82 kcal. mole⁻¹, which is the sum of two bond energies, i.e. D(Cl-COCl) + D(Cl-CO). By comparison with the values, D(H₃C-COCH₃)/D(H₃C-CO) = 72/18 = 4.0 for CH₃COC(=O)Cl/D(Cl-CO) = 4.3 for CH₃COCl(g), the ratio of D(Cl-COCl)/D(Cl-CO) is estimated to be 4.0 for COCl₂(g). Hence the enthalpy change for the reaction COCl₂(g) = COCl(g) + Cl(g) is calculated as 82 x (4/5) = 65.6 kcal. mole⁻¹. Using the ΔH_f⁰ value obtained, the heat of formation for COCl(g) is derived to be -15 ± 10 kcal. mole⁻¹.

Heat Capacity and Entropy.

The vibrational frequencies were reported by M. E. Jécox and D. E. Milligan, J. Chem. Phys. 43, 866 (1965).

The bond distances and angle were estimated by Jécox and Milligan, loc. cit. Due to the presence of one unpaired electron on C atom, the ground state quantum weight is calculated to be 2. The three principal moments of inertia are: I_A = 1.29987 x 10⁻³⁶, I_B = 7.1580 x 10⁻⁴⁰, and I_C = 1.37145 x 10⁻³⁸ g. cm.²

CARBON DICHLORIDE (CCl₂)

(IDEAL GAS)

GFW = 82.91715

Point Group C_{2v}

ΔHf°₀ = 56.7 ± 5 kcal/mol

S°_{298.15} = 63.4 ± 0.5 gibbs/mol

ΔHf°_{298.15} = 57.0 ± 5 kcal/mol

Ground State Quantum Weight = 1

Carbon Dichloride (CCl₂)

(Ideal Gas)

GFW = 82.91715

T, °K	Cp°	S° -(C°-H° ₂₉₈)/T	gibbs/mol	H°-H° ₂₉₈	ΔHf° kcal/mol	ΔGf°	Log Kp
0	8.900	INFINITE	INFINITE	-2.1722	56.724	56.724	INFINITE
100	8.922	53.086	72.287	-1.920	56.816	56.043	-122.482
200	9.120	49.520	64.363	-1.023	57.050	56.836	-39.835
298	11.054	43.392	56.832	0.000	57.000	56.791	-39.871
300	11.075	43.461	57.001	.020	57.001	54.377	-39.613
400	11.984	46.781	61.839	1.177	57.082	53.489	-29.225
500	12.559	49.522	64.709	2.406	57.139	52.584	-22.985
600	12.949	51.888	65.710	3.683	57.169	51.670	-18.821
700	13.259	53.668	67.338	4.993	57.176	50.753	-15.866
800	13.546	55.057	67.420	6.334	57.172	49.835	-13.614
900	13.835	57.269	67.711	7.703	57.164	48.918	-11.879
1000	14.132	59.742	68.641	9.101	57.162	48.001	-10.491
1100	14.428	60.103	70.531	10.529	57.170	47.084	-9.355
1200	14.713	61.371	71.382	11.986	57.191	46.167	-8.408
1300	14.975	62.559	72.197	13.471	57.225	45.247	-7.607
1400	15.206	63.677	72.977	14.980	57.274	44.325	-6.919
1500	15.401	64.733	73.726	16.511	57.335	43.398	-6.323
1600	15.557	65.732	74.445	18.059	57.405	42.465	-5.800
1700	15.677	66.679	75.138	19.621	57.484	41.531	-5.339
1800	15.762	67.578	75.804	21.193	57.566	40.589	-4.928
1900	15.816	68.432	76.446	22.772	57.651	39.644	-4.560
2000	15.843	69.244	77.066	24.355	57.734	38.695	-4.228
2100	15.847	70.017	77.668	25.940	57.817	37.741	-3.926
2200	15.834	70.754	78.243	27.524	57.892	36.781	-3.654
2300	15.806	71.457	78.802	29.106	57.963	35.823	-3.404
2400	15.767	72.129	79.344	30.685	58.026	34.859	-3.174
2500	15.721	72.772	79.868	32.260	58.081	33.891	-2.963
2600	15.668	73.387	80.376	33.829	58.126	32.923	-2.767
2700	15.612	73.978	80.869	35.393	58.162	31.952	-2.586
2800	15.554	74.544	81.347	36.951	58.188	30.983	-2.418
2900	15.495	75.089	81.812	38.504	58.204	30.010	-2.262
3000	15.436	75.613	82.263	40.050	58.209	29.036	-2.115
3100	15.378	76.119	82.702	41.591	58.205	28.065	-1.979
3200	15.322	76.604	83.126	43.126	58.190	27.093	-1.850
3300	15.267	77.077	83.545	44.655	58.164	26.120	-1.730
3400	15.215	77.532	83.949	46.179	58.130	25.152	-1.617
3500	15.165	77.972	84.344	47.698	58.085	24.178	-1.510
3600	15.118	78.398	84.728	49.213	58.033	23.212	-1.409
3700	15.073	78.812	85.103	50.722	57.970	22.247	-1.314
3800	15.030	79.213	85.469	52.227	57.900	21.282	-1.224
3900	14.990	79.603	85.827	53.728	57.821	20.322	-1.139
4000	14.952	79.982	86.176	55.225	57.734	19.361	-1.056
4100	14.917	80.351	86.517	56.719	57.641	18.399	-.981
4200	14.883	80.710	86.851	58.209	57.539	17.445	-.908
4300	14.852	81.060	87.177	59.695	57.430	16.490	-.836
4400	14.822	81.401	87.497	61.179	57.316	15.542	-.772
4500	14.793	81.734	87.809	62.660	57.195	14.590	-.709
4600	14.769	82.059	88.116	64.138	57.069	13.647	-.648
4700	14.745	82.376	88.416	65.614	56.938	12.706	-.591
4800	14.722	82.686	88.710	67.087	56.800	11.765	-.536
4900	14.701	82.990	88.998	68.558	56.658	10.831	-.483
5000	14.681	83.281	89.281	70.027	56.512	9.895	-.433
5100	14.662	83.577	89.558	71.495	56.362	8.963	-.384
5200	14.645	83.861	89.831	72.960	56.207	8.037	-.338
5300	14.628	84.140	90.098	74.424	56.048	7.111	-.293
5400	14.613	84.414	90.361	75.886	55.885	6.191	-.251
5500	14.598	84.682	90.619	77.346	55.717	5.274	-.210
5600	14.584	84.945	90.872	78.805	55.547	4.355	-.170
5700	14.571	85.203	91.121	80.263	55.372	3.437	-.132
5800	14.559	85.456	91.366	81.720	55.195	2.520	-.095
5900	14.548	85.705	91.607	83.175	55.013	1.606	-.060
6000	14.537	85.949	91.844	84.629	54.828	.720	-.026

Mar. 31, 1965; Dec. 31, 1968

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	1
[4000]	[3]
[17500]	[1]

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	
721 (1)	
721 (1)	
[3501] (1)	
748 (1)	

Bond Distance: C-Cl = [1.76] Å

Bond Angle: Cl-C-Cl = [100 ± 10°]

Product of Moments of Inertia: I_AI_BI_C = [1.1017] × 10⁻¹¹⁴ g³cm⁶

Heat of Formation

Shapiro and Jacox (1) have measured mass-spectrometrically the appearance potentials 12.2 and 14.7 eV for the processes CHCl₃(g) + e⁻ → CCl₂(g) + HCl(g) + 2e⁻ and C₂Cl₄(g) + e⁻ → CCl₂(g) + CCl₂(g) + 2e⁻, respectively. The difference in these two processes gives ΔHf° = 2.5 eV (57.65 kcal/mol) for the reaction C₂Cl₄(g) + HCl(g) → CCl₂(g) + CHCl₃(g) which leads to ΔHf°₂₉₈ (CCl₂, g) = 57.32 kcal/mol, using JANAF ΔHf°₂₉₈ = -2.97, -22.063 and -24.7 kcal/mol for C₂Cl₄(g), HCl(g) and CHCl₃(g), respectively. Since the authors claimed that the experimental error was probably 5 kcal/mol, the value, 57 ± 5 kcal/mol, is adopted for the heat of formation.

Heat Capacity and Entropy

Milligan and Jacox (2) have found two stretching fundamentals (721 and 748 cm⁻¹) for the CCl₂ radical in the infrared and ultraviolet spectra by matrix-isolation, and proposed a bent molecular structure (the valence angle = 100 ± 10°) with a ground singlet state which was based on the analogy with the electronic absorption spectrum of CF₂. L. Andrews (3) has confirmed all these observations in his infrared spectrometric studies of dichlorocarbene in solid argon, and made vibrational assignment to the fundamentals and also eliminated the possibility of a linear molecular structure for CCl₂. The bending frequency (350 cm⁻¹) is estimated by the valence force method (4), using the same ratio of bending over stretching force constants from CF₂(g) (5). The bond distance is estimated to be the same as that of CCl₄(g) measured by Bartell et al (6). The three principal moments of inertia are I_A = 2.1028 × 10⁻³⁹, I_B = 21.4013 × 10⁻³⁹, and I_C = 23.5840 × 10⁻³⁹ g cm².

The triplet low lying electronic level of 4000 cm⁻¹ is estimated by analogy with that of CF₂(g). The other level of 17,500 cm⁻¹ is also estimated based on a weak band appearing between 4400 and 5600 Å in the spectra of CCl₂ observed by Milligan and Jacox (2).

References

- (1) J. S. Shapiro and F. P. Lossing, J. Phys. Chem. **72**, 1552 (1968).
- (2) D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 703 (1967).
- (3) L. Andrews, J. Chem. Phys. **48**, 979 (1968).
- (4) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co. Inc., New York, 1945.
- (5) JANAF CF₂(g) table dated Sept. 30, 1966.
- (6) L. S. Bartell, L. O. Brockway and R. H. Schwendeman, J. Chem. Phys. **23**, 1854 (1955).

Point Group C_{2v}

Ground State Quantum Weight = 1

S_{298.15} = 71.91 ± 0.05 gibbs/mol

ΔHf° = -116.5 ± 2 kcal/mol

ΔHf°_{298.15} = -117.5 ± 2 kcal/mol

Dichlorodifluoromethane (CCl₂F₂)GF_W = 120.9140

(Ideal Gas)

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log K _p
0	9.473	57.674	INFINITE	3.553	-116.497	INFINITE
100	14.005	55.665	84.926	2.725	-117.074	249.663
200	17.307	71.911	73.396	1.546	-117.399	121.266
298	17.307	71.911	-0.000	-0.000	-117.500	79.315
300	17.359	72.018	71.911	-0.032	-117.501	78.784
400	19.463	77.351	72.423	1.691	-117.486	57.383
500	21.276	81.926	74.037	3.944	-117.414	44.540
600	22.371	85.907	75.691	6.130	-117.307	35.999
700	23.136	89.444	77.066	8.270	-117.152	29.326
800	23.687	91.754	78.100	10.260	-116.952	24.775
900	24.087	93.356	80.758	13.140	-116.615	21.775
1000	24.369	97.912	82.348	15.544	-116.776	18.938
1100	24.621	100.248	83.971	18.015	-116.637	16.020
1200	24.802	102.396	85.326	20.597	-116.385	14.066
1300	24.943	104.304	86.446	23.475	-116.231	12.166
1400	25.063	106.243	88.046	25.475	-116.231	11.661
1500	25.158	107.975	89.318	27.966	-116.101	10.452
1600	25.237	109.601	90.335	30.506	-115.974	9.396
1700	25.303	111.133	91.702	33.033	-115.948	8.464
1800	25.358	112.594	93.409	35.415	-115.906	7.638
1900	25.406	113.994	95.409	38.105	-115.848	6.898
2000	25.446	115.258	97.634	40.647	-115.491	6.234
2100	25.482	116.500	99.932	43.194	-115.376	5.633
2200	25.512	117.686	99.694	45.743	-115.289	5.080
2300	25.536	118.809	99.721	48.291	-115.081	4.574
2400	25.563	119.869	99.721	50.839	-114.965	4.134
2500	25.563	120.952	99.589	53.408	-114.965	3.715
2600	25.602	121.956	100.430	55.968	-114.672	3.329
2700	25.619	122.923	101.245	58.559	-114.784	2.971
2800	25.647	123.754	102.034	61.184	-114.784	2.631
2900	25.659	124.464	102.804	63.855	-114.624	2.311
3000	25.659	125.024	103.551	66.621	-114.552	2.043
3100	25.670	125.466	104.276	69.787	-114.485	1.774
3200	25.744	126.274	104.992	72.951	-114.424	1.522
3300	25.778	127.000	105.694	76.115	-114.320	1.282
3400	25.797	127.648	106.380	79.482	-114.320	1.062
3500	25.705	128.563	106.994	79.062	-114.276	0.853
3600	25.712	130.307	107.631	81.633	-114.239	0.654
3700	25.718	131.012	108.254	84.205	-114.207	0.467
3800	25.730	132.366	109.556	89.350	-114.180	0.281
3900	25.735	133.018	110.037	91.923	-114.145	0.121
4000	25.735	133.018	110.037	91.923	-114.145	0.039
4100	25.739	133.653	110.605	94.497	-114.135	3.583
4200	25.744	134.274	111.161	97.071	-114.132	6.456
4300	25.752	134.874	111.700	99.645	-114.120	9.336
4400	25.752	135.471	112.220	102.220	-114.110	12.201
4500	25.755	136.050	112.762	104.796	-114.151	15.066
4600	25.759	136.616	113.275	107.371	-114.187	17.940
4700	25.762	137.170	113.777	109.947	-114.168	20.814
4800	25.767	137.714	114.264	112.514	-114.244	23.688
4900	25.770	138.244	114.754	115.100	-114.244	26.564
5000	25.770	138.764	115.229	117.677	-116.278	29.435
5100	25.772	139.275	115.695	120.254	-114.317	32.304
5200	25.775	139.775	116.154	122.832	-114.359	35.179
5300	25.779	140.268	116.608	125.410	-114.402	38.054
5400	25.779	141.221	117.047	127.987	-114.459	40.929
5500	25.781	141.221	117.047	130.565	-114.515	43.804
5600	25.763	141.686	117.910	133.143	-114.575	46.679
5700	25.765	142.162	118.772	135.722	-114.640	49.551
5800	25.768	142.631	119.631	138.301	-114.701	52.426
5900	25.768	143.031	119.484	140.879	-114.781	55.301
6000	25.789	143.465	119.555	143.458	-114.858	58.176

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

Vibrational Frequencies and Degeneracies

ω_1 , cm ⁻¹	ω_2 , cm ⁻¹	ω_3 , cm ⁻¹	ω_4 , cm ⁻¹
1099 (1)	457.5 (1)	436 (1)	
261.5 (1)	322 (1)	1162 (1)	
667.2 (1)	922 (1)	446 (1)	
Bond Distance: C-Cl = 1.77 ± 0.02 Å C-F = 1.33 ± 0.02 Å			
Bond Angle: F-C-F = 109.5 ± 3° Cl-C-Cl = 108.5 ± 2°			
Product of the Moments of Inertia: I _A I _B I _C = 2.5841 × 10 ⁻¹¹³ g ³ cm ⁻⁶			
Heat of Formation			

Mears and Stahl (1) investigated several heats of reaction involving CF₄, CF₃Cl, CF₂Cl₂, CFCI₃, CCl₄, HF and HCl. Using JANAF values for all compounds except CF₂Cl₂ and CFCI₃ we obtain the following observations:

- ΔHf^o (CCl₃F, g) = -70.12 ± 1.1 kcal/mol
- ΔHf^o (CCl₂F₂, g) = -116.53 ± 1.5 kcal/mol
- ΔHf^o (CCl₃F, g) - ΔHf^o (CCl₂F₂, g) = -49.39 ± 1.0 kcal/mol
- ΔHf^o (CCl₂F₂, g) - 2ΔHf^o (CCl₃F, g) = 20.34 ± 1.0 kcal/mol
- ΔHf^o (CCl₃F, g) - 2ΔHf^o (CCl₂F₂, g) = 165.47 ± 1.0 kcal/mol

The sum of the squares of the deviations is smallest when ΔHf^o (CCl₂F₂, g) = -117.5 kcal/mol and ΔHf^o (CCl₃F, g) = -69 kcal/mol, and all the values are within their uncertainty ranges.

Petersen and Pitzer (2) obtained an approximate equilibrium constant for the reaction 2CCl₃F(g) + CCl₄(g) = 3CCl₂F₂(g) of log K₄₀₀ = -3.0. This on 3rd law reduction gives ΔH^o = 7.64 kcal and with ΔHf^o (CCl₂F₂, g) = -117.9 kcal/mol. ΔHf^o (CCl₄, g) = -22.94 kcal/mol this yields ΔHf^o (CCl₃F, g) = 20.34 ± 1.0 kcal/mol.

Kirkbride and Davidson (3) investigated the reaction of potassium with the chlorofluoromethanes and obtained

ΔHf^o (CCl₂F₂, g) = -115.1 ± 2 kcal/mol and ΔHf^o (CCl₃F, g) = -72.9 ± 4 kcal/mol after correction with JANAF auxiliary data. Wartenberg and Schiefer (4) investigated the same reaction and we obtain, after correction with JANAF auxiliary data, ΔHf^o (CCl₂F₂, g) = -112.7 kcal/mol and ΔHf^o (CCl₃F, g) = -63.1 kcal/mol. Kolesov et al. (4) have reported analogous data for the reaction with sodium which, after correction with JANAF auxiliary data, yields

ΔHf^o (CCl₂F₂, g) = -114.4 ± 3.5 kcal/mol.

We adopt the values calculated above from Mears and Stahl (1), since they have a high degree of internal consistency and also lead to a realistic progression in the heats of atomization in going from CF₄ to CCl₄. With the adopted heats of formation, the successive replacement of F by Cl changes the atomization heats by 43.8, 41.6, 38.5 and 36.0 kcal.

Heat Capacity and Entropy

Classen (5) chose the frequencies given above from his own gas-phase Raman measurements and the infrared values of earlier investigators. The values are in good agreement with the assignment of Plyler and Benedict (6). Masi (7) has measured the gas phase heat capacities at 243, 273, 318 and 363°K, within this range our adopted heat capacities are from .3 to .7% high. The entropies agree to within 0.05% and further adjustment to obtain better fits was not considered necessary. The molecular structure was determined from the microwave measurements of Long et al. (7). The individual moments of inertia were: I_A = 31.928 × 10⁻³⁹ g cm², I_B = 21.216 × 10⁻³⁹ g cm², and I_C = 38.148 × 10⁻³⁹ g cm².

References

- W. H. Mears and R. F. Stahl, IUPAC Thermochemical Bulletin 2, 5 (1956).
- F. W. Kirkbride and F. G. Davidson, Nature 174, 79 (1954).
- H. Wartenberg and J. Schiefer, Z. Anorg. Chem. 228, 326 (1955).
- V. P. Kolesov, I. D. Zenkov, and S. M. Skuratov, Russ. J. Phys. Chem. (English Trans.) 37, 378 (1963).
- H. H. Classen, J. Chem. Phys. 22, 50 (1954).
- E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std. 47, 202 (1951).
- M. W. Long, Q. Williams, and T. L. Weatherly, J. Chem. Phys. 33, 508 (1960).
- D. E. Petersen and K. S. Pitzer, J. Phys. Chem. 63, 1252 (1957).
- J. F. Masi, J. Amer. Chem. Soc. 74, 4738 (1952) and 75, 2276 (1953).

T, °K.	C _p	S° est. mole ⁻¹ deg ⁻¹	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f kcal. mole ⁻¹	ΔF°	Log K _F
0	8.000	55.000	INF	0	55.192	-	INF
100	11.559	59.012	1.252	2.973	55.192	-	55.192
200	13.700	67.816	1.000	1.252	55.192	-	55.192
298	13.823	67.801	0.766	0.766	55.192	-	55.192
300	13.823	67.801	0.766	0.766	55.192	-	55.192
400	15.266	73.055	0.922	1.066	55.192	-	55.192
500	16.981	78.687	1.076	1.220	55.192	-	55.192
600	17.515	81.307	1.220	1.366	55.192	-	55.192
700	17.924	83.664	1.366	1.512	55.192	-	55.192
800	18.251	85.800	1.512	1.658	55.192	-	55.192
900	18.500	87.739	1.658	1.804	55.192	-	55.192
1000	18.693	89.512	1.804	1.950	55.192	-	55.192
1100	18.853	91.145	1.950	2.096	55.192	-	55.192
1200	18.986	92.660	2.096	2.242	55.192	-	55.192
1300	19.096	94.077	2.242	2.388	55.192	-	55.192
1400	19.186	95.392	2.388	2.534	55.192	-	55.192
1500	19.262	96.632	2.534	2.680	55.192	-	55.192
1600	19.326	97.802	2.680	2.826	55.192	-	55.192
1700	19.379	98.909	2.826	2.972	55.192	-	55.192
1800	19.423	99.959	2.972	3.118	55.192	-	55.192
1900	19.459	100.955	3.118	3.264	55.192	-	55.192
2000	19.504	101.906	3.264	3.410	55.192	-	55.192
2100	19.536	102.814	3.410	3.556	55.192	-	55.192
2200	19.568	103.684	3.556	3.702	55.192	-	55.192
2300	19.597	104.524	3.702	3.848	55.192	-	55.192
2400	19.625	105.336	3.848	3.994	55.192	-	55.192
2500	19.650	106.066	3.994	4.140	55.192	-	55.192
2600	19.672	106.724	4.140	4.286	55.192	-	55.192
2700	19.691	107.314	4.286	4.432	55.192	-	55.192
2800	19.707	107.839	4.432	4.578	55.192	-	55.192
2900	19.721	108.299	4.578	4.724	55.192	-	55.192
3000	19.735	108.699	4.724	4.870	55.192	-	55.192
3100	19.699	109.544	4.870	5.016	55.192	-	55.192
3200	19.709	110.170	5.016	5.162	55.192	-	55.192
3300	19.727	111.365	5.162	5.308	55.192	-	55.192
3400	19.735	111.937	5.308	5.454	55.192	-	55.192
3500	19.743	112.493	5.454	5.600	55.192	-	55.192
3600	19.750	113.035	5.600	5.746	55.192	-	55.192
3700	19.750	113.035	5.746	5.892	55.192	-	55.192
3800	19.752	114.075	5.892	6.038	55.192	-	55.192
3900	19.752	114.075	6.038	6.184	55.192	-	55.192
4000	19.757	114.575	6.184	6.330	55.192	-	55.192
4100	19.772	115.083	6.330	6.476	55.192	-	55.192
4200	19.777	115.560	6.476	6.622	55.192	-	55.192
4300	19.785	116.000	6.622	6.768	55.192	-	55.192
4400	19.785	116.000	6.768	6.914	55.192	-	55.192
4500	19.789	116.904	6.914	7.060	55.192	-	55.192
4600	19.793	117.339	7.060	7.206	55.192	-	55.192
4700	19.799	117.765	7.206	7.352	55.192	-	55.192
4800	19.802	118.176	7.352	7.498	55.192	-	55.192
4900	19.802	118.590	7.498	7.644	55.192	-	55.192
5000	19.805	118.990	7.644	7.790	55.192	-	55.192
5100	19.807	119.383	7.790	7.936	55.192	-	55.192
5200	19.810	120.765	7.936	8.082	55.192	-	55.192
5300	19.810	120.765	8.082	8.228	55.192	-	55.192
5400	19.816	120.878	8.228	8.374	55.192	-	55.192
5500	19.816	120.878	8.374	8.520	55.192	-	55.192
5600	19.818	121.236	8.520	8.666	55.192	-	55.192
5700	19.820	121.586	8.666	8.812	55.192	-	55.192
5800	19.820	121.586	8.812	8.958	55.192	-	55.192
5900	19.824	122.270	8.958	9.104	55.192	-	55.192
6000	19.825	122.603	9.104	9.250	55.192	-	55.192

June 30, 1961

CARBONYL DICHLORIDE (COCl₂) (IDEAL GAS)

ΔH°_f = -52.2 ± 0.8 kcal. mole⁻¹
Point Group C_{2v}
ΔH°_f 298.15 = -52.2 ± 0.8 kcal. mole⁻¹
S°_{298.15} = 67.816 cal. deg⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

(J, cm ⁻¹)	(570) (1)	(1827) (1)	(285) (1)	(849) (1)	(440) (1)	(585) (1)
------------------------	-----------	------------	-----------	-----------	-----------	-----------

Interatomic distances: C-O 1.166 ± 0.002 Å
C1-O 2.589 ± 0.001
C1-Cl 2.884 ± 0.001
C-Cl 1.746 ± 0.004
Cl-C-Cl angle 111.3 ± 0.1°

Moments of inertia: I_A = 1.0690 X 10⁻³⁸ g. cm.² I_B = 2.4489 X 10⁻³⁸ I_C = 3.5291 X 10⁻³⁸ σ = 2

Heat of Formation

J. Thomsen, Thermochemische Untersuchungen, Barth, Leipzig, 1882, Vol. 2, p. 361, reports the heat of alkali line hydrolysis of COCl₂, from which ΔH°_f 298.15 is calculated to be -54.4 ± 0.3 kcal. mole⁻¹. From the heat of combustion of COCl₂ in O₂ and H₂, reported by Thomsen, op. cit., p. 363, ΔH°_f 298.15 is calculated to be -51.73 ± 0.43 kcal. mole⁻¹. M. Bodenstein and H. Plaut, Z. Phys. Chem. 110, 399 (1924), J. A. Christiansen, ibid. 103, 99 (1923), and M. Bodenstein and O. Duanat, ibid. 61, 437 (1908), report 10 values of K_p from 647° to 876°K for the reaction CO + Cl₂ ⇌ COCl₂. These yield -25.91 ± 0.04 kcal. for ΔH°_f 298.15, whence ΔH°_f 298.15 for COCl₂ is -52.33 ± 0.62 kcal. mole⁻¹. The average of the 5 foregoing values of ΔH°_f 298.15, weighted for the uncertainties, is adopted here. Values calculated from the degrees of dissociation of COCl₂ from 374° to 778°K, reported by R. H. Atkinson, C. T. Heycock, and W. J. Pope, J. Chem. Soc. 117, 1410 (1920), range from -47.06 to -53.11 kcal. mole⁻¹ and are ignored.

Heat Capacity and Entropy

The vibrational frequencies were assigned by E. Catalano and K. S. Pitzer, J. Am. Chem. Soc. 80, 1054 (1958), on the basis of their own infra-red spectra and other data. The molecular dimensions listed above were deduced from microwave spectra by G. W. Robinson, J. Chem. Phys. 21, 1741 (1953), and are confirmed by electron-diffraction values compiled by P. W. Allen and L. E. Sutton, Acta Cryst. 2, 46 (1950). The moments of inertia are weighted for the isotopes and were calculated from Robinson's dimensions by M. F. Olafson and J. B. Ott, J. Am. Chem. Soc. 82, 2689 (1960). Olafson and Ott, loc. cit., determined S°_{298.15} experimentally to be 67.81 cal. deg⁻¹ mole⁻¹, with which the value calculated here agrees.

CCl₂ 20

Trichloromethyl (CCl₃)
(Ideal Gas)

GFW = 118.37015

TRICHLOROMETHYL (CCl₃)

(IDEAL GAS)

Point Group D_{3h}

GFW = 118.37015

 $\Delta H_f^\circ = 19.15 \pm 2 \text{ kcal/mol}$ $\Delta H_f^\circ(298.15) = 19 \pm 2 \text{ kcal/mol}$ $S_{298.15}^\circ = 70.92 \pm 1.5 \text{ gibbs/mol}$

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

in cm⁻¹

[450] (1)

[460] (1)

898 (2)

[240] (2)

Bond Distance: C-Cl = [1.74] Å

Bond Angle: Cl-C-Cl = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [3.8215 \times 10^{-113}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

Benson (1) has reanalysed the kinetic data of Sullivan and Davidson (2) for the reaction $\text{Br}_2(\text{g}) + \text{CHCl}_3(\text{g}) = \text{HBr}(\text{g}) + \text{CH}_2\text{Cl}_2(\text{g})$ and has obtained from it the heat of the initial step, $\text{Br}(\text{g}) + \text{CHCl}_3(\text{g}) = \text{CCl}_3(\text{g}) + \text{HBr}(\text{g})$, as $8.2 \pm 1 \text{ kcal/mol}$. Substituting this value and $\Delta H_f^\circ(298) (\text{Br}) = 26.74 \text{ kcal/mol}$, $\Delta H_f^\circ(298) (\text{CHCl}_3) = -24.66 \text{ kcal/mol}$ and $\Delta H_f^\circ(298) (\text{HBr}) = -8.71 \text{ kcal/mol}$, we obtain $\Delta H_f^\circ(298) (\text{CCl}_3, \text{g}) = 19 \pm 2 \text{ kcal/mol}$, which is adopted here.

Heat Capacity and Entropy

Walsh (3) has predicted that CCl_3 is non-planar on the basis of his orbital correlation diagram. Andrews (4) indicates that his matrix infrared observations of the symmetric and antisymmetric stretches are consistent with a non-planar C_3v structure and a near tetrahedral angle. The antisymmetric stretch has been confirmed by Current and Burdett (5). They rationalize the absence of the symmetric stretch and claim support of the C_3v structure. Rogers et al. (6) have made a thorough search for the symmetric stretch and did not find it in the region where it was reported by Andrews (4). Thus, they conclude that since only the antisymmetric stretch has been confirmed, the possibility of a planar D_3h molecule cannot be excluded. Hagat et al. (7) have observed the NMR spectrum of trapped CCl_3 and find it consistent with a planar molecule. The absence of the symmetric stretch strongly implies a planar configuration, and we adopt such a configuration until more definitive proof of the non-planarity can be obtained. The remaining vibrational frequencies are estimated by comparison with those of BCl_3 . The bond length was estimated as 1.74 Å by Andrews (4) from a correlation with related molecules. The individual moments of inertia are $I_A = I_B = 2.6734 \times 10^{-38} \text{ g cm}^2$ and $I_C = 5.3468 \times 10^{-38} \text{ g cm}^2$.

References

1. S. W. Benson, *J. Chem. Phys.*, **43**, 2044 (1965).
2. J. H. Sullivan and N. Davidson, *J. Chem. Phys.*, **19**, 143 (1951).
3. A. D. Walsh, *J. Chem. Soc. (London)*, **1953**, 2301 (1953).
4. L. Andrews, *J. Chem. Phys.*, **48**, 972 (1968).
5. J. H. Current and J. K. Burdett, *J. Phys. Chem.*, **73**, 3504 (1969).
6. E. E. Rogers, S. Abramowitz, M. E. Jacob and D. E. Milligan, *J. Chem. Phys.*, **52**, 2198 (1970).
7. M. Hagat, N. Leray and J. Roncin, *Vysokomolekulyarnye Soedineniya*, Vsesoyuz. Khim. Obshch. D. I. Mendeleeva, **11**, 223 (1966).

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	3.392	19.151	INFINITE	
100	9.795	57.405	62.694	2.549	19.089	43.686	
200	13.070	65.271	72.246	1.395	18.923	21.000	23.013
298	15.212	70.918	79.918	0.000	19.000	22.093	16.195
300	15.245	71.012	80.018	-0.028	19.002	22.112	16.109
400	16.658	75.606	71.535	1.628	19.111	23.133	12.639
500	17.564	79.428	72.742	3.343	19.227	24.126	10.545
600	18.156	82.066	74.135	5.131	19.333	25.095	9.141
700	18.555	85.517	75.563	6.968	19.428	26.049	7.133
800	18.895	88.744	77.020	8.842	19.512	27.017	5.133
900	19.035	90.244	78.320	10.732	19.582	27.917	3.679
1000	19.184	92.259	79.615	12.643	19.647	28.836	2.303
1100	19.297	94.092	80.849	14.567	19.702	29.765	1.112
1200	19.385	95.775	82.023	16.502	19.751	30.697	0.185
1300	19.459	97.273	83.147	18.446	19.795	31.621	-0.781
1400	19.509	98.647	84.224	20.392	19.827	32.534	-1.681
1500	19.555	100.121	85.224	22.345	19.857	33.434	-2.514
1600	19.592	101.384	86.195	24.303	19.883	34.283	-3.282
1700	19.623	102.573	87.123	26.264	19.906	35.185	-4.023
1800	19.650	103.700	88.017	28.234	19.926	36.102	-4.721
1900	19.672	104.772	88.867	30.214	19.943	37.022	-5.381
2000	19.691	105.768	89.687	32.162	19.951	37.877	-6.019
2100	19.708	106.729	90.476	34.131	19.961	38.773	-6.635
2200	19.722	107.646	91.235	36.103	19.965	39.697	-7.221
2300	19.735	108.523	91.965	38.075	19.973	40.650	-7.775
2400	19.745	109.363	92.675	40.050	19.981	41.623	-8.303
2500	19.755	110.169	93.359	42.025	19.986	42.615	-8.803
2600	19.764	110.944	94.021	44.001	19.997	43.622	-9.273
2700	19.772	111.690	94.661	45.978	19.992	44.647	-9.713
2800	19.778	112.410	95.282	47.953	19.987	45.693	-10.123
2900	19.785	113.104	95.882	49.923	19.982	46.761	-10.503
3000	19.791	113.774	96.470	51.912	19.977	47.842	-10.853
3100	19.796	114.423	97.039	53.892	19.972	48.942	-11.183
3200	19.800	115.052	97.592	55.871	19.968	50.063	-11.493
3300	19.805	115.661	98.131	57.852	19.963	51.203	-11.783
3400	19.810	116.250	98.656	59.834	19.958	52.363	-12.053
3500	19.812	116.827	99.166	61.813	19.954	53.542	-12.303
3600	19.815	117.385	99.664	63.795	19.952	54.742	-12.533
3700	19.818	117.928	100.151	65.776	19.949	55.963	-12.743
3800	19.821	118.457	100.625	67.756	19.947	57.203	-12.933
3900	19.823	118.971	101.089	69.734	19.945	58.463	-13.103
4000	19.826	119.473	101.543	71.723	19.940	59.743	-13.253
4100	19.828	119.963	101.986	73.706	19.937	61.043	-13.393
4200	19.830	120.441	102.420	75.689	19.934	62.363	-13.513
4300	19.832	120.900	102.843	77.669	19.931	63.703	-13.613
4400	19.834	121.343	103.256	79.645	19.928	65.063	-13.693
4500	19.836	121.769	103.657	81.619	19.925	66.443	-13.753
4600	19.837	122.185	104.066	83.622	19.922	67.843	-13.793
4700	19.839	122.672	104.456	85.666	19.919	69.263	-13.813
4800	19.841	123.139	104.834	87.746	19.916	70.703	-13.823
4900	19.843	123.589	105.201	89.866	19.913	72.163	-13.823
5000	19.844	123.999	105.558	91.958	19.910	73.643	-13.813
5100	19.845	124.392	105.901	93.942	19.906	75.143	-13.793
5200	19.845	124.778	106.207	95.927	19.902	76.663	-13.763
5300	19.846	125.152	106.499	97.911	19.898	78.203	-13.723
5400	19.847	125.519	106.776	99.894	19.894	79.763	-13.673
5500	19.847	125.791	107.040	101.881	19.890	81.343	-13.613
5600	19.848	126.148	107.272	103.865	19.886	82.943	-13.543
5700	19.849	126.500	107.483	105.845	19.882	84.563	-13.463
5800	19.850	126.843	107.676	107.820	19.878	86.203	-13.373
5900	19.851	127.176	107.853	109.790	19.874	87.863	-13.273
6000	19.851	127.518	108.050	111.845	19.870	89.543	-13.163

Trichlorofluoromethane (CCl₃F)

(Ideal Gas) GFW = 137.3686

T, °K	C _p ^o	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	0.000	0.000	0.000	0.000	0.000	0.000	INFINITE
100	10.377	56.377	56.377	56.377	56.377	56.377	14.805
200	15.394	67.203	75.612	1.682	69.006	62.702	68.517
298	18.646	74.002	74.002	0.000	69.000	59.604	43.691
300	18.695	74.117	74.002	0.035	68.969	59.546	43.379
400	20.211	84.617	78.266	4.175	68.736	53.305	29.300
500	21.423	92.367	82.367	6.445	68.584	50.236	18.298
600	22.475	98.568	86.515	8.700	68.386	47.194	12.735
700	23.412	103.395	89.814	11.188	68.210	44.160	8.070
800	24.258	107.129	92.685	13.605	68.058	41.130	4.210
900	24.938	110.029	95.184	16.085	67.902	38.215	0.352
1000	25.491	112.628	97.436	18.568	67.694	35.259	7.005
1200	25.953	115.569	99.814	21.066	67.530	32.316	5.886
1300	26.163	117.579	99.443	23.579	67.372	29.389	4.941
1400	26.332	119.479	99.109	26.027	67.214	26.471	4.132
1500	26.473	121.192	98.812	28.427	67.066	23.566	3.434
1600	26.584	122.734	98.543	30.774	66.920	20.673	2.824
1700	26.672	124.132	98.294	33.070	66.776	17.784	2.286
1800	26.745	125.408	98.065	35.316	66.637	14.909	1.810
1900	26.804	126.584	97.854	37.514	66.502	12.048	1.396
2000	26.853	127.680	97.652	39.666	66.368	9.192	1.002
2100	26.895	128.705	97.458	41.774	66.236	6.317	0.657
2200	26.932	129.668	97.272	43.837	66.103	3.469	0.345
2300	26.963	130.568	97.094	45.855	65.971	0.599	0.059
2400	26.989	131.407	96.921	47.828	65.840	-2.260	-0.442
2500	27.011	132.187	96.752	49.754	65.711	-5.032	-0.942
2600	27.029	132.918	96.587	51.631	65.585	-7.804	-1.442
2700	27.043	133.599	96.426	53.458	65.460	-10.576	-1.942
2800	27.054	134.230	96.268	55.234	65.336	-13.348	-2.442
2900	27.062	134.818	96.113	56.960	65.212	-16.120	-2.942
3000	27.067	135.363	95.960	58.636	65.088	-18.892	-3.442
3100	27.071	135.874	95.809	60.261	64.964	-21.664	-3.942
3200	27.073	136.350	95.660	61.836	64.840	-24.436	-4.442
3300	27.074	136.791	95.513	63.361	64.716	-27.208	-4.942
3400	27.074	137.197	95.368	64.836	64.592	-30.000	-5.442
3500	27.073	137.568	95.224	66.261	64.468	-32.772	-5.942
3600	27.071	137.904	95.080	67.636	64.344	-35.544	-6.442
3700	27.067	138.205	94.937	68.961	64.220	-38.316	-6.942
3800	27.062	138.471	94.794	70.236	64.096	-41.088	-7.442
3900	27.056	138.702	94.651	71.461	63.972	-43.860	-7.942
4000	27.049	138.900	94.508	72.636	63.848	-46.632	-8.442
4100	27.041	139.064	94.365	73.761	63.724	-49.404	-8.942
4200	27.032	139.194	94.222	74.836	63.600	-52.176	-9.442
4300	27.022	139.290	94.079	75.861	63.476	-54.948	-9.942
4400	27.011	139.353	93.936	76.836	63.352	-57.720	-10.442
4500	27.000	139.384	93.793	77.761	63.228	-60.492	-10.942
4600	26.988	139.384	93.650	78.636	63.104	-63.264	-11.442
4700	26.975	139.353	93.507	79.461	62.980	-66.036	-11.942
4800	26.962	139.290	93.364	80.236	62.856	-68.808	-12.442
4900	26.949	139.194	93.221	81.011	62.732	-71.580	-12.942
5000	26.936	139.064	93.078	81.786	62.608	-74.352	-13.442
5100	26.923	138.900	92.935	82.561	62.484	-77.124	-13.942
5200	26.909	138.702	92.792	83.286	62.360	-79.896	-14.442
5300	26.895	138.471	92.649	84.011	62.236	-82.668	-14.942
5400	26.882	138.205	92.506	84.686	62.112	-85.440	-15.442
5500	26.869	137.904	92.363	85.311	61.988	-88.212	-15.942
5600	26.856	137.568	92.220	85.886	61.864	-90.984	-16.442
5700	26.843	137.194	92.077	86.411	61.740	-93.756	-16.942
5800	26.830	136.791	91.934	86.936	61.616	-96.528	-17.442
5900	26.817	136.353	91.791	87.461	61.492	-99.300	-17.942
6000	26.804	135.874	91.648	87.936	61.368	-102.072	-18.442

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

Point Group C_{3v}

$S_{298.15}^{\circ} = 74.00 \pm 0.05$ gibbs/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_1, cm^{-1} ω_2, cm^{-1}

349.5 (1) 241 (2)

535.3 (1) 398 (2)

1085 (1) 847 (2)

Bond Distance: C-Cl = 1.76 Å C-F = 1.33 Å

Bond Angle: Cl-C-Cl = $109^{\circ}40'$ F-C-Cl = $109^{\circ}28'$

Product of the Moments of Inertia: $I_{AB}I_C = 5.73499 \times 10^{-113} \text{ g cm}^{-6}$ $\sigma = 3$

Heat of Formation

Wears and Stahl (1) investigated several heats of reaction involving CF_4 , CF_3Cl , CF_2Cl_2 , CFCl_3 , CCl_4 , HF and HCl.

Using JANAF values for all compounds except CF_2Cl_2 and CFCl_3 , we obtain the following observations:

1. $\Delta H_{298}^{\circ}(\text{CCl}_3\text{F}, g) = -70.12 \pm 1.1$ kcal/mol
2. $\Delta H_{298}^{\circ}(\text{CCl}_2\text{F}_2, g) = -116.53 \pm 1.5$ kcal/mol
3. $\Delta H_{298}^{\circ}(\text{CCl}_2\text{F}_2, g) - \Delta H_{298}^{\circ}(\text{CCl}_3\text{F}, g) = -49.39 \pm 1.0$ kcal/mol
4. $\Delta H_{298}^{\circ}(\text{CCl}_2\text{F}_2, g) - 2\Delta H_{298}^{\circ}(\text{CCl}_3\text{F}, g) = 20.34 \pm 1.0$ kcal/mol
5. $\Delta H_{298}^{\circ}(\text{CCl}_3\text{F}, g) - 2\Delta H_{298}^{\circ}(\text{CCl}_2\text{F}_2, g) = 165.47 \pm 1.0$ kcal/mol

The sum of the squares of the deviations is smallest when $\Delta H_{298}^{\circ}(\text{CCl}_2\text{F}_2, g) = -117.5$ kcal/mol and $\Delta H_{298}^{\circ}(\text{CCl}_3\text{F}, g) = -69$ kcal/mol, and all the values are within their uncertainty ranges.

Petersen and Pitzer (2) obtained an approximate equilibrium constant for the reaction $\text{CClF}_3(g) + 2\text{CCl}_4(g) = 3\text{CCl}_3\text{F}(g)$ of $\log K_{1400} = -4.5$. This on 3rd law reduction gives $\Delta H_{298}^{\circ} = 10.56$ kcal and with $\Delta H_{298}^{\circ}(\text{CClF}_3, g) = -169.2$ kcal/mol and $\Delta H_{298}^{\circ}(\text{CCl}_4, g) = -22.94$ kcal/mol this yields $\Delta H_{298}^{\circ}(\text{CCl}_3\text{F}, g) = -68.2$ kcal/mol.

Kirkbridge and Davidson (2) investigated the reaction of potassium with the chlorofluoromethanes and obtained $\Delta H_{298}^{\circ}(\text{CCl}_2\text{F}_2, g) = -115.1 \pm 2$ kcal/mol and $\Delta H_{298}^{\circ}(\text{CCl}_3\text{F}, g) = -72.9 \pm 4$ kcal/mol after correction with JANAF auxiliary data. Wartenberg and Schiefer (3) investigated the same reaction and we obtain, after correction with JANAF

auxiliary data, $\Delta H_{298}^{\circ}(\text{CCl}_2\text{F}_2, g) = -112.7$ kcal/mol and $\Delta H_{298}^{\circ}(\text{CCl}_3\text{F}, g) = -63.1$ kcal/mol. Baibuz (4) has reported $\Delta H_{298}^{\circ}(\text{CCl}_3\text{F}, g) = -66.4 \pm 2.1$ from heat of explosion measurements. A correlation of his other results would indicate that this value is not negative enough, possibly by as much as 3 kcal.

We adopt the values calculated above from Wears and Stahl (1), since they have a high degree of internal consistency and also lead to a realistic progression in the heats of atomization in going from CF_4 to CCl_4 . With the adopted heats of formation, the successive replacement of F by Cl changes the atomization heats by 43.8, 41.6, 38.5 and 36.0 kcal.

Heat Capacity and Entropy

Claassen (5) chose the frequencies given above from his own gas phase Raman measurements and the infrared values of earlier investigators. The values are in good agreement with the assignment of Plyler and Benedict (6), and the matrix studies of King (7). The molecular structure was determined from the microwave measurements of Long et al. (8). The individual moments of inertia were: $I_A = I_C = 34.301 \times 10^{-39} \text{ g cm}^2$ and $I_B = 40.744 \times 10^{-39} \text{ g cm}^2$.

References

1. W. H. Mears and R. F. Stahl, IUPAC Thermochemical Bulletin 2, 5 (1955).
2. F. W. Kirkbridge and F. G. Davidson, Nature 174, 79 (1954).
3. H. Wartenberg and J. Schiefer, Z. Anorg. Chem. 278, 326 (1955).
4. V. F. Baibuz, Dokl. Akad. Nauk SSSR, 140 1358 (1961).
5. H. H. Claassen, J. Chem. Phys. 22, 50 (1954).
6. E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std. 47, 202 (1951).
7. S. T. King, J. Chem. Phys. 19, 1321 (1956).
8. M. W. Long, Q. Williams, and T. L. Weatherly, J. Chem. Phys. 33, 508 (1960).
9. D. E. Petersen and K. S. Pitzer, J. Phys. Chem. 61, 1252 (1957).

CARBON TETRACHLORIDE (CCl₄)
 (IDEAL GAS)
 GFW = 153.82315
 Point Group T_d
 S_{298.15} = 74.02 ± 0.01 gibbs/mol
 ΔH_{f,0}⁰ = -22.42 ± 0.5 kcal/mol
 ΔH_{f,298.15}⁰ = -22.94 ± 0.5 kcal/mol

Ground State Quantum Weight = 1
 Bond Distance: C-Cl = 1.760 Å
 Bond Angle: Cl-C-Cl = 109.47°
 Product of the Moments of Inertia: I_AI_BI_C = 1.14972 × 10⁻¹¹² g²cm⁶
 σ = 12

Vibrational Frequencies and Degeneracies

g, cm ⁻¹
458 (1)
216 (2)
776 (3)
314 (3)

Heat of Formation
 Hu and Sinks (1) have measured the heat of combustion of CCl₄(l) in the rotating platinum bomb calorimeter, using As₂O₃ solution as the reducing agent. They reported ΔH_{c,298}⁰ = -86.02 kcal/mol for CCl₄(l) + 2H₂O(l) + CO₂(g) + 4HCl(600H₂O, aq) which leads to ΔH_{f,298}⁰(CCl₄, l) = -30.69 kcal/mol, using ΔH_{f,298}⁰ = -94.051, -39.823 and -88.315 kcal/mol for CO₂(g), HCl(600H₂O, aq) and H₂O(l), respectively (2). The standard deviation of five combustion runs was 10.074 kcal/mol. Employing the heat of vaporization of CCl₄(l) at 298°K as 7.75 kcal/mol (3), we obtain ΔH_{f,298}⁰(CCl₄, g) = -22.94 kcal/mol which is adopted in the tabulation.

L. Smith et al. (5), based on the combustion data of E. Efring (2), re-evaluated the heat of combustion of carbon tetrachloride at 18.7°C as ΔH_{c,18.7}⁰ = -567.5 cal/g for CCl₄(l) + 2H₂O(l) + CO₂(g) + 4HCl(600H₂O). This value needs to be further corrected for a change in the heat of oxidation of As₂O₃(s) and calculated to 25°C to give ΔH_{c,298}⁰ = -88.105 kcal/mol, ΔH_{c,298}⁰ = -87.513 kcal/mol, ΔH_{f,298}⁰(CCl₄, l) = -29.20 kcal/mol and ΔH_{f,298}⁰(CCl₄, g) = -21.45 kcal/mol.

C. A. Neugebauer (7) has measured the heat of reaction of CCl₄ with Hg in presence of hydrogen in the stationary bomb calorimeter and then derived the heat of formation, ΔH_{f,298}⁰(CCl₄, l) = -32.3 ± 2 kcal/mol which yields ΔH_{f,298}⁰(CCl₄, g) = -24.55 ± 2 kcal/mol. V. F. Baibuz (8), using an explosion technique, obtained ΔH_{f,298}⁰(CCl₄, g) = -24.6 ± 1.9 kcal/mol. Bodenstern and Gunther (9) have measured calorimetrically ΔH_{f,293}⁰ = -62.57 ± 0.35 kcal/mole for CCl₄(g) + 2H₂(g) + C(c) + 4HCl(g). They calibrated their calorimeter by means of the reaction H₂(g) + Cl₂(g) + 2HCl(g) for which they took ΔH_{f,293}⁰ = -44 kcal/mol. Their data have been re-evaluated to give ΔH_{f,298}⁰(CCl₄, g) = -25.68 kcal/mol, but no correction is applied for the heat of formation of carbon which was not the reference state "graphite" formed in the reaction. Domalski and Armstrong (10) reviewed several cases of active carbon formed in similar reactions and quoted a heat of formation of carbon from 1.9 to 3.95 kcal/mol. If this correction is applied to the data of Bodenstern, their heat of formation of CCl₄(g) should be 2 to 4 kcal/mol less negative than -25.68 kcal/mol.

Heat Capacity and Entropy

Bartell, Brockway and Schwendeman (11) have measured the bond distance as 1.760 ± 0.004 Å by the electron diffraction measurement. The assigned fundamental vibrational frequencies are obtained from Shimanouchi's selection (12) in which they are essentially the same as those frequencies determined from Raman and infrared spectra by Glasen (13). The three principal moments of inertia are I_A = I_B = I_C = 48.627 × 10⁻³⁹ g cm².

References

- (1) A. T. Hu, G. C. Sinke, presented at the 23rd Calorimetry Conference, Midland, Mich., 1968.
- (2) U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
- (3) D. L. Hildenbrand and R. A. McDonald, J. Phys. Chem. 53, 1521 (1959).
- (4) E. Efring, Diss., University of Lund, 1938.
- (5) L. Smith, L. Bjallerup, S. Krook and H. Westmark, Acta Chem. Scand. 7, 65 (1953).
- (6) S. Sumner and S. Thoren, Acta Chem. Scand. 18, 1528 (1964).
- (7) C. A. Neugebauer, Diss. Abstr. 17, 1478 (1957).
- (8) V. F. Baibuz, Dokl. Akad. Nauk. SSSR. 140, 1358 (1961).
- (9) M. Bodenstern and P. Gunther, 48th General Meeting of the Am. Electrochem. Soc., Chicago, April 22, 1926; Angew. Chem. 33, 875 (1926).
- (10) E. S. Domalski and G. T. Armstrong, J. Res. Natl. Bur. Stds. 71A, 105 (1967).
- (11) L. S. Bartell, L. O. Brockway and R. H. Schwendeman, J. Chem. Phys. 23, 1854 (1955).
- (12) T. Shimanouchi, U. S. Natl. Bur. Std. NBS-RS-56, 1967.
- (13) H. W. Glasen, J. Chem. Phys. 22, 50 (1954).

Carbon Tetrachloride (CCl₄)
 (Ideal Gas) GFW = 153.82315

T, °K	C _p ⁰	S ⁰ - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	Log K _p
0	11.291	0.000	INFINITE	22.420	INFINITE
100	11.291	57.033	4.120	22.420	INFINITE
200	16.629	56.669	22.420	22.420	4.825
298	19.933	74.019	1.812	23.048	17.600
300	19.979	74.142	0.037	22.937	9.299
400	21.916	80.180	2.140	22.740	5.137
500	23.088	85.207	4.395	22.510	2.663
600	23.623	89.486	6.743	22.278	1.032
700	24.106	93.197	9.151	22.051	0.191
800	24.638	96.466	11.600	21.833	-1.122
900	24.874	99.382	14.076	21.624	-1.638
1000	25.047	102.012	16.572	21.422	-2.160
1100	25.178	104.406	19.085	21.227	-2.586
1200	25.279	106.601	21.607	21.040	-2.934
1300	25.359	108.628	24.139	20.861	-3.227
1400	25.423	110.510	26.678	20.686	-3.477
1500	25.474	112.265	29.223	20.517	-3.691
1600	25.517	113.911	31.773	20.353	-3.877
1700	25.552	115.459	34.324	20.192	-4.041
1800	25.582	116.920	36.883	20.036	-4.184
1900	25.608	118.304	39.443	19.882	-4.312
2000	25.629	119.618	42.005	19.735	-4.426
2100	25.648	120.869	44.566	19.588	-4.528
2200	25.664	122.063	47.134	19.450	-4.620
2300	25.679	123.204	49.701	19.313	-4.704
2400	25.691	124.297	52.270	19.181	-4.781
2500	25.702	125.346	54.840	19.055	-4.850
2600	25.712	126.354	57.410	18.934	-4.914
2700	25.721	127.325	59.982	18.818	-4.972
2800	25.729	128.260	62.554	18.709	-5.027
2900	25.736	129.163	65.126	18.605	-5.077
3000	25.742	130.036	67.701	18.509	-5.124
3100	25.748	130.880	70.276	18.418	-5.167
3200	25.753	131.698	72.851	18.335	-5.206
3300	25.758	132.490	75.424	18.259	-5.245
3400	25.762	133.259	78.003	18.188	-5.281
3500	25.766	134.006	80.579	18.127	-5.314
3600	25.770	134.732	83.156	18.070	-5.346
3700	25.773	135.436	85.733	18.020	-5.375
3800	25.776	136.125	88.310	17.977	-5.403
3900	25.779	136.795	90.886	17.940	-5.430
4000	25.782	137.448	93.466	17.910	-5.455
4100	25.784	138.084	96.044	17.884	-5.479
4200	25.787	138.706	98.623	17.862	-5.501
4300	25.789	139.312	101.202	17.850	-5.523
4400	25.791	139.905	103.781	17.840	-5.544
4500	25.793	140.485	106.360	17.836	-5.563
4600	25.794	141.052	108.939	17.834	-5.582
4700	25.797	141.607	111.518	17.834	-5.600
4800	25.799	142.150	114.098	17.844	-5.617
4900	25.799	142.682	116.678	17.854	-5.634
5000	25.800	143.203	119.258	17.866	-5.650
5100	25.801	143.714	121.838	17.881	-5.665
5200	25.803	144.215	124.418	17.899	-5.680
5300	25.804	144.706	126.999	17.920	-5.694
5400	25.805	145.189	129.579	17.944	-5.708
5500	25.806	145.662	132.160	17.970	-5.721
5600	25.807	146.127	134.740	17.998	-5.734
5700	25.808	146.584	137.321	18.030	-5.746
5800	25.809	147.033	139.902	18.062	-5.758
5900	25.809	147.474	142.484	18.096	-5.770
6000	25.810	147.908	145.064	18.136	-5.781

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1968

$$\Delta H_f^\circ = 60.1 \pm 2 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = 61 \pm 2 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 50.889 \pm 0.01 \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	2
77.11	2
[25000]	4
42705	2
49452	2
$\omega_e \times \rho_e = 11.10 \text{ cm}^{-1}$	$\sigma = 1$
$\alpha_e = 0.0184 \text{ cm}^{-1}$	$\rho_e = 1.2667 \text{ \AA}$

Heat of Formation

M. Farber et al. (1) have studied the weight change of graphite in CF_4 at high temperatures. Our reanalysis of their data uses the equilibrium constants for CF_4 , CF_3 and CF_2 from the JANAF Tables (2); the only other C-F species considered is assumed to be CF. This treatment yields negative values for the CF pressure except at the highest temperature, where 3rd law analysis of the equilibrium constant yields $\Delta H_{298}^\circ(CF, g) = 59.4 \text{ kcal/mol}$. Farber et al. also investigated mass-spectrometrically the vapor species present at equilibrium and followed the intensities of CF^+ and F^+ . From a second law treatment of the intensities they report $\Delta H_{2300}^\circ(CF, g) = 62.0 \text{ kcal/mol}$, or $\Delta H_{298}^\circ(CF, g) = 64 \text{ kcal/mol}$.

Porter et al. (3) have investigated the A-X band system under high dispersion. From an analytical extrapolation of the 10 observed levels they reported a dissociation energy of $126.9 \pm 2.9 \text{ kcal/mol}$, which yields $\Delta H_{298}^\circ(CF, g) = 61.9 \pm 2.9 \text{ kcal/mol}$. The predissociation limit of $CF(g)$ has been reported by Thrush and Zwolnick (4) as $\leq 132 \text{ kcal/mol}$; Kuzakov and Tatiievsky (5) determined the same quantity as $\leq 133 \text{ kcal/mol}$. These results yield $\Delta H_{298}^\circ(CF, g) \geq 55 \text{ kcal/mol}$. Thrush and Zwolnick (4) also report a predissociation limit for the reaction $CF_2 \rightarrow CF + F$ which is $\leq 140 \text{ kcal/mol}$. This value has now been shown to be erroneous (see the CF_2 table for details).

Modica (6) has studied the equilibrium $CF_2 \rightarrow CF + F$ in a shock tube in the range 2880° to $3400^\circ K$. Since functions for CF_2 , CF and F are well established, the data were analyzed using 2nd and 3rd law treatments. The 2nd law analysis gives $\Delta H_{298}^\circ = 107.2 \pm 7.6 \text{ kcal/mol}$, in agreement with the value reported by Modica. The 3rd law analysis yields $\Delta H_{298}^\circ = 134.9 \pm 7.2 \text{ kcal/mol}$ and a drift of $9.7 \pm 2.5 \text{ eu}$. The excessive drift indicates that the reported equilibrium constants do not represent the stated reaction.

Andrews and Barrow (7) report a dissociation energy of 114 kcal from an extrapolation of four B state levels. This extrapolation is considered unreliable by Porter et al. (3) since this state is formed from an avoided crossing and is likely to be perturbed.

The adopted value of $\Delta H_{298}^\circ(CF, g)$ is $61 \pm 2 \text{ kcal/mol}$, which is within the uncertainties and ranges of the acceptable investigations.

Heat Capacity and Entropy

The vibrational and rotational constants are from Porter et al. (3); the higher electronic levels are those reported by Andrews and Barrow (7), except that the B state is now considered to be $^2\Sigma$. The estimated level at 25000 cm^{-1} is proposed in order to explain the low bond dissociation energy of C_2F_2 by analogy with the reasoning used by Simons (8) for C_2F_4 . This level would be a $^2\Sigma$ level and could correlate with the ground state atoms.

References

1. M. Farber, M. A. Frisch, and H. C. Ko, Trans. Faraday Soc. **55**, 3202 (1959).
2. JANAF Thermochemical Tables; CF_4 dated 6-30-69; CF_3 dated 6-30-69; CF_2 dated 6-30-70.
3. T. L. Porter, D. E. Mann and N. Acquista, J. Mol. Spectry, **15**, 228 (1965).
4. B. A. Thrush and J. J. Zwolnick, Trans. Faraday Soc. **53**, 582 (1957).
5. Yu. Ya. Kuzakov and V. M. Tatiievsky, Opt. i. Spektroskopiya **5**, 699 (1958).
6. A. P. Modica, J. Chem. Phys. **44**, 1585 (1966).
7. E. B. Andrews and R. F. Barrow, Proc. Phys. Soc. (London), **64A**, 481 (1951).
8. J. P. Simons, Nature **205**, 1308 (1965).

Dec. 31, 1950; Mar. 31, 1961; Sept. 30, 1966; Dec. 31, 1967; June 30, 1970

CF

Cyanogen Fluoride (FCN)

(Ideal Gas) GFW = 45 .01625

CFN

CYANOGEN FLUORIDE (FCN)

(IDEAL GAS)

GFW = 45.01625

Point Group $C_{\infty v}$ $\Delta H_f^\circ = 8.5 \pm 4$ kcal/mol $S^\circ_{298.15} = 53.85 \pm 0.2$ gibbs/mol $\Delta H_f^\circ_{298.15} = 8.6 \pm 4$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

 ω_e, cm^{-1}

1077 (1)

[420] (2)

2290 (1)

 $\sigma = 1$

Bond Distances: C-F = 1.262 Å C-N = 1.159 Å

Bond Angle: F-C-N = 180°

Rotational Constants: $B_0 = 0.3531 \text{ cm}^{-1}$

Heat of Formation

Davis and Okabe (1) have determined the dissociation energy of FCN to F(g) and CN(g) by measuring the threshold energies of incident photon radiation to produce F^2CN which is monitored by its fluorescence. The dissociation energy determined by this technique is ≤ 111 kcal/mol with an uncertainty of about 1 kcal in the determination of the limit.

Dibeler and Liston (2) have reported a dissociation energy of ≤ 115.6 kcal/mol from the threshold of the CN^+ ion as determined by photoionization.

We adopt a median value of 113.1 ± 2.5 kcal/mol which leads to $\Delta H_f^\circ(\text{FCN}, g) = 8.6 \pm 4$ kcal/mol with auxiliary JANAF values for F(g) and CN(g).

Heat Capacity and Entropy

The molecular structure and bond lengths and angle were determined using microwave spectroscopy by Tyler and Sheridan (3). The vibrational frequencies were reported by Aynsley et. al. (4) from the infra-red spectrum, except for the bending frequency which is estimated from the values for ClCN, BrCN and ICN, by comparison of bending force constants. The reasonable limits for this value as calculated from generous limits on the bending force constant are 405-450 cm^{-1} .

References:

1. D. D. Davis and H. Okabe, J. Chem. Phys. **49**, 5526 (1968).
2. V. H. Dibeler and S. K. Liston, J. Chem. Phys. **47**, 4548 (1967).
3. J. K. Tyler and J. Sheridan, Trans. Faraday Soc. **59**, 2661 (1963).
4. E. E. Aynsley, R. E. Dodd, and R. Little, Proc. Chem. Soc. (London), **1959**, 265 (1959).

T, °K	C_p	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔC_p°	Log Kp
0	1.000	INFINITE	INFINITE	2.455	8.484	INFINITE
100	7.900	52.438	1.728	1.486	8.484	1.486
200	8.900	50.037	5.273	8.519	7.509	6.206
298	10.113	53.846	53.846	8.400	6.999	5.129
300	10.130	53.908	53.846	.019	8.401	6.086
400	10.934	56.939	54.254	1.074	8.437	3.517
500	11.582	59.447	55.049	2.199	8.728	2.586
600	12.031	61.596	55.945	3.379	8.758	5.295
700	12.438	63.482	56.907	4.603	8.767	1.473
800	12.779	65.166	57.836	5.864	8.765	4.134
900	13.066	66.688	58.736	7.157	8.753	3.560
1000	13.306	68.077	59.602	8.476	8.737	.652
1100	13.508	69.355	60.431	9.817	8.715	2.409
1200	13.677	70.538	61.225	11.176	8.689	.335
1300	13.820	71.639	61.984	12.551	8.658	.213
1400	13.942	72.668	62.711	13.940	8.627	.109
1500	14.045	73.633	63.407	15.339	8.592	.070
1600	14.133	74.542	64.075	16.748	8.556	.058
1700	14.210	75.402	64.716	18.165	8.514	.127
1800	14.275	76.216	65.333	19.590	8.474	.188
1900	14.333	76.989	65.926	21.020	8.438	.242
2000	14.383	77.726	66.498	22.456	8.396	.290
2100	14.427	78.428	67.049	23.896	8.354	.334
2200	14.465	79.100	67.582	25.341	8.308	.373
2300	14.500	79.744	68.097	26.789	8.262	.409
2400	14.530	80.362	68.595	28.241	8.214	.441
2500	14.556	80.956	69.078	29.695	8.165	.471
2600	14.582	81.527	69.555	31.152	8.113	.499
2700	14.604	82.078	69.999	32.612	8.060	.524
2800	14.624	82.609	70.440	34.073	8.007	.547
2900	14.642	83.123	70.869	35.536	7.950	.568
3000	14.656	83.620	71.286	37.002	7.891	.588
3100	14.673	84.100	71.691	38.468	7.832	.607
3200	14.687	84.567	72.086	39.936	7.769	.624
3300	14.699	85.019	72.472	41.405	7.704	.640
3400	14.711	85.458	72.847	42.876	7.638	.655
3500	14.721	85.884	73.213	44.346	7.569	.669
3600	14.731	86.299	73.571	45.820	7.498	.682
3700	14.740	86.703	73.921	47.294	7.424	.694
3800	14.748	87.096	74.262	48.768	7.349	.706
3900	14.756	87.479	74.596	50.243	7.271	.717
4000	14.763	87.853	74.923	51.719	7.190	.727
4100	14.769	88.217	75.243	53.196	7.107	.736
4200	14.776	88.573	75.556	54.673	7.021	.745
4300	14.781	88.921	75.863	56.151	6.933	.754
4400	14.787	89.261	76.163	57.629	6.841	.762
4500	14.792	89.593	76.456	59.108	6.747	.769
4600	14.797	89.919	76.747	60.588	6.650	.776
4700	14.801	90.237	77.031	62.068	6.551	.783
4800	14.805	90.549	77.309	63.548	6.448	.789
4900	14.809	90.854	77.583	65.029	6.343	.795
5000	14.813	91.153	77.851	66.510	6.234	.801
5100	14.816	91.446	78.115	67.991	6.122	.806
5200	14.819	91.734	78.374	69.473	6.007	.811
5300	14.823	92.016	78.629	70.955	5.890	.816
5400	14.825	92.294	78.879	72.438	5.769	.820
5500	14.828	92.566	79.126	73.920	5.643	.824
5600	14.831	92.833	79.368	75.403	5.516	.828
5700	14.833	93.095	79.606	76.886	5.384	.832
5800	14.836	93.353	79.841	78.370	5.249	.836
5900	14.838	93.607	80.072	79.854	5.111	.839
6000	14.840	93.856	80.300	81.337	4.969	.842

Dec. 31, 1960; June 30, 1961; June 30, 1969

CFN

T, °K.	$\left(\frac{C_p}{\text{cal. mole}^{-1}\text{deg.}^{-1}} \right)$		$\left(\frac{S^\circ - (F^\circ - H_{298}^\circ)/T}{\text{cal. mole}^{-1}\text{deg.}^{-1}} \right)$		$\left(\frac{H^\circ - H_{298}^\circ}{\text{cal. mole}^{-1}} \right)$		Log K _P
	C _p	S°	-(F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	
0	7.069	50.185	INFINITE	-2.484	-41.139	-41.139	INFINITE
100	7.969	50.185	67.074	-1.689	-41.062	-41.062	91.675
200	8.476	55.826	60.187	-0.872	-41.014	-42.857	46.830
298	9.305	59.363	59.363	0.000	-41.000	-43.766	32.080
300	9.320	59.420	59.363	0.017	-41.000	-43.784	31.895
400	10.068	64.542	60.742	2.034	-41.058	-45.629	19.944
500	10.768	68.541	62.722	2.034	-41.058	-45.629	19.944
600	11.310	66.554	61.322	3.139	-41.124	-46.538	16.951
700	11.748	66.331	62.199	4.293	-41.210	-47.433	14.809
800	12.093	63.066	63.066	5.486	-41.308	-48.315	13.093
900	12.365	61.365	64.116	6.722	-41.408	-49.187	11.699
1000	12.607	72.682	64.722	7.960	-41.528	-50.043	10.936
1100	12.791	73.892	65.501	9.230	-41.646	-50.890	10.110
1200	12.940	75.012	66.248	10.517	-41.768	-51.724	9.420
1300	13.065	76.052	66.967	11.827	-41.897	-52.549	8.854
1400	13.168	77.014	67.659	13.157	-42.032	-53.366	8.399
1500	13.251	77.936	68.303	14.450	-42.161	-54.167	7.952
1600	13.323	78.794	68.932	15.779	-42.298	-54.965	7.508
1700	13.384	79.603	69.536	17.111	-42.436	-55.751	7.167
1800	13.436	80.360	70.117	18.455	-42.580	-56.522	6.864
1900	13.479	81.077	70.676	19.811	-42.728	-57.280	6.595
2000	13.521	81.750	71.214	21.151	-42.874	-58.065	6.345
2100	13.555	82.451	71.734	22.505	-43.024	-58.821	6.121
2200	13.581	83.082	72.230	23.872	-43.181	-59.559	5.910
2300	13.601	83.646	72.700	25.252	-43.345	-60.283	5.710
2400	13.616	84.136	73.149	26.584	-43.501	-60.990	5.529
2500	13.625	84.583	73.644	27.949	-43.667	-61.774	5.400
2600	13.674	85.359	74.084	29.315	-43.837	-62.494	5.253
2700	13.690	85.815	74.511	30.683	-44.011	-63.208	5.116
2800	13.701	86.186	74.924	32.049	-44.189	-63.916	4.989
2900	13.719	86.895	75.329	33.424	-44.369	-64.616	4.869
3000	13.731	87.320	75.721	34.797	-44.554	-65.313	4.758
3100	13.742	87.770	76.102	36.171	-44.742	-66.009	4.653
3200	13.751	88.207	76.474	37.545	-44.935	-66.684	4.554
3300	13.758	88.621	76.836	38.918	-45.132	-67.350	4.460
3400	13.770	89.041	77.189	40.297	-45.332	-68.030	4.373
3500	13.778	89.440	77.533	41.675	-45.537	-68.696	4.289
3600	13.785	89.829	77.869	43.053	-45.744	-69.356	4.210
3700	13.791	90.206	78.199	44.432	-45.956	-70.000	4.133
3800	13.797	90.574	78.519	45.812	-46.171	-70.631	4.059
3900	13.803	90.933	78.832	47.191	-46.391	-71.246	3.995
4000	13.808	91.282	79.139	48.572	-46.613	-71.929	3.930
4100	13.813	91.623	79.440	49.953	-46.840	-72.561	3.868
4200	13.816	91.956	79.734	51.334	-47.071	-73.184	3.808
4300	13.822	92.281	80.021	52.715	-47.306	-73.801	3.750
4400	13.826	92.599	80.304	54.099	-47.543	-74.418	3.696
4500	13.829	92.910	80.581	55.482	-47.784	-75.029	3.644
4600	13.833	93.214	80.852	56.865	-48.029	-75.629	3.593
4700	13.836	93.511	81.119	58.248	-48.277	-76.216	3.544
4800	13.839	93.803	81.379	59.632	-48.527	-76.814	3.497
4900	13.842	94.088	81.636	61.016	-48.785	-77.403	3.452
5000	13.845	94.368	81.888	62.400	-49.044	-77.987	3.409
5100	13.847	94.642	82.135	63.785	-49.308	-78.567	3.367
5200	13.849	94.911	82.374	65.171	-49.576	-79.144	3.326
5300	13.852	95.175	82.617	66.555	-49.844	-79.709	3.286
5400	13.854	95.434	82.852	67.940	-50.117	-80.263	3.248
5500	13.856	95.688	83.083	69.326	-50.394	-80.815	3.211
5600	13.858	95.938	83.311	70.711	-50.675	-81.369	3.175
5700	13.860	96.183	83.534	72.097	-50.960	-81.918	3.140
5800	13.862	96.424	83.754	73.483	-51.247	-82.454	3.107
5900	13.863	96.661	83.971	74.870	-51.538	-82.988	3.074
6000	13.865	96.894	84.185	76.256	-51.833	-83.522	3.042

MOL. WT. = 47.00895

(IDEAL GAS)

Point Group C_s

S°_{298.15} = [59] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

ω_e , cm.⁻¹

1018 (1)

826 (1)

1855 (1)

C-O = [1.18] Å

C-O = [1.34] Å

P-C-O = [135] °

Product of the Moments of Inertia: I_AI_BI_C = [2.1986 x 10⁻¹¹⁶] g.³ cm.⁶

Bond Distance: C-P = [1.34] Å

Bond Angle: P-C-O = [135] °

Heat of Formation.

The enthalpy change (ΔH_f°) for the reaction COF₂(g) = CO(g) + 2F(g) was calculated as 180.5 kcal. mole⁻¹. By analogy with D(Cl-COCl)/D(Cl-CO), the value of D(F-COF)/D(F-CO) was taken to be 4. Based on ΔH_f° = 180.5 x (4/5) = 128.4 kcal. mole⁻¹ for the reaction COF₂(g) = CO(g) + F(g), the heat of formation for COF(g) was derived as -41 ± 15 kcal. mole⁻¹.

Heat Capacity and Entropy.

The vibrational frequencies were reported by D. E. Milligen, M. E. Jacob, A. M. Bass, J. J. Comeford and D. E. Mann, J. Chem. Phys. 42, 3187 (1965). The bond distances and angle were estimated by comparison with those for HFCO (g). Due to the presence of one unpaired electron on C atom, the ground state quantum weight is calculated to be 2. The three principal moments of inertia are: I_A = 7.8757 x 10⁻³⁹, I_B = 3.3980 x 10⁻⁴⁰, and I_C = 8.2155 x 10⁻³⁹ g. cm.²

Point Group C_{2v}S_{298,15} = 57.53 ± 0.01 gibbs/molΔH_{f,0}⁰ = -43.6 ± 1.5 kcal/molΔH_{f,298,15} = -43.5 ± 1.5 kcal/molCarbon Difluoride (CF₂)

GFW = 50.00795

(Ideal Gas)

T, °K	Cp ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal/mol	ΔH _f ^c	Log Kp
0	-0.000	-0.000	INFINITE	-2.475	-43.613	INFINITE
100	7.961	48.404	55.199	-1.680	-43.527	66.766
200	8.402	54.018	56.354	-0.867	-43.492	49.221
298	9.309	57.533	57.533	-0.000	-43.500	33.575
300	9.327	57.591	57.534	-0.017	-43.501	33.379
400	10.300	60.410	57.911	1.000	-43.534	25.456
500	11.105	62.799	58.656	2.071	-43.589	20.604
600	11.716	64.680	59.524	3.214	-43.656	17.516
700	12.158	66.170	60.504	4.444	-43.740	15.046
800	12.468	67.376	61.615	5.768	-43.827	13.136
900	12.675	68.356	62.843	7.193	-43.926	11.752
1000	12.850	69.123	64.019	8.719	-44.032	10.835
1100	13.100	70.458	65.821	10.396	-44.144	10.259
1200	13.214	71.559	67.332	12.187	-44.266	9.906
1300	13.291	72.461	68.593	14.040	-44.397	9.704
1400	13.341	73.201	69.626	15.934	-44.514	9.626
1500	13.374	73.811	70.469	17.841	-44.617	9.600
1600	13.397	74.344	71.055	19.746	-44.703	9.600
1700	13.412	74.801	71.515	21.641	-44.775	9.619
1800	13.420	75.181	71.879	23.521	-44.835	9.631
1900	13.425	75.491	72.169	25.381	-44.881	9.631
2000	13.425	75.757	72.400	27.221	-44.915	9.620
2100	13.420	75.981	72.581	29.041	-44.939	9.597
2200	13.412	76.161	72.721	30.841	-44.953	9.571
2300	13.400	76.301	72.821	32.621	-44.958	9.541
2400	13.384	76.401	72.891	34.381	-44.954	9.504
2500	13.363	76.461	72.931	36.121	-44.941	9.461
2600	13.339	76.481	72.941	37.841	-44.919	9.409
2700	13.312	76.461	72.931	39.541	-44.888	9.349
2800	13.282	76.401	72.891	41.221	-44.848	9.279
2900	13.249	76.311	72.821	42.881	-44.799	9.199
3000	13.214	76.191	72.721	44.521	-44.741	9.109
3100	13.177	76.041	72.591	46.141	-44.674	9.009
3200	13.138	75.861	72.431	47.741	-44.599	8.899
3300	13.097	75.651	72.241	49.321	-44.516	8.779
3400	13.054	75.411	72.021	50.881	-44.426	8.649
3500	13.009	75.141	71.771	52.421	-44.329	8.509
3600	12.963	74.841	71.491	53.941	-44.226	8.359
3700	12.916	74.511	71.181	55.441	-44.109	8.199
3800	12.868	74.151	70.841	56.921	-43.980	8.029
3900	12.819	73.771	70.471	58.381	-43.839	7.849
4000	12.769	73.371	70.071	59.821	-43.688	7.659
4100	12.718	72.941	69.641	61.241	-43.528	7.459
4200	12.666	72.481	69.181	62.641	-43.359	7.249
4300	12.613	72.001	68.691	64.021	-43.182	7.029
4400	12.559	71.501	68.171	65.381	-42.998	6.799
4500	12.504	71.001	67.621	66.721	-42.808	6.559
4600	12.448	70.481	67.041	68.041	-42.613	6.309
4700	12.391	69.941	66.431	69.341	-42.414	6.049
4800	12.333	69.381	65.791	70.621	-42.211	5.779
4900	12.274	68.801	65.121	71.881	-42.005	5.499
5000	12.214	68.201	64.431	73.121	-41.796	5.209
5100	12.153	67.581	63.721	74.341	-41.584	4.909
5200	12.091	66.941	62.991	75.541	-41.368	4.599
5300	12.028	66.281	62.241	76.721	-41.148	4.279
5400	11.964	65.601	61.471	77.881	-40.924	3.949
5500	11.899	64.901	60.681	79.021	-40.696	3.609
5600	11.833	64.181	59.871	80.141	-40.464	3.259
5700	11.766	63.441	59.041	81.241	-40.228	2.909
5800	11.698	62.681	58.191	82.321	-39.988	2.549
5900	11.629	61.901	57.321	83.381	-39.743	2.179
6000	11.559	61.101	56.431	84.421	-39.493	1.809

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Sept. 30, 1966; June 30, 1970

Electronic Levels and Quantum Weights

State	E _i , cm ⁻¹	E _i , cm ⁻¹	State	E _i , cm ⁻¹	E _i , cm ⁻¹
X ¹ A ₁	0	1	A ³ B ₁	16000	3
			A ³ B ₂	37226	1

Vibrational Frequencies and Degeneracies

ω ₁ , cm ⁻¹	ω ₂ , cm ⁻¹	ω ₃ , cm ⁻¹
1222 (1)	665 (1)	1110 (1)

Bond Distance: C-F = 1.300 Å Bond Angle: F-C-F = 104.9°

Product of the Moments of Inertia: I_AI_BI_C = 4.87886 × 10⁻¹¹⁶ g³ cm⁶

Heat of Formation

Thrush and Zwoelenik (1) reported a predissociation limit for CF₂ + CF + F; however, Harsigny et al. (2) have since observed in emission the assumed predissociated level, and others above it, which invalidates the reported limit.

Walter et al. (3) have obtained the photoionization threshold at 0°K for onset of the reaction C₂F₄ + e⁻ → CF₂⁺ + CF₂ + 2e⁻, as 14.63 ± 0.04 eV (337.37 Kcal). The ionization potential of CF₂ has been reported as 11.7 eV (4), 11.8 ± 0.3 eV (5) and 11.86 ± 0.1 eV (6). Since these values were obtained by electron impact methods, there may be excess energy involved. Thus, adopting the lowest value as 11.7 ± 0.2 eV, we obtain ΔH_{f,298}⁰(CF₂, g) = -44.4 ± 2.5 Kcal/mol (2). All previous electron impact methods are considered superseded by this photoionization result.

Modica and LaGraff (8) determined equilibrium constants for the reaction (A) C₂F₄ + 2CF₂ by use of a shock tube to achieve high temperatures and ultra violet absorption to detect the CF₂ concentration. Carlson (9) has studied the same reaction using a similar technique, and also Zmbov et al. (5) have investigated this equilibrium in a mass spectrometer. A 2nd and 3rd law analysis of all three sets of data is given below along with our recalculated equilibrium data of Farber et al. (10) for the reaction (B) C + 2F + CF₂ from weight loss experiments in the system C + CF₄.

Kinetic methods were used by Edwards and Small (11) to study the equilibrium (C) CHF₃Cl(g) ⇌ CF₂(g) + HCl(g). They analysed their data by assuming that the only other equilibrium occurring was 2CF₂(g) ⇌ C₂F₄(g), and fit their kinetic data by 6.21 ± 3.0 Kcal, thus ΔE = 49.6 ± 3.0 and ΔH₃₀₀ = 51.4 ± 3 Kcal, which yields ΔH_{f,298}⁰(CF₂) = -42 ± 4 Kcal/mol (2). They also obtained the activation energy of reaction (A) as 70.36 ± 1.3 Kcal. Dalby (12) has reported the activation energy of the reverse of (A) as 1.2 ± 0.2 Kcal, thus, ΔE_a = 69.2 ± 1.3 and ΔH₃₀₀ = 71.0 ± 1.3 Kcal, which yields ΔH_{f,298}⁰(CF₂) = -42.6 ± 1.0 Kcal/mol (2). Gozzo and Patrick (13) also investigated the kinetics of reaction C and obtained activation energies of 51.4 ± 2.5 and 14.4 ± 5 Kcal, the latter value being corrected for the activation energy of CF₂ recombination (12). Thus, we obtain ΔE_a = 37 ± 7 and ΔH₁₀₀₀ = 39 ± 7 Kcal, which yields ΔH_{f,298}⁰(CF₂) = -54 ± 9 Kcal/mol (2).

Modica and LaGraff (14) investigated the kinetics of CHF₃ decomposition by a mass spectrometer coupled to a shock tube. They investigated the pressure dependence of the rate and concluded that at the high pressure limit P₀ = 58.4 ± 2.2 Kcal. Taking this value as ΔH_f⁰ for the reaction (D) CHF₃(g) + CF₂(g) + HF(g) ⇌ HF(g) + CF₂(g) we obtain ΔH_{f,298}⁰(CF₂) = -41.3 ± 2.5 Kcal/mol (2). However, any activation energy of the reverse reaction (D) will make this value more negative. Since values of the reverse activation energy of analogous reaction (C) range from 6.2 to 14.4 Kcal, it appears likely that reverse reaction (D) will have a significant activation energy; thus, ΔH_{f,298}⁰(CF₂) < -41.3 ± 2.5 Kcal. Tschukow-Roux (15) has investigated the same reaction in a shock tube, but was unable to obtain sufficient variation of rate with pressure to calculate the high pressure limit.

**ΔH_{f,298}⁰(CF₂, g)

Reference	Points	Range, °K	2nd Law	3rd Law	Drift
9. A	35*	1165-1940	0.5727	0.5727	-0.320
10. B	11	1127-1244	77.3 ± 2.1	75.13 ± 0.72	-0.350
10. B	11	2023-2474	-73.8 ± 1.4	-80.04 ± 1.0	-41.15 ± 1.5
					-42.3 ± 1.0

*Points omitted due to failure of a statistical test **Calculated from the 3rd law heat of reaction.

A median value of ΔH_{f,298}⁰(CF₂, g) covering the area of maximum probability is adopted as -43.5 ± 1.5 Kcal/mol.

Heat Capacity and Entropy

The structure of CF₂ has been reported by Powell and Lide (16) from microwave measurements and has been confirmed by Mathews (17) from the fine structure of the 2500Å absorption band. Mathews also reported ω₂ and Herr and Pimentel (18) reported ω₃, both from gas phase studies. Milligan et al. (19) have observed all three vibrations in matrix-isolated CF₂ as 1222, 665 and 1102 cm⁻¹. The electronic levels are from Mathews (17) with the triplet level estimated by Simons (20) to explain the low C-C bond energy of 70 Kcal in C₂F₄. The individual moments of inertia are I_A = 0.9512 × 10⁻³⁹ g cm², I_B = 6.7020 × 10⁻³⁹ g cm², and I_C = 7.6532 × 10⁻³⁹ g cm².

References

1. B. A. Thrush and J. J. Zwoelenik, Trans. Faraday Soc. 59, 582 (1963).
2. L. Marsigny, J. Perrin, J. Lebreton, and R. Lagrange, Comp. Rend. 286C, 507 (1968).
3. T. A. Walter, C. Livshitz, and W. A. Chupka, and J. Berkowitz, J. Chem. Phys. 48, 1057 (1968).
4. I. P. Fisher, J. B. Homar, and F. P. Lossing, J. Amer. Chem. Soc. 87, 957 (1965).
5. K. F. Zmbov, O. M. Uy, and J. L. Margrave, J. Amer. Chem. Soc. 90, 5090 (1968).
6. R. F. Potte, J. Chem. Phys. 42, 2607 (1965).
7. J. W. P. Smith, J. Chem. Phys. 42, 2607 (1965).
8. A. P. Modica and J. E. LaGraff, J. Chem. Phys. 43, 3383 (1965).
9. G. A. Carlson, Sandia Laboratories, Albuquerque, N. M., private communication, April 7, 1970.
10. M. Farber, M. A. Frish, and H. C. Ko, Trans. Faraday Soc. 65, 3202 (1969).
11. J. W. Edwards and P. A. Small, Ind. Eng. Chem. Fundamentals 4, 396 (1965).
12. P. Dalby, J. Chem. Phys. 41, 2297 (1964).
13. E. Gozzo and J. Patrick, J. Chem. Phys. 42, 2607 (1965).
14. A. P. Modica and J. E. LaGraff, J. Chem. Phys. 44, 3375 (1966).
15. E. Tschukow-Roux, J. Chem. Phys. 42, 3639 and 2049 (1965).
16. F. X. Powell and D. R. Lide, J. Chem. Phys. 45, 1067 (1966).
17. C. W. Mathews, J. Chem. Phys. 45, 1068 (1966) and Can. J. Phys. 45, 1068 (1967).
18. K. F. Zmbov, O. M. Uy, and J. L. Margrave, Appl. Opt. 4, 25 (1965).
19. D. E. Milligan, D. E. F. Mann, M. F. Jacob, and R. A. Misch, J. Chem. Phys. 41, 1199 (1964) and D. E. Milligan and M. F. Jacob, J. Chem. Phys. 43, 2265 (1965).
20. J. P. Simons, Nature 205, 1308 (1965) and J. Chem. Soc. (London), 3406 (1965).

Point Group C_{2v}

$$\Delta H_f^\circ = -152.0 \pm 0.4 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -152.7 \pm 0.4 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 61.85 \pm 0.02 \text{ gibbs/mol}$$

$$\text{Ground State Quantum Weight} = 1$$

Carbonyl Fluoride (COF₂)

$$\text{CFW} = 66.0074$$

(Ideal Gas)

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log Kp
0	0.000	INFINITE	-	2.657	-151.958	-	INFINITE
100	8.004	51.917	70.536	-	-150.218	-	310.556
200	9.296	57.767	62.820	-	-150.493	-	164.100
298	11.294	61.851	61.851	-	-152.700	-	109.710
300	11.330	61.921	61.851	1.225	-152.701	-	108.520
400	13.092	65.432	62.318	1.285	-152.651	-	80.695
500	14.460	68.507	63.255	2.626	-152.961	-	63.987
600	15.495	71.240	64.362	4.197	-153.048	-	52.841
700	16.305	73.693	65.729	5.719	-153.121	-	43.730
800	16.924	75.912	66.665	7.382	-153.162	-	36.674
900	17.406	77.935	67.824	9.099	-153.235	-	31.247
1000	17.786	79.789	68.929	10.660	-153.279	-	30.526
1100	18.089	81.499	69.995	12.454	-153.319	-	27.480
1200	18.334	83.084	71.021	14.475	-153.355	-	24.945
1300	18.533	84.559	72.006	16.319	-153.391	-	22.793
1400	18.697	85.939	72.952	18.161	-153.423	-	20.950
1500	18.834	87.234	73.862	20.058	-153.458	-	19.353
1600	18.949	88.453	74.736	21.947	-153.492	-	17.956
1700	19.046	89.605	75.577	23.847	-153.526	-	16.722
1800	19.129	90.696	76.387	25.756	-153.562	-	15.626
1900	19.201	91.732	77.168	27.672	-153.599	-	14.644
2000	19.262	92.719	77.921	29.596	-153.638	-	13.761
2100	19.316	93.660	78.648	31.525	-153.678	-	12.961
2200	19.363	94.559	79.351	33.459	-153.724	-	12.234
2300	19.404	95.421	80.031	35.379	-153.771	-	11.570
2400	19.441	96.248	80.690	37.339	-153.823	-	10.961
2500	19.474	97.042	81.328	39.285	-153.878	-	10.401
2600	19.503	97.806	81.947	41.234	-153.937	-	9.883
2700	19.529	98.543	82.548	43.186	-153.999	-	9.404
2800	19.552	99.253	83.132	45.140	-154.065	-	8.959
2900	19.573	99.940	83.700	47.096	-154.137	-	8.544
3000	19.592	100.604	84.252	49.054	-154.213	-	8.157
3100	19.609	101.247	84.790	51.014	-154.291	-	7.794
3200	19.625	101.869	85.314	52.976	-154.376	-	7.454
3300	19.639	102.473	85.825	54.939	-154.464	-	7.135
3400	19.653	103.060	86.323	56.904	-154.557	-	6.834
3500	19.665	103.630	86.810	58.870	-154.655	-	6.550
3600	19.676	104.184	87.285	60.837	-154.756	-	6.281
3700	19.686	104.723	87.749	62.805	-154.861	-	6.027
3800	19.696	105.248	88.202	64.774	-154.974	-	5.786
3900	19.704	105.760	88.646	66.744	-155.090	-	5.558
4000	19.713	106.259	89.080	68.715	-155.209	-	5.341
4100	19.720	106.746	89.505	70.686	-155.334	-	5.136
4200	19.727	107.221	89.921	72.659	-155.463	-	4.936
4300	19.734	107.685	90.329	74.632	-155.596	-	4.748
4400	19.740	108.139	90.729	76.605	-155.735	-	4.568
4500	19.746	108.583	91.121	78.580	-155.877	-	4.397
4600	19.751	109.017	91.505	80.555	-156.023	-	4.232
4700	19.756	109.442	91.882	82.530	-156.175	-	4.074
4800	19.761	109.858	92.252	84.506	-156.331	-	3.922
4900	19.765	110.265	92.616	86.482	-156.491	-	3.777
5000	19.769	110.665	92.973	88.459	-156.656	-	3.638
5100	19.773	111.056	93.323	90.436	-156.826	-	3.504
5200	19.777	111.440	93.668	92.413	-156.999	-	3.374
5300	19.780	111.817	94.007	94.391	-157.177	-	3.249
5400	19.784	112.187	94.340	96.369	-157.361	-	3.129
5500	19.787	112.550	94.665	98.348	-157.548	-	3.013
5600	19.790	112.906	94.991	100.327	-157.740	-	2.902
5700	19.793	113.256	95.308	102.306	-157.937	-	2.794
5800	19.795	113.601	95.620	104.285	-158.137	-	2.689
5900	19.798	113.939	95.928	106.265	-158.342	-	2.586
6000	19.800	114.272	96.231	108.245	-158.552	-	2.480

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; Mar. 31, 1965; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}
965 (1)	1249 (1)
1928 (1)	584 (1)
826 (1)	774 (1)

$$\text{Bond Distances: C-F} = 1.312 \text{ \AA} \quad \text{C-O} = 1.174 \text{ \AA}$$

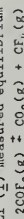
$$\text{Bond Angle: F-C-F} = 108^\circ \quad \text{F-C-O} = 128^\circ 1'$$

$$\text{Product of the Moments of Inertia: } I_A I_B I_C = 7.243 \times 10^{-115} \text{ g}^3 \text{ cm}^6$$

$$\sigma = 2$$

Heat of Formation

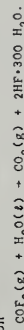
Ruff and Li (1) measured equilibrium constants for the reaction



in the temperature range 573-1273°K. These equilibrium data were recently analyzed by Stull, Westrum, and Sinke (2).

Their third law analysis of the data clearly indicates that the three low temperature points are in error and should not be used in calculating ΔH₂₉₈°. They reported, ΔH₂₉₈° = -12 ± 3 kcal/mol, based upon an average of the five high temperature points. Combining this result with the heat of formation of carbon dioxide and carbon tetrafluoride (3), we derive,

$$\Delta H_f^\circ(\text{COF}_2, \text{g}) = -152.5 \pm 3.3 \text{ kcal/mol.}$$

Wartenberg and Ritaris (4) measured the heat of hydrolysis of CF₂O. They reported, ΔH_r = -26.7 ± 0.2 kcal/mol, for the reactionCombining this result with heat of formation data for carbon dioxide and HF(ΔH_f°(HF·300 H₂O) = -76.84 kcal/mol (5)), we derive,

$$\Delta H_f^\circ(\text{CF}_2\text{O}, \text{g}) = -152.7 \pm 0.4 \text{ kcal/mol.}$$

Armstrong, Coyle, and Krieger (6) measured the heats of combustion of CH₄ in O₂-F₂ mixtures and found ΔH₂₉₈°(CF₂O, g) = -154.8 kcal/mol. The value calculated from Wartenberg's data is adopted here.

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Hopper et al. (7) and are in good agreement with the results of Lovall et al. (8) and Nielsen et al. (9). The molecular constants are from the microwave studies of Laurie et al. (10) and are in reasonable agreement with the electron-diffraction work of Brown and Livingston (11). Individual moments of inertia calculated from the rotational constants of Laurie et al. (10) are I_A = 7.105 × 10⁻³⁹ g cm², I_B = 7.144 × 10⁻³⁹ g cm², and I_C = 14.27 × 10⁻³⁹ g cm².

References

1. O. Ruff and S. Li, Z. Anorg. Chem., **242**, 272 (1939).
2. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," John Wiley & Sons, Inc., New York, 1959, p. 80.
3. JANAF Thermochemical Tables, The Dow Chemical Co., June 30, 1969.
4. H. von Wartenberg and G. Ritaris, Z. Anorg. Chem., **258**, 358 (1949).
5. Ref. 3, Dec. 31, 1968.
6. G. T. Armstrong, C. F. Coyle, and L. A. Krieger, WADC TR 58-541, October, 1958.
7. M. J. Hopper, J. W. Russell, and J. Overend, J. Chem. Phys., **48**, 3765 (1968).
8. R. J. Lovell, C. V. Stephenson, E. A. Jones, J. Chem. Phys., **23**, 1953 (1954).
9. A. H. Nielsen, T. G. Burke, P. J. H. Holtz, and E. A. Jones, J. Chem. Phys., **20**, 586 (1952).
10. V. W. Laurie, D. T. Pence, and R. H. Jackson, J. Chem. Phys., **32**, 2395 (1962).
11. T. T. Brown and R. L. Livingston, J. Amer. Chem. Soc., **74**, 6094 (1952).

Trifluoromethyl (CF₃)

(Ideal Gas)

GFW = 69.00635

CF₃Point Group C_{3v}S_{298.15} = 63.329 ± 1.0 gibbs/mol

Ground State Quantum Weight = 2

ΔH_f⁰ = -111.7 ± 1.0 kcal/molΔH_f⁰_{298.15} = -112.4 ± 1.0 kcal/mol

Vibrational Frequencies and Degeneracies		
ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
1090 (1)	1259 (2)	
701 (1)	(500) (2)	

Bond Distance: C-F = [1.33] Å

Bond Angle: F-C-F = [112°]

Product of the Moments of Inertia: I_AI_BI_C = {9.608 × 10⁻¹¹⁵} g³ cm⁶

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₃X (X = H, Cl, Br, I, CF₃). Details of the input data and the adjustment are given in (1). Kinetic data provide the most consistent paths to ΔH_f⁰ of CF₃(g). Forward and reverse activation energies for the reactions CHF₃(g) + X(g) → CF₃(g) + HX(g) have been reported for X = Cl by Coomber (2), for X = Br by Amphlett (3), and for X = I by Goy (4). Increases of about 0.3 kcal/mol in the reverse activation energies for X = Cl and Br were proposed by Arthur (5) on the basis of additional data. Combining these values and reducing to 298.15°K, we get ΔH_r⁰ = 2.93 ± 0.7 (X = Cl), 18.89 ± 0.7 (X = Br), and 35.5 ± 3 kcal/mol at 298.15°K for X = I. Coomber (2) reviewed data for the analogous reactions with X = CH₃ and CD₃; these yield ΔH_r⁰ = 0.6 ± 2 kcal/mol at 298.15°K for X = CH₃. Activation energies have also been reported (6) for CF₃I(g) + I(g) → CF₃(g) + I₂(g) from which we derive the average value ΔH_r⁰ = 17.1 ± 2 kcal/mol. The data of Tschuikow-Roux (7) for C₂F₆(g) + 2CF₃(g), recalculated as suggested by Coomber (8) but with JANAF functions, yield ΔH_r⁰ = 97.6 ± 6 kcal/mol. Differences between the calculated and observed values of ΔH_r⁰ are all less than half of the uncertainties assigned to the observed values.

The thorough discussion of photoionization data by Noutary (9) emphasized that CF₃⁺ is formed with large amounts of excess energy both during ionization of CF₃ and during fragmentation of other fluorides. The amount of excess energy varies with the parent molecule. This may also be involved in electron-impact studies and could account for some of the discrepancies in bond-dissociation energies derived from appearance potentials and ionization potentials. Such data have been summarized by Coomber (10). Ionization data were omitted from the simultaneous adjustment due to uncertainty in the amounts of excess energy. Also omitted was the mass-spectrometric study of 3C₂F₄(g) + 4CF₃(g) → 2C₂F₆(g) + 2C(CF₃)₂(g) by Ehler (11) which gave ΔH_f⁰ = -102 ± 3 kcal/mol. The discrepancy of 10 kcal/mol suggests that the data may not represent equilibrium for the above reaction. This reaction was one of many which resulted from heating MnF₃ in an effusion cell made of graphite.

Heat Capacity and Entropy

The bond length is assumed to be 1.33 Å by comparison with the molecules CF₃X, and the bond angle is estimated from molecular-orbital calculations of Morokuma (12) and Pople and coworkers (13). The nonplanar structure is consistent with electron-spin-resonance spectra (14) of CF₃ in krypton and xenon matrices, with infrared spectra of CF₃ in various matrices (15) and in the gaseous phase (16), and with photoionization spectra (17). The observed vibrational fundamentals of Carlson (18) are confirmed by the matrix spectra of Milligan (19). The latter estimated ν₄ to be in the range of 500 to 600 cm⁻¹. We choose the lower value by comparison with CF₃H, SiF₃H and SiF₃ (18).

The uncertainty in ν₄ corresponds to an uncertainty in the entropy of 0.4 eu at 300°K and 0.7 eu at 1000°K. Coomber (2) and Amphlett (13) used kinetic data to derive entropies of 63.2 eu at 350°K and 71.5 eu at 600°K. The calculated entropies from this table are higher by 2.0 and 1.7 eu, respectively. These differences are only slightly larger than our estimate of the uncertainty in the kinetic results. We estimate the overall uncertainty in the calculated entropies as 1.0 eu at 298°K and 1.6 eu at 1000°K.

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFPRC Contract Nr. F04611-67-C-0009, Dow Chemical Co., July, 1969.
2. J. W. Coomber and E. Whittle, Trans. Faraday Soc. 52, 2183 (1956).
3. J. C. Amphlett and E. Whittle, Trans. Faraday Soc. 52, 2130 (1956).
4. N. A. Goy, A. Lord, and H. O. Fritchard, J. Phys. Chem. 71, 1086 (1967).
5. N. A. Goy, A. Lord, and H. O. Fritchard, J. Phys. Chem. 71, 1086 (1967).
6. Reference (4) Table III; G. S. Laurence, Trans. Faraday Soc. 63, 1155 (1967).
7. E. Tschuikow-Roux, J. Chem. Phys. 43, 2251 (1965).
8. J. W. Coomber and E. Whittle, Trans. Faraday Soc. 63, 1394 (1967).
9. C. J. Noutary, J. Res. Nat. Bur. Stand. 72A, 479 (1968).
10. J. W. Coomber and E. Whittle, Trans. Faraday Soc. 63, 2656 (1967).
11. T. C. Ehler, J. Phys. Chem. 71, 1086 (1967).
12. D. Morokuma, L. Pedersen and H. Karplus, J. Chem. Phys. 48, 4801 (1968).
13. D. K. Morokuma, P. A. Dobosh and J. A. Pople, J. Chem. Phys. 48, 4803 (1968); M. S. Gordon and J. A. Pople, J. Chem. Phys. 49, 4643 (1968).
14. R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 43, 2704 (1965).
15. E. C. Milligan, M. E. Jacox and J. J. Cornford, J. Chem. Phys. 44, 4058 (1966).
16. G. Carlson, J. Chem. Phys. 44, 4053 (1966).
17. C. Lifshitz and W. A. Chupka, J. Chem. Phys. 47, 3039 (1967).
18. D. E. Milligan and M. E. Jacox, J. Chem. Phys. 49, 5330 (1968).
19. J. C. Amphlett and E. Whittle, Trans. Faraday Soc. 63, 2695 (1967).

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Sept. 30, 1964; June 30, 1969

Point Group C_{3v}

$$\Delta H_f^\circ = -139.4 \pm 0.8 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -139.4 \pm 0.8 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -139.4 \pm 0.8 \text{ kcal/mol}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
1074 (1)	1185 (2)
742 (1)	539 (2)
284 (1)	260 (2)

$$\text{Bond Distance: C-F} = 1.332 \text{ \AA} \quad \text{C-I} = 2.130 \text{ \AA}$$

$$\text{Bond Angle: F-C-F} = 108.3 \pm 1^\circ \quad \text{F-C-I} = 110.62^\circ$$

$$\text{Product of the Moments of Inertia: } I_A I_B I_C = 4.4095 \times 10^{-113} \text{ g}^3 \text{ cm}^6$$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₃X (X = H, Cl, Br, I, CF₃) and C₂F₆. Details of the input data and the adjustment are given in (1). Lord, Goy and Fritchard (2, 3) report equilibrium data for the reactions CF₃X(g) + I₂(g) = CF₃I(g) + XI(g) where X = H, Cl, and Br. In addition to these prime links, there is a weak link to CF₃ through kinetic studies of CF₃I(g) + I(g) = CF₃(g) + I₂(g). Data for this reaction (3, 12) yield the average value $\Delta H_f^\circ = 17.1 \pm 2 \text{ kcal/mol}$ at 298.15°K.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction studies by Bowen (4), Anderson (5), and Mong and Schomaker (6). Differences among the data are small. The results of Anderson are adopted since they are intermediate between the others. Microwave data (7) are consistent with the adopted parameters. Infrared spectra of the gas were observed by several investigators (8, 9, 10) and Raman spectra of the liquid were obtained by Edgell and May (10). The vibrational assignments of (9, 10) are in close agreement. These assignments are adopted but preference is given to frequencies observed for the gas. In particular, ν_6 is taken as 260 cm⁻¹ (from overtone and combination bands of the gas) rather than 265 cm⁻¹ (from the Raman spectra of the liquid). The approximate values of ν_2 , ν_3 and ν_6 have been confirmed by analysis (11) of absorption spectra in the UV.

The thermodynamic functions of this table are essentially the same as those calculated by (9). Uncertainty in the entropy is estimated to vary from 0.15 to 0.6 gibbs/mol over the range from 300 to 1000°K. Uncertainty in ν_6 and neglect of anharmonicity are the major sources of error. Discussions of the magnitude of anharmonic effects appear on the tables for CClF₃(g) and CF₄(g). The principal moments of inertia are $I_A = 14.71 \times 10^{-39}$ and $I_B = I_C = 54.75 \times 10^{-39} \text{ g cm}^2$.

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFRL Contract Nr. F04611-67-C-0009, Dow Chemical Co., July, 1969.
2. A. Lord, C. A. Goy and H. O. Pritchard, J. Phys. Chem. **71**, 2705 (1967).
3. C. A. Goy, A. Lord and H. O. Pritchard, J. Phys. Chem. **71**, 1086 (1967).
4. H. J. M. Bowen, Trans. Faraday Soc. **50**, 444 (1954).
5. R. E. Anderson, Dissertation Abstracts **13**, 50 (1968).
6. C. Mong and V. Schomaker, J. Chem. Phys. **28**, 1010 (1958).
7. J. Sheridan and M. Gordy, J. Chem. Phys. **20**, 591 (1952).
8. E. K. Plyler and N. Acquista, J. Res. Nat. Bur. Stand. **118**, 92 (1952).
9. P. R. McGee, F. F. Cleveland, A. G. Meister and C. E. Decker, J. Chem. Phys. **21**, 242 (1953).
10. W. F. Edgell and C. E. May, J. Chem. Phys. **22**, 1808 (1954).
11. L. H. Sutcliffe and A. D. Walsh, Trans. Faraday Soc. **57**, 873 (1961).
12. G. S. Laurence, Trans. Faraday Soc. **53**, 1155 (1957).

Trifluoroiodomethane (CF₃I)
(Ideal Gas) GFW = 195.91075

T, °K	C _p ^o	S ^o	-(C _p ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	10.000	59.000	1M1M1E	3.527	-139.393	-139.393	1M1M1E
100	10.006	59.006	1M1M1E	3.527	-139.393	-139.393	1M1M1E
200	10.016	59.016	1M1M1E	3.527	-139.393	-139.393	1M1M1E
298	16.955	73.498	73.498	.000	-140.800	-136.503	100.040
300	17.002	73.603	73.498	.031	-140.806	-136.477	99.423
400	19.230	76.815	74.194	1.649	-142.975	-137.671	97.487
500	20.646	81.296	75.176	3.857	-146.258	-132.413	97.487
600	21.996	87.198	77.194	6.002	-148.187	-129.250	97.079
700	22.819	90.654	78.675	8.245	-148.095	-126.100	96.370
800	23.418	93.743	80.544	10.559	-147.990	-122.966	95.563
900	23.862	96.546	82.167	12.865	-147.876	-119.850	94.663
1000	24.196	99.060	83.732	15.328	-147.760	-116.737	93.685
1100	24.457	101.379	85.233	17.761	-147.642	-113.642	92.579
1200	24.661	103.516	86.669	20.217	-147.521	-110.554	91.335
1300	24.824	105.497	88.042	22.692	-147.405	-107.478	90.000
1400	24.955	107.362	89.355	25.181	-147.296	-104.410	88.597
1500	25.063	109.107	90.617	27.682	-147.174	-101.351	87.125
1600	25.152	110.687	91.817	30.193	-147.063	-98.302	85.597
1700	25.227	112.215	92.972	32.712	-146.953	-95.257	84.024
1800	25.290	113.656	94.082	35.238	-146.847	-92.221	82.406
1900	25.341	115.026	95.150	37.770	-146.743	-89.190	80.745
2000	25.381	116.326	96.175	40.307	-146.641	-86.160	79.045
2100	25.431	117.568	97.165	42.848	-146.543	-83.139	77.302
2200	25.466	118.752	98.119	45.392	-146.450	-80.125	75.524
2300	25.496	119.885	99.041	47.941	-146.358	-77.108	73.727
2400	25.521	120.970	100.000	50.490	-146.268	-74.088	71.900
2500	25.547	122.013	100.775	53.045	-146.186	-71.059	69.951
2600	25.568	123.015	101.630	55.601	-146.111	-68.033	67.895
2700	25.587	123.981	102.440	58.159	-146.036	-65.004	65.724
2800	25.604	124.910	103.260	60.720	-145.963	-62.000	63.424
2900	25.620	125.810	104.060	63.283	-145.892	-59.000	61.000
3000	25.633	126.679	104.732	65.842	-145.836	-56.115	58.466
3100	25.646	127.520	105.453	68.406	-145.776	-53.123	55.745
3200	25.657	128.334	106.156	70.971	-145.723	-50.134	52.900
3300	25.667	129.126	106.840	73.538	-145.670	-47.150	50.000
3400	25.676	129.899	107.500	76.107	-145.618	-44.178	47.000
3500	25.686	130.635	108.157	78.673	-145.569	-41.178	43.951
3600	25.694	131.356	108.791	81.242	-145.553	-38.195	40.800
3700	25.701	132.062	109.411	83.812	-145.523	-35.214	37.600
3800	25.708	132.746	110.016	86.383	-145.497	-32.222	34.350
3900	25.716	133.416	110.607	88.953	-145.470	-29.222	31.050
4000	25.720	134.067	111.186	91.525	-145.459	-26.271	27.700
4100	25.726	134.702	111.751	94.097	-145.449	-23.293	24.350
4200	25.731	135.322	112.305	96.670	-145.443	-20.311	21.000
4300	25.736	135.926	112.846	99.242	-145.437	-17.311	17.650
4400	25.740	136.519	113.379	101.817	-145.441	-14.311	14.300
4500	25.744	137.098	113.900	104.391	-145.457	-11.378	10.950
4600	25.748	137.664	114.410	106.966	-145.471	-8.396	7.600
4700	25.751	138.217	114.911	109.541	-145.491	-5.416	4.250
4800	25.754	138.758	115.400	112.116	-145.510	-2.436	0.900
4900	25.758	139.290	115.886	114.692	-145.534	0.581	-2.450
5000	25.761	139.811	116.357	117.266	-145.564	3.531	-5.800
5100	25.763	140.321	116.822	119.844	-145.626	6.503	-9.150
5200	25.766	140.822	117.278	122.429	-145.674	9.495	-12.500
5300	25.769	141.314	117.728	125.016	-145.722	12.487	-15.850
5400	25.771	141.798	118.169	127.604	-145.765	15.464	-19.200
5500	25.773	142.267	118.603	130.151	-145.850	18.452	-22.550
5600	25.775	142.731	119.030	132.729	-145.920	21.440	-25.900
5700	25.777	143.186	119.450	135.306	-145.977	24.427	-29.250
5800	25.779	143.636	119.860	137.884	-146.034	27.415	-32.600
5900	25.781	144.077	120.269	140.462	-146.165	30.410	-35.950
6000	25.783	144.510	120.670	143.041	-146.258	33.400	-39.300

June 30, 1969

CF₃I

Carbon Tetrafluoride (CF₄)

(Ideal Gas) CFW = 88.00475

CARBON TETRAFLUORIDE (CF₄)

(IDEAL GAS)

GFW = 88.00475

Point Group T_d $\Delta H_f^\circ = -221.61 \pm 0.3 \text{ kcal/mol}$ $S_{298.15}^\circ = 62.454 \pm 0.06 \text{ gibbs/mol}$ $\Delta H_f^\circ = -221.61 \pm 0.3 \text{ kcal/mol}$

Ground State Quantum Weight = 1

 $\Delta H_f^\circ = -221.61 \pm 0.3 \text{ kcal/mol}$

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log K _p
0	-	-	-	-	-	-	INFINITE
100	8.304	50.729	INFINITE	3.043	-221.611	-221.611	INFINITE
200	11.332	57.306	63.686	2.242	-222.214	-222.214	478.902
298	14.592	62.454	63.686	1.276	-222.726	-215.026	235.643
300	14.592	62.454	63.686	1.276	-222.726	-215.026	235.643
400	17.304	67.139	63.686	0.271	-223.045	-212.301	154.661
500	19.290	71.225	64.294	3.465	-223.326	-205.041	69.623
600	20.741	74.077	65.759	5.471	-223.362	-201.379	73.352
700	21.699	76.126	67.300	7.600	-223.350	-197.559	51.013
800	22.216	77.432	68.799	9.849	-223.280	-193.594	46.235
900	23.166	83.617	70.362	12.110	-223.280	-190.398	40.614
1000	23.613	86.282	71.832	14.450	-223.216	-186.744	36.380
1100	23.960	88.550	73.250	16.829	-223.144	-183.104	32.655
1200	24.232	90.656	74.614	19.239	-223.064	-179.467	29.505
1300	24.433	92.511	75.933	21.684	-222.976	-175.840	26.684
1400	24.631	94.144	77.179	24.129	-222.899	-172.213	24.564
1500	24.777	96.119	78.386	26.599	-222.815	-168.594	22.536
1600	24.899	97.722	79.545	29.083	-222.731	-164.985	20.536
1700	25.001	99.234	80.659	31.578	-222.646	-161.377	18.547
1800	25.091	100.661	81.741	34.084	-222.561	-157.770	16.567
1900	25.161	102.024	82.784	36.595	-222.482	-154.179	14.587
2000	25.224	103.317	83.799	39.115	-222.401	-150.584	12.607
2100	25.279	104.549	84.720	41.640	-222.323	-146.997	10.627
2200	25.327	105.726	85.648	44.170	-222.250	-143.414	8.647
2300	25.369	106.851	86.548	46.704	-222.181	-139.831	6.667
2400	25.406	107.933	87.435	49.244	-222.109	-136.251	4.687
2500	25.439	108.971	88.256	51.786	-222.045	-132.677	2.707
2600	25.468	109.969	89.072	54.332	-221.984	-129.102	0.727
2700	25.494	110.934	90.824	56.880	-221.926	-125.529	-1.253
2800	25.516	111.869	92.534	59.432	-221.876	-121.954	-3.233
2900	25.535	112.758	94.181	61.983	-221.822	-118.381	-5.213
3000	25.558	113.620	95.870	64.536	-221.774	-114.803	-7.193
3100	25.575	114.459	97.500	67.095	-221.735	-111.226	-9.173
3200	25.589	115.269	99.074	69.653	-221.699	-107.650	-11.153
3300	25.601	116.053	100.594	72.214	-221.670	-104.073	-13.133
3400	25.618	116.823	102.061	74.774	-221.639	-100.496	-15.113
3500	25.630	117.566	103.481	77.336	-221.614	-96.919	-17.093
3600	25.641	118.288	104.854	79.900	-221.594	-93.342	-19.073
3700	25.649	118.984	106.184	82.465	-221.575	-89.765	-21.053
3800	25.656	119.651	107.469	85.031	-221.559	-86.188	-23.033
3900	25.669	120.342	108.911	87.597	-221.537	-82.611	-25.013
4000	25.677	120.992	110.316	90.164	-221.517	-79.034	-26.993
4100	25.685	121.626	111.684	92.732	-221.504	-75.457	-28.973
4200	25.692	122.244	113.016	95.301	-221.500	-71.880	-30.953
4300	25.698	122.849	114.304	97.864	-221.500	-68.303	-32.933
4400	25.704	123.440	115.551	100.430	-221.539	-64.726	-34.913
4500	25.710	124.016	116.761	103.011	-221.667	-61.149	-36.893
4600	25.715	124.583	117.933	105.592	-221.701	-57.572	-38.873
4700	25.725	125.134	119.164	108.174	-221.741	-53.995	-40.853
4800	25.732	125.676	120.359	110.759	-221.781	-50.418	-42.833
4900	25.739	126.208	121.506	113.299	-221.837	-46.841	-44.813
5000	25.743	126.728	122.616	115.872	-221.894	-43.264	-46.793
5100	25.737	127.236	123.694	118.446	-221.957	-39.687	-48.773
5200	25.744	127.736	124.736	121.020	-222.025	-36.110	-50.753
5300	25.747	128.226	125.736	123.604	-222.095	-32.533	-52.733
5400	25.750	128.709	126.709	126.168	-222.161	-28.956	-54.713
5500	25.750	129.182	127.643	128.743	-222.267	-25.379	-56.693
5600	25.753	129.646	130.196	131.318	-222.360	-21.802	-58.673
5700	25.759	130.099	131.694	133.894	-222.459	-18.225	-60.653
5800	25.761	130.559	133.159	136.474	-222.556	-14.648	-62.633
5900	25.761	130.990	134.606	139.046	-222.673	-11.071	-64.613
6000	25.764	131.423	136.039	141.622	-222.790	-7.494	-66.593

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Sept. 30, 1964; June 30, 1969

CF 4

Vibrational Frequencies and Degeneracies

 $\frac{\omega}{\text{cm}^{-1}}$ $\frac{\omega}{\text{cm}^{-1}}$

908.5 (1)

1783.0 (3)

435.0 (2)

631.5 (3)

 $\sigma = 12$ $I_A I_B I_C = 3.1489 \times 10^{-114} \text{ g cm}^2$

Bond Angle: F-C-F = 109.47°

Bond Distance: C-F = 1.320 Å

Product of the Moments of Inertia: $I_A I_B I_C = 3.1489 \times 10^{-114} \text{ g cm}^2$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of HF(g), HF(50 H₂O) and five closely related fluorides. Adjustment of 73 selected observations relating the 7 variables gives the following heats of formation in kcal/mol at 298.15°K: HF(g), -65.14 ± 0.2; HF(50 H₂O), -76.78 ± 0.1; NaF(s), -137.52 ± 0.2; BF₃(g), -271.42 ± 0.4; CF₄(g), -223.04 ± 0.3; NF₃(g), -31.43 ± 0.3; and C₂F₄(polymer), -198.2 ± 0.7. The ± values are estimates of the overall uncertainty including systematic error. Further details of the simultaneous adjustment are given in (1).

The selected value is essentially the same as that obtained by Greenberg and Hubbard (2) in their thorough calorimetric study of the combustion in fluorine of natural and synthetic graphite. Their result is confirmed by the data of Domalski and Armstrong (3) for combustion of graphite-Teflon mixtures. Reliable data (1) also link CF₄(g) with HF(n H₂O), NF₃(g) and C₂F₄(polymer). Armstrong (1, 3) critically reviewed the more uncertain data which were omitted from the adjustment.

Heat Capacity and Entropy

The fundamental vibrations are those observed in the gas-phase Raman spectra by Monostori and Weber (3) and the gas-phase infrared spectra by Haki et al. (5) and Chalmers and McKean (7). The frequencies are essentially the same as those selected by Shimanouchi (8) who also lists earlier spectral studies. Electron-diffraction studies of the gas were reported by Thornton (9) and Hoffman and Livingston (10). The adopted bond length is the average of these two results which differ by only 0.006 Å. The principal moments of inertia are $I_A = I_B = I_C = 14.657 \times 10^{-39} \text{ g cm}^2$.

The most significant uncertainty in the calculated thermodynamic functions is due to neglect of anharmonic contributions. Estimates for these contributions were given by Barho (11) and Albright et al. (12), and functions calculated with anharmonic terms were given by McBride et al. (13). Differences between McBride and this JANAF table vary from 0.1 to 0.75 gibbs/mol in Cp° and 0.05 to 0.49 gibbs/mol in S° over the range from 300 to 1000°K. Measurements (14) of Cp° (303-473°K) suggest that anharmonic contributions are significant, but the data are not sufficiently accurate to test the calculations of McBride (13). Heat capacity data (15) for the condensed phases were reviewed by Kelley and King (16) who derived S°_{298.15} = 62.8 ± 0.5 gibbs/mol for CF₄(g).

References

1. A. N. Syverud, Report AFPL-TR-69-70, Jan., 1969.
2. E. Greenberg and W. N. Hubbard, J. Phys. Chem., **72**, 222 (1968).
3. E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Stand., **71A**, 105 (1967).
4. G. T. Armstrong, U. S. Nat. Bur. Stand., Report 9003, 1-18 (1966).
5. B. Monostori and A. Weber, J. Chem. Phys., **33**, 1887 (1960).
6. A. Maki, E. K. Plyler and R. Thibault, J. Chem. Phys., **37**, 1899 (1962).
7. A. Chalmers and D. C. McKean, Spectrochim. Acta **22**, 251 (1966).
8. T. Shimanouchi, U. S. Nat. Bur. Stand., NBS-NBS 6, 11 (1967).
9. C. G. Thornton, Dissertation Abstracts **14**, 604 (1954); R. L. Livingston, Ann. Rev. Phys. Chem., **5**, 397 (1954).
10. C. W. W. Hoffman and R. L. Livingston, J. Chem. Phys., **21**, 565 (1953).
11. W. Barho, Kältetechnik **17**, 219 (1965).
12. L. F. Albright, W. C. Galeger and K. K. Innes, J. Am. Chem. Soc., **76**, 6017 (1954).
13. B. J. McBride, J. S. Helme, J. G. Ehlers and S. Gordon, NASA SP-3001, 156 (1963).
14. Y. Huang and J. J. Martin, A. I. Ch. E. J., **10**, 89 (1964).
15. A. Eucken and E. Schröder, Z. Phys. Chem., **148**, 307 (1939).
16. K. K. Kelley and E. G. King, U. S. Bur. Mines Bull., **592**, 1961.

CF 4

Point Group C_{2v} $\Delta H_f^\circ = -181.9 \pm 3 \text{ kcal/mol}$ $S_{298.15}^\circ = 77.06 \pm 0.7 \text{ gibbs/mol}$ $\Delta H_f^\circ = -182.8 \pm 3 \text{ kcal/mol}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
1294.4 (1)	679.0 (1)	1223.2 (1)
1262.5 (1)	584.1 (1)	607.5 (1)
947.3 (1)	433.7 (1)	250.0 (1)
882.1 (1)	227.5 (1)	Internal rotation

Bond Distances: C-F = $1.331 \text{ \AA}$ F-O = $1.42 \text{ \AA}$ C-O = $1.431 \text{ \AA}$ Bond Angles: C-O-F = (103.2°) F-C-F = (109.5°) Product of Moments of Inertia: $I_A I_B I_C = 1.138 \times 10^{-113} \text{ g}^3 \text{ cm}^6$

Heat of Formation

Porter and Cady (1) measured equilibrium constants for the reaction

 $\text{CF}_3\text{OF(g)} \rightleftharpoons \text{COF}_2\text{(g)} + \text{F}_2\text{(g)}$

in the temperature range 630-750°K. Equilibrium constants were also determined with excess fluorine added to the system.

Second and third law analyses of these data yield the following heats of reaction:

	ΔH_{298}° 2nd law	ΔH_{298}° 3rd law	Drift
Set 1	27.65 ± 0.2	30.10	3.6 ± 0.3
Set added fluorine	25.11 ± 0.3	30.09	7.2 ± 0.5

The third law analyses indicate significant trends within each set of equilibrium data. If the entire error is assigned to the free energy functions, then the drifts in the third law analysis imply that the free energy functions for CF₃OF should be increased by 3.6 or 7.2 gibbs/mol. However, the real error in these free energy functions is probably no larger than 1 gibbs/mol in the temperature range of the experimental data. Apparently, the equilibrium reaction investigated by Porter and Cady (1) was affected by side reactions possibly involving perfluorodimethyl peroxide. However, since the only other approach to the heat of formation of CF₃OF involves bond energies, we adopt the third law value, $\Delta H_f^\circ = 30.1 \text{ kcal/mol}$, and derive $\Delta H_{298}^\circ(\text{CF}_3\text{OF, g}) = -182.8 \pm 3 \text{ kcal/mol}$ with $\Delta H_{298}^\circ(\text{COF}_2, \text{g}) = -152.7 \pm 0.4 \text{ kcal/mol}$ (2).

Czarnowski et al. (3) recently determined the O-F bond energy in CF₃OF from kinetic studies on the thermal decomposition of CF₃OF in the presence of SO₃. They reported the value $D(\text{O-F}) = 43.5 \pm 0.5 \text{ kcal/mol}$. Combining this result with the following data,

 $\Delta H_{298}^\circ(\text{C, g}) = 170.89 \pm 0.45 \text{ kcal/mol}$ (4) $\Delta H_{298}^\circ(\text{F, g}) = 18.96 \pm 0.40 \text{ kcal/mol}$ (5) $\Delta H_{298}^\circ(\text{O, g}) = 59.559 \pm 0.03 \text{ kcal/mol}$ (6) $D(\text{C-O}) = 117.4 \text{ kcal/mol}$ (from $\Delta H_{298}^\circ(\text{CF}_4, \text{g}) = -223.04 \pm 0.3 \text{ kcal/mol}$ (7))we derive $\Delta H_{298}^\circ(\text{CF}_3\text{OF, g}) = -173.8 \text{ kcal/mol}$.

The value determined from Porter and Cady's equilibrium data is adopted here. H_{298}° is determined to be -4.086 kcal/mol .

Heat Capacity and Entropy

The vibrational frequencies are from the infrared and Raman studies of Wilt and Jones (9) and are in reasonable agreement with nine of the twelve expected fundamentals observed by Lagemann et al. (10). Bond lengths and angles are estimated quantities chosen by Wilt and Jones (9). Individual moments of inertia calculated from these estimated molecular constants are $I_A = 14.723 \times 10^{-39} \text{ g cm}^2$, $I_B = 27.796 \times 10^{-39} \text{ g cm}^2$, and $I_C = 27.801 \times 10^{-39} \text{ g cm}^2$. The contributions of hindered internal rotation to the thermodynamic properties of CF₃OF are from the tables of Pitzer and Gwinn (11). The reduced moment of inertia, I_r , and the potential barrier, V_0 , are from the work of Wilt and Jones (9) and are:

$$I_r = 2.939 \times 10^{-39} \text{ g cm}^2$$

$$V_0 = 1130 \text{ cal/mol } (V_{12} = 56 \text{ cm}^{-1})$$

References

1. R. S. Porter and G. H. Cady, J. Amer. Chem. Soc., **79**, 5678 (1957).
2. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, Dec. 31, 1969.
3. J. Czarnowski, L. Castellano, and H. J. Schumacher, Chem. Commun., **20**, 1755 (1968).
4. R. S. Porter, J. Amer. Chem. Soc., **81**, 5678 (1959).
5. Ref. 2, Sept. 30, 1965.
6. Ref. 2, June 30, 1962.
7. Ref. 2, June 30, 1962.
8. L. S. Gould, "Inorganic Reactions and Structure," Revised Ed., Holt, Rinehart, and Winston, New York, 1962, p. 138.
9. P. Wilt and E. A. Jones, J. Inorg. Nucl. Chem., **30**, 2933 (1966).
10. P. Wilt and E. A. Jones, J. Mol. Spectry., **20**, 1768 (1952).
11. K. S. Pitzer and W. D. Gwinn, J. Chem. Phys., **10**, 428 (1942).

Mar. 31, 1965; Dec. 31, 1969

Methylidyne (CH)

(Ideal Gas)

GFW = 13.01912

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o)/T	cal/mol ΔH ^o	ΔG ^o	Log K _p
0	4.993	∞	∞	141.178	141.178	∞
100	4.999	30.099	-2.084	141.178	141.178	∞
200	4.999	44.920	-1.382	141.178	141.178	∞
300	4.999	54.758	-0.884	141.178	141.178	∞
400	4.972	61.721	-0.608	142.000	134.082	-90.246
500	4.972	67.764	-0.431	142.000	133.973	-97.599
600	4.972	72.771	-0.315	142.000	133.973	-97.599
700	4.972	76.833	-0.231	142.000	133.973	-97.599
800	4.972	80.000	-0.171	142.000	133.973	-97.599
900	4.972	82.333	-0.128	142.000	133.973	-97.599
1000	4.972	83.921	-0.094	142.000	133.973	-97.599
1100	4.972	85.764	-0.068	142.000	133.973	-97.599
1200	4.972	87.833	-0.048	142.000	133.973	-97.599
1300	4.972	90.111	-0.032	142.000	133.973	-97.599
1400	4.972	92.600	-0.019	142.000	133.973	-97.599
1500	4.972	95.300	-0.008	142.000	133.973	-97.599
1600	4.972	98.200	-0.001	142.000	133.973	-97.599
1700	4.972	101.300	0.000	142.000	133.973	-97.599
1800	4.972	104.600	0.000	142.000	133.973	-97.599
1900	4.972	108.100	0.000	142.000	133.973	-97.599
2000	4.972	111.800	0.000	142.000	133.973	-97.599
2100	4.972	115.700	0.000	142.000	133.973	-97.599
2200	4.972	119.800	0.000	142.000	133.973	-97.599
2300	4.972	124.100	0.000	142.000	133.973	-97.599
2400	4.972	128.600	0.000	142.000	133.973	-97.599
2500	4.972	133.300	0.000	142.000	133.973	-97.599
2600	4.972	138.200	0.000	142.000	133.973	-97.599
2700	4.972	143.300	0.000	142.000	133.973	-97.599
2800	4.972	148.600	0.000	142.000	133.973	-97.599
2900	4.972	154.100	0.000	142.000	133.973	-97.599
3000	4.972	159.800	0.000	142.000	133.973	-97.599
3100	4.972	165.700	0.000	142.000	133.973	-97.599
3200	4.972	171.800	0.000	142.000	133.973	-97.599
3300	4.972	178.100	0.000	142.000	133.973	-97.599
3400	4.972	184.600	0.000	142.000	133.973	-97.599
3500	4.972	191.300	0.000	142.000	133.973	-97.599
3600	4.972	198.200	0.000	142.000	133.973	-97.599
3700	4.972	205.300	0.000	142.000	133.973	-97.599
3800	4.972	212.600	0.000	142.000	133.973	-97.599
3900	4.972	220.100	0.000	142.000	133.973	-97.599
4000	4.972	227.800	0.000	142.000	133.973	-97.599
4100	4.972	235.700	0.000	142.000	133.973	-97.599
4200	4.972	243.800	0.000	142.000	133.973	-97.599
4300	4.972	252.100	0.000	142.000	133.973	-97.599
4400	4.972	260.600	0.000	142.000	133.973	-97.599
4500	4.972	269.300	0.000	142.000	133.973	-97.599
4600	4.972	278.200	0.000	142.000	133.973	-97.599
4700	4.972	287.300	0.000	142.000	133.973	-97.599
4800	4.972	296.600	0.000	142.000	133.973	-97.599
4900	4.972	306.100	0.000	142.000	133.973	-97.599
5000	4.972	315.800	0.000	142.000	133.973	-97.599
5100	4.972	325.700	0.000	142.000	133.973	-97.599
5200	4.972	335.800	0.000	142.000	133.973	-97.599
5300	4.972	346.100	0.000	142.000	133.973	-97.599
5400	4.972	356.600	0.000	142.000	133.973	-97.599
5500	4.972	367.300	0.000	142.000	133.973	-97.599
5600	4.972	378.200	0.000	142.000	133.973	-97.599
5700	4.972	389.300	0.000	142.000	133.973	-97.599
5800	4.972	400.600	0.000	142.000	133.973	-97.599
5900	4.972	412.100	0.000	142.000	133.973	-97.599
6000	4.972	423.800	0.000	142.000	133.973	-97.599

CH

METHYLDIYNE (CH)

(IDEAL GAS)

GFW = 13.01912

Ground State Configuration $2^1\Pi$ $\Delta H_f^\circ = 141.2 \pm 0.1$ kcal/mol $S_{298.15}^\circ = 43.72 \pm 0.01$ gibbs/mol $\Delta H_f^\circ = 142.0 \pm 0.1$ kcal/mol

Electronic Levels and Multiplicities

e_i , cm ⁻¹	g_i
0	2
17.9	2
[4500]	4
23150	4
25949	2
31821	2

 $\omega_e X_e = 84.29$ cm⁻¹ $\sigma = 1$ $a_e = 0.5339$ cm⁻¹ $r_e = 1.1198$ Å

Heat of Formation

G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950, reanalyzed the rotational predissociation reported by T. Shidei, Japan J. Phys. 11, 23 (1936), and concluded that $D_0^\circ = 80.0$ kcal/mol (3.47 eV). This yields $\Delta H_f^\circ(298.15^\circ\text{K}, g) = 142.0$ kcal/mol and is the adopted value.

R. G. Brewer and F. L. Kester, J. Chem. Phys. 40, 812 (1964), have confirmed the value as 142 ± 5 kcal/mol, from an equilibrium study of the temperature variation of the intensity of the $\lambda_{2,2}^1\Pi$ emission band.

M. Linevsky, J. Chem. Phys. 47, 1495 (1967), determined the concentration of CH radicals in equilibrium with 1 atm. of hydrogen gas, by application of a high resolution spectro-photographic technique to three electronic transitions in absorption.

A third law analysis, using the present functions, of 27 determinations in the temperature range 3065 - 3155°K yielded $\Delta H_f^\circ(298.15^\circ\text{K}, g) = 142.01 \pm 1.28$ kcal/mol with a negligible drift. This value is in excellent agreement with the spectroscopic predissociation value.

Heat Capacity and Entropy

The vibrational and rotational constants and electronic levels are from Herzberg, loc. cit., with the exception of the estimated $\frac{1}{2}\epsilon$ level. All the constants have been adjusted to the normal isotopic abundances for both carbon and hydrogen. The $\frac{1}{2}\epsilon$ level is estimated from the ab initio calculations of A. C. Hurley, Proc. Roy. Soc. (London), 249A, 402 (1959), which include electron correlation effects. Earlier LCAO calculations had predicted the $\frac{1}{2}\epsilon$ level to be the ground state, but J. Higuchi, J. Chem. Phys. 22, 1339 (1954), used LCAO-SCF calculations and obtained the $\frac{1}{2}\epsilon$ level at 800 cm⁻¹. M. Krauss and J. F. Wöhner, J. Chem. Phys. 23, 1287 (1955), using essentially the same technique as Hurley, obtained $\frac{1}{2}\epsilon$ at 3000 cm⁻¹.

Monochloromethylene (CHCl)

(Ideal Gas) GFW = 48.47212

Point Group C_s $\Delta H_f^\circ = [79.9 \pm 10] \text{ kcal/mol}$ $S_{298.15}^\circ = 56.12 \pm 0.05 \text{ gibbs/mol}$ $\Delta H_f^\circ = [80 \pm 10] \text{ kcal/mol}$

Ground State Quantum Weight = 1

T, °K	Cp ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	Log Kp
100	7.000	47.000	INFINITE	2.427	78.939	INFINITE
150	8.170	52.750	56.900	1.830	80.047	86.497
200	8.170	56.118	56.118	.000	80.000	76.270
300	8.793	56.173	56.118	.016	79.998	76.287
400	9.498	56.799	56.472	1.905	79.905	76.283
500	10.146	58.499	57.152	1.913	79.792	76.257
600	10.786	62.895	57.962	2.960	79.677	72.610
700	11.434	64.606	58.791	4.071	79.572	71.442
800	12.040	66.176	59.617	5.247	79.493	70.266
900	12.604	67.634	60.479	6.486	79.448	69.137
1000	13.247	69.001	61.217	7.788	79.430	68.093
1100	13.720	70.286	61.984	9.133	79.445	66.848
1200	14.104	71.487	62.777	10.525	79.484	65.702
1300	14.403	72.639	63.486	11.951	79.538	64.551
1400	14.654	73.775	64.112	13.402	79.604	63.397
1500	14.879	74.779	64.614	14.873	79.675	62.230
1600	14.881	75.666	65.464	16.357	79.746	61.071
1700	14.941	76.591	66.092	17.848	79.815	59.903
1800	14.970	77.466	66.699	19.344	79.878	58.729
1900	14.975	78.283	67.286	20.841	79.934	57.554
2000	14.964	79.053	67.854	22.339	79.981	56.374
2100	14.942	79.753	68.403	23.834	80.020	55.194
2200	14.912	80.487	68.935	25.326	80.047	54.009
2300	14.879	81.169	69.450	26.816	80.065	52.827
2400	14.843	81.800	69.943	28.303	80.076	51.641
2500	14.807	82.387	70.433	29.788	80.069	50.454
2600	14.771	82.927	70.903	31.273	80.057	49.273
2700	14.737	83.484	71.358	32.739	80.035	48.086
2800	14.704	84.019	71.801	34.211	80.004	46.906
2900	14.672	84.534	72.231	35.684	79.964	45.734
3000	14.645	85.031	72.650	37.149	79.913	44.544
3100	14.618	85.511	73.057	38.609	79.858	43.367
3200	14.593	85.975	73.453	40.069	79.799	42.191
3300	14.571	86.428	73.840	41.527	79.738	41.016
3400	14.550	86.868	74.218	42.984	79.674	39.871
3500	14.531	87.290	74.593	44.437	79.589	38.674
3600	14.513	87.689	74.962	45.890	79.455	37.508
3700	14.497	88.066	75.292	47.340	79.352	36.345
3800	14.482	88.419	75.633	48.789	79.284	35.186
3900	14.466	88.749	75.968	50.237	79.240	34.030
4000	14.456	89.075	76.298	51.683	79.006	32.878
4100	14.445	89.572	76.614	53.128	78.878	31.719
4200	14.434	89.920	76.926	54.572	78.744	30.573
4300	14.425	90.251	77.233	56.015	78.603	29.427
4400	14.415	90.591	77.532	57.457	78.459	28.285
4500	14.406	90.915	77.826	58.898	78.307	27.142
4600	14.398	91.231	78.114	60.338	78.151	26.010
4700	14.390	91.541	78.396	61.777	77.990	24.880
4800	14.382	91.847	78.673	63.216	77.823	23.752
4900	14.377	92.140	78.945	64.653	77.651	22.626
5000	14.370	92.430	79.212	66.091	77.477	21.505
5100	14.364	92.715	79.474	67.528	77.296	20.385
5200	14.358	92.998	79.731	68.964	77.111	19.272
5300	14.353	93.279	80.000	70.399	76.921	18.164
5400	14.347	93.555	80.253	71.836	76.727	17.059
5500	14.342	93.799	80.477	73.269	76.527	15.954
5600	14.337	94.057	80.717	74.703	76.324	14.852
5700	14.332	94.311	80.953	76.115	76.115	13.753
5800	14.327	94.565	81.185	77.509	75.902	12.653
5900	14.323	94.805	81.415	78.899	75.682	11.553
6000	14.318	95.046	81.640	80.284	75.463	10.448

Dec. 31, 1969

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	1
[3000]	3
12288	1

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	
[2800] (1)	
1201 (1)	
815 (1)	

Bond Distance: C-H = 1.12 Å C-Cl = 1.889 Å

Bond Angle: H-C-Cl = 103.4°

Product of the Moments of Inertia: $I_A I_B I_C = 3.9877 \times 10^{-117} \text{ g}^3 \text{ cm}^6$

Heat of Formation

The heat of formation can be estimated as the average of those of the CH₂ and CCl₂ radicals, which gives $\Delta H_f^\circ(\text{CHCl}, g) = 74.5 \pm 15 \text{ kcal/mol}$. A better value for the heat of formation can be obtained by considering the reactions $\text{CHCl} + \text{CH} + \text{Cl}$ and $\text{CHCl} + \text{CCl} + \text{H}$. When $\Delta H_f^\circ(\text{CCl}, g) = 74.5 \text{ kcal/mol}$ is substituted into the above equations it gives $D_{\text{C-Cl}} = 98 \text{ kcal}$ and $D_{\text{C-H}} = 98 \text{ kcal}$. Although these values are not unreasonable the $D_{\text{C-H}}$ value appears to be too high compared to that in CFH. Thus, we adopt $\Delta H_f^\circ(\text{CHCl}, g) = 80 \text{ kcal/mol}$ which gives $D_{\text{C-Cl}} = 91 \text{ kcal}$ and $D_{\text{C-H}} = 92 \text{ kcal}$.

Heat Capacity and Entropy

The structure and electronic levels of the molecule have been established by Merer and Travis (1) from an analysis of the rotational structure of the visible absorption bands. The estimated triplet state is based on the electronic levels of CCl₂ and CH₂ as given in these tables. The vibrational levels are from Iacox and Milligan (2) who investigated the infrared spectrum of matrix-isolated CHCl, and also estimated the missing frequency.

² The individual moments of inertia are $I_A = 4.6455 \times 10^{-39} \text{ g cm}^2$, $I_B = 1.780 \times 10^{-40} \text{ g cm}^2$, and $I_C = 4.8235 \times 10^{-39} \text{ g cm}^2$.

References

1. A. J. Merer and D. N. Travis, Can. J. Phys. **44**, 575 (1966).
2. M. E. Iacox and D. E. Milligan, J. Chem. Phys. **47**, 1626 (1967).

Chlorodi fluoromethane (CHClF₂) (Ideal Gas) GFW = 86.4689

CHLORODIFLUOROMETHANE (CHClF₂) (IDEAL GAS) GFW = 86.4689

Point Group C_{2v}
S_{298.15} = 87.126 ± 0.2 gibbs/mol
Ground State Quantum Weight = 1
ΔH_f⁰ = -113.6 ± 3 kcal/mol
ΔH_{298.15}⁰ = -115.1 ± 3 kcal/mol

CHClF₂

T, °K	Cp*	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	Kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	-	2.967	-113.596	-	INFINITE
100	6.368	55.720	77.369	-2.165	-114.230	-112.235	245.289
200	10.930	62.245	68.286	-1.209	-114.717	-110.045	120.252
298	13.653	67.126	67.126	-	-115.100	-107.668	78.922
300	13.701	67.211	67.126	-0.925	-115.107	-107.622	78.402
400	17.039	71.465	67.493	1.517	-115.393	-105.080	57.413
500	17.649	75.268	68.637	3.215	-115.597	-102.478	44.793
600	19.221	78.649	70.196	5.072	-115.735	-99.640	36.367
700	20.871	81.694	71.624	7.089	-115.824	-97.102	30.342
800	22.550	84.490	73.047	9.267	-115.862	-94.745	25.561
900	24.250	86.980	74.467	11.262	-115.860	-92.561	21.489
1000	25.965	89.301	75.836	13.444	-115.820	-90.574	17.887
1100	27.696	91.466	77.159	15.716	-115.665	-88.504	14.627
1200	29.440	93.440	78.434	18.008	-115.483	-86.353	11.687
1300	31.196	95.241	79.661	20.312	-115.271	-84.122	8.947
1400	32.962	96.880	80.840	22.537	-115.031	-81.812	6.397
1500	34.738	98.367	81.976	25.066	-114.763	-79.425	4.032
1600	36.524	100.735	83.069	27.485	-114.474	-76.960	1.900
1700	38.320	102.933	84.123	29.893	-114.159	-74.520	0.971
1800	40.126	104.994	85.146	32.297	-113.821	-72.102	0.509
1900	41.942	106.941	86.138	34.742	-113.463	-69.703	0.263
2000	43.768	108.775	87.095	37.221	-113.083	-67.320	0.146
2100	45.604	110.506	87.980	39.690	-112.683	-64.953	0.067
2200	47.450	112.139	88.865	42.158	-112.263	-62.603	0.027
2300	49.306	113.675	89.743	44.625	-111.823	-60.263	0.007
2400	51.172	115.119	90.613	47.093	-111.363	-57.933	0.002
2500	53.048	116.475	91.476	49.560	-110.883	-55.603	0.000
2600	54.934	117.756	92.333	52.027	-110.383	-53.273	0.000
2700	56.830	118.966	93.186	54.493	-109.863	-50.943	0.000
2800	58.736	120.106	94.033	56.959	-109.323	-48.613	0.000
2900	60.652	121.179	94.876	59.425	-108.763	-46.283	0.000
3000	62.578	122.191	95.712	61.891	-108.183	-43.953	0.000
3100	64.514	123.146	96.543	64.357	-107.583	-41.623	0.000
3200	66.460	124.056	97.370	66.823	-106.963	-39.293	0.000
3300	68.416	124.924	98.191	69.289	-106.323	-36.963	0.000
3400	70.382	125.751	99.000	71.755	-105.663	-34.633	0.000
3500	72.358	126.539	99.799	74.221	-104.983	-32.303	0.000
3600	74.344	127.289	100.588	76.687	-104.283	-29.973	0.000
3700	76.340	128.004	101.367	79.153	-103.563	-27.643	0.000
3800	78.346	128.686	102.137	81.619	-102.823	-25.313	0.000
3900	80.362	129.336	102.900	84.085	-102.063	-22.983	0.000
4000	82.388	129.956	103.656	86.551	-101.283	-20.653	0.000
4100	84.424	130.548	104.406	89.017	-100.483	-18.323	0.000
4200	86.470	131.114	105.146	91.483	-99.663	-15.993	0.000
4300	88.526	131.656	105.876	93.949	-98.823	-13.663	0.000
4400	90.592	132.176	106.600	96.415	-97.963	-11.333	0.000
4500	92.668	132.676	107.317	98.881	-97.083	-9.003	0.000
4600	94.754	133.156	108.017	101.347	-96.183	-6.673	0.000
4700	96.850	133.616	108.706	103.813	-95.263	-4.343	0.000
4800	98.956	134.056	109.386	106.279	-94.323	-2.013	0.000
4900	101.072	134.476	110.056	108.745	-93.363	0.317	0.000
5000	103.200	134.876	110.716	111.211	-92.383	2.647	0.000
5100	105.340	135.256	111.366	113.677	-91.383	4.977	0.000
5200	107.490	135.616	112.016	116.143	-90.363	7.307	0.000
5300	109.650	135.956	112.656	118.609	-89.323	9.637	0.000
5400	111.820	136.276	113.286	121.075	-88.263	11.967	0.000
5500	114.000	136.576	113.906	123.541	-87.183	14.297	0.000
5600	116.190	136.856	114.516	126.007	-86.083	16.627	0.000
5700	118.390	137.116	115.116	128.473	-84.963	18.957	0.000
5800	120.600	137.356	115.706	130.939	-83.823	21.287	0.000
5900	122.820	137.576	116.286	133.405	-82.663	23.617	0.000
6000	125.060	137.776	116.856	135.871	-81.483	25.947	0.000

Dec. 31, 1960; Sept. 30, 1961; Sept. 30, 1964; June 30, 1970

Heat of Formation
Edwards and Small (1) determined a single equilibrium constant at 600°C for the reaction 2CHClF₂(g) + C₂F₆(g) + 2HCl(g). The value was not obtained directly but was obtained by extrapolation to eliminate the effects of side reactions. The equilibrium constant was used with JANAF free energy functions (2) to obtain ΔH_f⁰ = -115.1 kcal/mol, which yields ΔH_f⁰ (CHClF₂, g) = -115.1 kcal/mol. An uncertainty of ±3 kcal/mol corresponds to an uncertainty of about ±50% in the equilibrium constant.

Heat Capacity and Entropy

The gas phase vibrational frequencies have been observed in the Raman by Holzer and Moser (3); they do not see anything in the 1350 cm⁻¹ region as reported in the liquid by Glockler and Edgell (4). Plyler and Benedict (5) in their assignment replaced an 831 cm⁻¹ frequency by 1178 cm⁻¹. We essentially adopt Glockler and Edgell's assignment with updated gas phase values for the observed frequencies. The microwave spectrum has been analysed by McLay and Mann (6) and Beeson et al. (7), who derive bond lengths and angles in excellent agreement with each other. The values given by Beeson et al. are adopted here.

Neelson and White (8) have measured the low temperature heat capacity and heat of vaporization and have reported an entropy in the gas phase at 232.5°C of 63.919 ± 0.28 gibbs/mol. This compares with 63.959 gibbs/mol calculated from our adopted functions.

The individual moments of inertia are I_A = 8.203 × 10⁻³⁹ g cm², I_B = 17.402 × 10⁻³⁹ g cm² and I_C = 24.060 × 10⁻³⁹ g cm².

References

1. J. W. Edwards and P. A. Small, Ind. Eng. Chem. Fundamentals **4**, 396 (1965).
2. JANAF Thermochemical Tables; C₂F₆ dated 6-30-69; HCl dated 9-30-64.
3. W. Holzer and H. Moser, J. Mol. Spectry, **20**, 185 (1966) and **25**, 123 (1968).
4. G. Glockler and W. F. Edgell, J. Chem. Phys. **9**, 224 (1941).
5. E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std. **47**, 202 (1951).
6. D. B. McLay and C. R. Mann, Can. J. Phys. **40**, 61 (1962).
7. E. L. Beeson, T. L. Weatherly and Q. Williams, J. Chem. Phys. **37**, 2926 (1962).
8. E. F. Neelson and D. White, J. Amer. Chem. Soc. **79**, 5618 (1957).

CHClF₂

Dichlorofluoromethane (CHCl₂F)

GFW = 102.9235

(Ideal Gas)

Point Group C_{2v} $\Delta H_f^\circ = [-66.36 \pm 3] \text{ kcal/mol}$ $S_{298.15}^\circ = 70.07 \pm 0.2 \text{ gibbs/mol}$ $\Delta H_f^\circ = [-67.7 \pm 3] \text{ kcal/mol}$

Ground State Quantum Weight = 1

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	Log K ^p
0	-0.000	INFINITE	3.177	-	-66.364	INFINITE
100	9.004	57.617	81.294	-2.359	-66.983	141.957
200	11.993	64.786	71.322	-6.7387	-68.563	68.563
298	14.578	70.069	70.069	-0.000	-69.700	60.423
300	14.623	70.159	70.048	.027	-67.705	63.986
400	17.265	77.174	70.670	1.402	-67.939	37.434
500	18.447	78.607	71.873	3.367	-68.098	24.201
600	19.701	82.087	73.291	5.277	-68.201	19.237
700	20.661	85.199	74.774	6.296	-68.260	15.066
800	21.017	87.507	76.205	7.275	-68.285	11.966
900	21.017	90.597	77.597	8.173	-68.285	10.196
1000	22.510	92.913	79.110	13.602	-68.259	9.291
1100	22.918	95.078	80.465	16.074	-68.216	7.936
1200	23.260	97.087	81.767	18.384	-68.159	6.906
1300	23.558	98.854	82.992	20.462	-68.090	6.135
1400	23.795	100.415	84.221	22.392	-68.015	5.035
1500	24.005	102.144	85.376	25.482	-67.933	4.327
1600	24.186	103.919	86.487	27.692	-67.848	3.709
1700	24.343	105.390	87.556	30.119	-67.757	3.164
1800	24.478	106.681	88.584	32.671	-67.661	2.688
1900	24.599	107.813	89.579	35.218	-67.570	2.288
2000	24.703	109.377	90.537	37.679	-67.476	1.860
2100	24.796	110.585	91.463	40.154	-67.380	1.509
2200	24.879	111.740	92.358	42.638	-67.287	1.301
2300	24.954	112.841	93.219	45.129	-67.197	1.091
2400	25.016	113.911	94.066	47.628	-67.104	.834
2500	25.075	114.933	94.880	50.133	-67.017	.463
2600	25.127	115.918	95.670	52.643	-66.933	.165
2700	25.177	116.863	96.438	55.158	-66.852	.035
2800	25.225	117.770	97.180	57.680	-66.773	.000
2900	25.266	118.649	97.910	60.201	-66.701	.524
3000	25.292	119.526	98.616	62.729	-66.633	8.009
3100	25.324	120.356	99.304	65.260	-66.568	.740
3200	25.351	121.141	100.028	67.813	-66.507	.483
3300	25.371	121.891	100.698	70.370	-66.450	.154
3400	25.406	122.639	101.266	72.949	-66.408	1.793
3500	25.429	123.436	101.869	75.411	-66.367	2.026
3600	25.450	124.152	102.498	77.955	-66.329	2.290
3700	25.467	124.829	103.149	80.480	-66.294	2.574
3800	25.487	125.529	103.674	83.093	-66.272	2.865
3900	25.504	126.191	104.243	85.599	-66.252	3.043
4000	25.520	126.837	104.800	88.150	-66.238	3.282
4100	25.534	127.468	105.349	90.703	-66.229	3.5293
4200	25.541	128.085	105.893	93.257	-66.229	3.786
4300	25.551	128.685	106.403	95.812	-66.229	4.046
4400	25.557	129.272	106.916	98.369	-66.237	4.272
4500	25.584	129.847	107.419	100.927	-66.250	4.519
4600	25.594	130.410	107.913	103.486	-66.267	4.765
4700	25.604	130.940	108.397	106.037	-66.287	5.015
4800	25.613	131.499	108.873	108.606	-66.319	5.266
4900	25.622	132.027	109.340	111.168	-66.351	5.5113
5000	25.630	132.545	109.799	113.731	-66.388	5.7589
5100	25.638	133.054	110.250	116.294	-66.430	6.0066
5200	25.652	134.039	111.129	121.923	-66.527	6.5034
5300	25.652	134.033	111.129	121.923	-66.527	6.5034
5400	25.668	134.519	111.558	123.969	-66.583	6.7514
5500	25.665	134.990	111.980	126.555	-66.644	7.0001
5600	25.670	135.452	112.395	129.121	-66.708	7.2482
5700	25.676	135.907	112.803	131.683	-66.778	7.4974
5800	25.681	136.353	113.205	134.257	-66.851	7.7465
5900	25.686	136.792	113.601	136.825	-66.930	7.9948
6000	25.691	137.224	113.992	139.394	-67.013	8.2430

Dec. 31, 1960; Sept. 30, 1964; June 30, 1970

Vibrational Frequencies and Degeneracies

ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}
3023 (1)	741 (1)	1242 (1)
1313 (1)	455 (1)	806 (1)
1079 (1)	270 (1)	368 (1)
Bond Distance: C-H = 1.09 Å C-Cl = 1.75 Å C-F = 1.367 Å		
Bond Angle: Cl-C-Cl = 112°12' F-C-Cl = 109° H-C-Cl = 109°45'		
Product of the Moments of Inertia: $I_A I_B I_C = 1.11593 \times 10^{-113} \text{ g}^3 \text{ cm}^6$		
$\sigma = 1$		

Heat of Formation

The change in heat of atomization by successive replacement of F by Cl in the CF₄ to CCl₄ series follows a regular pattern (see CCl₂F₂ table). A similar pattern is to be expected in the CHCl₃ series. The first replacement of the series is, in fact, 4 kcal higher than the mean versus 3.8 kcal higher in the CF₃-CCl₄ series. Thus, we have selected the atomization energy of the second and third replacements to continue this pattern. In this manner we have selected the atomization energy of CHCl₂F as 367.4 kcal which corresponds to ΔH_f° (CHCl₂F, g) = -57.7 kcal/mol. With this adopted value, the successive replacement of F by Cl changes the heat of atomization by 41.4, 37.3 and 33.0 kcal.

Heat Capacity and Entropy

Holzer (1) has reported the gas phase Raman spectrum which is in excellent agreement with the assignments of Plyler and Benedict (2). The only discrepancy is in ν_7 , which Plyler and Benedict assign at 1242 cm⁻¹, and Holzer (1) does not report a band in this region. Holzer does, however, report a band at 728 cm⁻¹ which has not been reported in the earlier liquid studies. There is strong evidence from correlations with CHCl₃ and CHF₃ that two frequencies should occur between 1220 and 1376 cm⁻¹. On this basis we adopt the assignment of Plyler and Benedict for ν_7 , while accepting the gas phase values of Holzer for the other frequencies. The extra band at 728 cm⁻¹ is not used. It is probable that the bands at 741 and 728 cm⁻¹ are due to Fermi resonance of ν_4 with $2\nu_9$; the unperturbed level would lie at 735 cm⁻¹. The symmetry classes of ν_4 and $2\nu_9$ are identical and thus Fermi resonance is allowed.

Nclay (3) has reported the molecular structure from his microwave investigations. The individual principal moments of inertia are $I_A = 12.053 \times 10^{-39} \text{ g cm}^2$, $I_B = 25.684 \times 10^{-39} \text{ g cm}^2$ and $I_C = 36.047 \times 10^{-39} \text{ g cm}^2$.

References

1. W. Holzer, J. Mol. Spectry, **25**, 123 (1968).
2. E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std. **47**, 202 (1951).
3. D. B. Nclay, Can. J. Phys. **42**, 720 (1964).

CHLOROFORM (CHCl₃)

(IDEAL GAS)

GFW = 119.3781

Chloroform (CHCl₃)

(Ideal Gas) GFW = 119.3781

Point Group C_{3v}

$\Delta H_f^\circ = -23.49 \pm 0.3 \text{ kcal/mol}$

$S_{298.15}^\circ = 70.628 \pm 0.01 \text{ gibbs/mol}$

$\Delta H_f^\circ = -24.66 \pm 0.3 \text{ kcal/mol}$

Ground State Quantum Weight = 1

T, °K	Cp°	$\frac{\text{kilbbs/mol}}{S^\circ} - \frac{(C^\circ - H^\circ_{298})}{T}$	H° - H° ₂₉₈	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0	9.000	INFINITE	3.383	23.686	23.686	INFINITE
100	9.637	57.180	82.642	24.089	47.430	21.159
200	12.978	64.933	71.975	19.363	21.459	12.335
298	15.627	70.628	70.628	24.660	16.868	12.324
300	15.671	70.724	70.628	24.664	16.780	12.324
400	17.747	75.532	71.629	24.826	14.125	7.717
500	19.266	79.664	72.545	24.919	11.437	4.999
600	20.378	83.280	74.039	24.966	8.736	3.182
800	21.872	89.365	77.337	24.978	5.929	1.802
1000	22.398	91.972	78.643	24.926	3.921	0.551
1500	24.160	103.000	86.533	24.050	2.075	0.454
2000	26.877	112.159	92.735	23.778	3.258	3.729
2500	29.513	120.262	99.268	22.905	3.986	4.041
3000	32.132	126.441	106.224	22.424	4.536	4.224
3500	34.748	131.592	112.659	22.082	4.992	4.402
4000	37.362	136.748	118.683	21.836	5.404	4.584
4500	39.976	141.904	124.319	21.686	5.776	4.766
5000	42.590	147.060	129.559	21.621	6.110	4.910
5500	45.204	152.216	134.399	21.656	6.454	5.054
6000	47.818	157.372	138.834	21.714	6.766	5.200
6500	50.432	162.528	142.868	21.788	7.046	5.346
7000	53.046	167.684	146.503	21.876	7.296	5.492
7500	55.660	172.840	149.737	21.976	7.516	5.638
8000	58.274	177.996	152.571	22.086	7.706	5.784
8500	60.888	183.152	155.005	22.206	7.866	5.930
9000	63.502	188.308	157.039	22.336	8.006	6.076
9500	66.116	193.464	158.673	22.476	8.156	6.222
10000	68.730	198.620	160.007	22.626	8.306	6.368
10500	71.344	203.776	161.141	22.786	8.456	6.514
11000	73.958	208.932	161.975	22.946	8.606	6.660
11500	76.572	214.088	162.509	23.106	8.756	6.806
12000	79.186	219.244	162.743	23.266	8.906	6.952
12500	81.800	224.400	162.677	23.426	9.056	7.098
13000	84.414	229.556	162.311	23.586	9.206	7.244
13500	87.028	234.712	161.645	23.746	9.356	7.390
14000	89.642	239.868	160.679	23.906	9.506	7.536
14500	92.256	245.024	159.413	24.066	9.656	7.682
15000	94.870	250.180	157.847	24.226	9.806	7.828
15500	97.484	255.336	155.981	24.386	9.956	7.974
16000	100.098	260.492	153.815	24.546	10.106	8.120
16500	102.712	265.648	151.349	24.706	10.256	8.266
17000	105.326	270.804	148.583	24.866	10.406	8.412
17500	107.940	275.960	145.417	25.026	10.556	8.558
18000	110.554	281.116	141.851	25.186	10.706	8.704
18500	113.168	286.272	136.885	25.346	10.856	8.850
19000	115.782	291.428	131.519	25.506	11.006	8.996
19500	118.396	296.584	124.753	25.666	11.156	9.142
20000	121.010	301.740	116.587	25.826	11.306	9.288
20500	123.624	306.896	107.021	25.986	11.456	9.434
21000	126.238	312.052	96.055	26.146	11.606	9.580
21500	128.852	317.208	83.689	26.306	11.756	9.726
22000	131.466	322.364	70.023	26.466	11.906	9.872
22500	134.080	327.520	55.157	26.626	12.056	10.018
23000	136.694	332.676	39.291	26.786	12.206	10.164
23500	139.308	337.832	22.425	26.946	12.356	10.310
24000	141.922	342.988	5.559	27.106	12.506	10.456
24500	144.536	348.144	-11.607	27.266	12.656	10.602
25000	147.150	353.300	-28.741	27.426	12.806	10.748
25500	149.764	358.456	-45.815	27.586	12.956	10.894
26000	152.378	363.612	-62.889	27.746	13.106	11.040
26500	154.992	368.768	-79.963	27.906	13.256	11.186
27000	157.606	373.924	-97.037	28.066	13.406	11.332
27500	160.220	379.080	-114.111	28.226	13.556	11.478
28000	162.834	384.236	-131.185	28.386	13.706	11.624
28500	165.448	389.392	-148.259	28.546	13.856	11.770
29000	168.062	394.548	-165.333	28.706	14.006	11.916
29500	170.676	399.704	-182.407	28.866	14.156	12.062
30000	173.290	404.860	-199.481	29.026	14.306	12.208
30500	175.904	410.016	-216.555	29.186	14.456	12.354
31000	178.518	415.172	-233.629	29.346	14.606	12.500
31500	181.132	420.328	-250.703	29.506	14.756	12.646
32000	183.746	425.484	-267.777	29.666	14.906	12.792
32500	186.360	430.640	-284.851	29.826	15.056	12.938
33000	188.974	435.796	-301.925	29.986	15.206	13.084
33500	191.588	440.952	-318.999	30.146	15.356	13.230
34000	194.202	446.108	-336.073	30.306	15.506	13.376
34500	196.816	451.264	-353.147	30.466	15.656	13.522
35000	199.430	456.420	-370.221	30.626	15.806	13.668
35500	202.044	461.576	-387.295	30.786	15.956	13.814
36000	204.658	466.732	-404.369	30.946	16.106	13.960
36500	207.272	471.888	-421.443	31.106	16.256	14.106
37000	209.886	477.044	-438.517	31.266	16.406	14.252
37500	212.500	482.200	-455.591	31.426	16.556	14.398
38000	215.114	487.356	-472.665	31.586	16.706	14.544
38500	217.728	492.512	-489.739	31.746	16.856	14.690
39000	220.342	497.668	-506.813	31.906	17.006	14.836
39500	222.956	502.824	-523.887	32.066	17.156	14.982
40000	225.570	507.980	-540.961	32.226	17.306	15.128
40500	228.184	513.136	-558.035	32.386	17.456	15.274
41000	230.798	518.292	-575.109	32.546	17.606	15.420
41500	233.412	523.448	-592.183	32.706	17.756	15.566
42000	236.026	528.604	-609.257	32.866	17.906	15.712
42500	238.640	533.760	-626.331	33.026	18.056	15.858
43000	241.254	538.916	-643.405	33.186	18.206	16.004
43500	243.868	544.072	-660.479	33.346	18.356	16.150
44000	246.482	549.228	-677.553	33.506	18.506	16.296
44500	249.096	554.384	-694.627	33.666	18.656	16.442
45000	251.710	559.540	-711.701	33.826	18.806	16.588
45500	254.324	564.696	-728.775	33.986	18.956	16.734
46000	256.938	569.852	-745.849	34.146	19.106	16.880
46500	259.552	575.008	-762.923	34.306	19.256	17.026
47000	262.166	580.164	-780.000	34.466	19.406	17.172
47500	264.780	585.320	-797.074	34.626	19.556	17.318
48000	267.394	590.476	-814.148	34.786	19.706	17.464
48500	270.008	595.632	-831.222	34.946	19.856	17.610
49000	272.622	600.788	-848.296	35.106	19.996	17.756
49500	275.236	605.944	-865.370	35.266	20.146	17.902
50000	277.850	611.100	-882.444	35.426	20.296	18.048
50500	280.464	616.256	-899.518	35.586	20.446	18.194
51000	283.078	621.412	-916.592	35.746	20.596	18.340
51500	285.692	626.568	-933.666	35.906	20.746	18.486
52000	288.306	631.724	-950.740	36.066	20.896	18.632
52500	290.920	636.880	-967.814	36.226	21.046	18.778
53000	293.534	642.036	-984.888	36.386	21.196	18.924
53500	296.148	647.192	-1001.962	36.546	21.346	19.070
54000	298.762	652.348	-1019.036	36.706	21.496	19.216
54500	301.376	657.504	-1036.110	36.866	21.646	19.362
55000	303.990	662.660	-1053.184	37.026	21.796	19.508
55500	306.604	667.816	-1070.258	37.186	21.946	19.654
56000	309.218	672.972	-1087.332	37.346	22.096	19.800
56500	311.832	678.128	-1104.406	37.506	22.246	19.946
57000	314.446	683.284	-1121.480	37.666	22.396	20.092
57500	317.060	688.440	-1138.554	37.826	22.546	20.238
58000	319.674	693.596	-1155.628	37.986	22.696	20.384
58500	322.288	698.752	-1172.702	38.146	22.846	20.530
59000	324.902	703.908	-1189.776	38.306	22.996	20.676
59500	327.516	709.064	-1206.850	38.466	23.146	20.822
60000	330.130	714.220	-1223.924	38.626	23.296	20.968

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1968

Heat of Formation
Hu and Sinke (1) have measured the heat of combustion of CHCl₃(l) in the rotating bomb calorimeter, using As₂O₃ solution as the reducing agent. The reported $\Delta H_{298}^\circ = -113.10 \text{ kcal/mol}$ for CHCl₃(l) + 0.5O₂ + H₂O(l) + CO₂(g) + 3HCl(600H₂O, aq) which leads to $\Delta H_{298}^\circ(\text{CHCl}_3, l) = -32.10 \text{ kcal/mol}$, using $\Delta H_{298}^\circ = -94.051, -39.873, -68.315 \text{ kcal/mol}$ for CO₂(g), HCl(600H₂O, aq) and H₂O(l), respectively (2). The standard deviation of six combustion runs was 0.09 kcal/mol. Employing the heat of vaporization of chloroform at 298°K as 7.44 kcal/mol (3), we obtain $\Delta H_{298}^\circ(\text{CHCl}_3, g) = -24.66 \text{ kcal/mol}$ which is adopted in the tabulation.

L. Smith et al. (4), based on the combustion data of E. Efring (5), re-evaluated the heat of combustion of chloroform at 18.7°C as $\Delta C_p^\circ/M = -347.7 \text{ cal/g}$ for CHCl₃(l) + 0.5O₂(g) + H₂O(l) + CO₂(g) + 3HCl(600H₂O, aq). This value needs to be further corrected for a change in the heat of oxidation of As₂O₃ (6) and calculated to 25°C to give $\Delta H_{298}^\circ = -113.44 \text{ kcal/mol}$, $\Delta H_{298}^\circ(\text{CHCl}_3, l) = -31.76 \text{ kcal/mol}$ and $\Delta H_{298}^\circ(\text{CHCl}_3, g) = -24.32 \text{ kcal/mol}$.

Heat Capacity and Entropy

The assigned fundamental vibrational frequencies are obtained from Shimanouchi's selection (7), based on infrared and Raman spectra measured by Nielsen and Ward (8), Madigan and Cleveland (9), Gibian and McKinney (10) and Stanevich and Yaroslavskii (11).

The bond distances and angles were obtained from the microwave spectra by Jen and Lide (12). The three principal moments of inertia are $I_A = I_B = 25.719 \times 10^{-39}$ and $I_C = 49.603 \times 10^{-39} \text{ g cm}^2$.

Monofluoromethylene (CHF)

(Ideal Gas)

GFW = 32.01752

Point Group C_s $\Delta H_f^\circ = [29.9 \pm 7] \text{ kcal/mol}$ $S_{298.15}^\circ = 53.35 \pm 0.05 \text{ gibbs/mol}$ $\Delta H_f^{298.15} = [30 \pm 7] \text{ kcal/mol}$

Ground State Quantum Weight = 1

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^c	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.989	44.609	2.366	20.933	20.933	INFINITE
200	7.986	44.518	1.591	26.087	26.087	62.945
300	8.013	44.415	1.000	30.400	30.400	34.137
398	8.271	53.355	-	36.372	36.372	19.191
400	8.279	53.406	-	36.349	36.349	19.195
500	8.810	55.857	0.15	25.151	25.151	13.742
600	9.347	57.845	0.69	23.984	23.984	10.485
700	9.919	59.645	1.779	20.533	20.533	6.327
800	10.795	61.210	3.760	21.763	21.763	6.795
900	11.749	63.916	4.820	20.692	20.692	5.653
1000	11.458	65.107	5.918	19.684	19.684	4.770
1100	11.727	66.212	7.084	18.616	18.616	4.068
1200	11.962	67.243	8.208	17.605	17.605	3.498
1300	12.171	68.209	9.392	16.612	16.612	3.025
1400	12.357	69.118	10.556	15.630	15.630	2.628
1500	12.526	69.976	11.826	14.664	14.664	2.289
1600	12.683	70.793	13.070	13.707	13.707	1.997
1700	12.830	71.563	15.604	12.758	12.758	1.743
1800	12.971	72.300	16.800	11.823	11.823	1.520
1900	13.110	73.005	18.200	10.893	10.893	1.323
2000	13.246	73.681	19.518	9.975	9.975	1.147
2100	13.382	74.331	20.849	9.053	9.053	0.990
2200	13.517	74.956	22.194	8.157	8.157	0.849
2300	13.653	75.560	23.553	7.256	7.256	0.721
2400	13.789	76.144	24.925	6.365	6.365	0.605
2500	13.925	76.710	26.311	5.476	5.476	0.499
2600	14.061	77.259	27.710	4.590	4.590	0.401
2700	14.195	77.792	29.123	3.711	3.711	0.312
2800	14.328	78.311	30.549	2.834	2.834	0.229
2900	14.458	78.816	31.949	1.961	1.961	0.153
3000	14.586	79.308	33.441	1.094	1.094	0.082
3100	14.709	79.788	34.906	0.233	0.233	0.016
3200	14.829	80.257	36.382	0.61	0.61	0.045
3300	14.943	80.715	37.871	1.503	1.503	0.103
3400	15.053	81.163	39.371	2.367	2.367	0.157
3500	15.157	81.601	40.881	3.296	3.296	0.207
3600	15.255	82.029	42.402	4.065	4.065	0.255
3700	15.347	82.448	43.932	4.943	4.943	0.300
3800	15.434	82.859	45.471	5.799	5.799	0.343
3900	15.513	83.261	47.019	6.653	6.653	0.383
4000	15.587	83.655	48.574	7.509	7.509	0.421
4100	15.655	84.040	50.136	8.363	8.363	0.457
4200	15.716	84.418	51.705	9.221	9.221	0.492
4300	15.821	85.152	53.279	10.079	10.079	0.524
4400	15.891	85.508	54.859	10.927	10.927	0.555
4500	15.965	85.958	56.443	11.742	11.742	0.585
4600	15.994	86.457	58.032	12.639	12.639	0.614
4700	15.997	86.999	59.624	13.449	13.449	0.641
4800	15.995	87.535	61.219	14.341	14.341	0.667
4900	15.989	88.065	62.816	15.191	15.191	0.692
5000	16.008	88.716	64.416	16.043	16.043	0.716
5100	16.023	89.305	66.016	16.896	16.896	0.739
5200	16.042	89.847	67.621	17.752	17.752	0.761
5300	16.064	90.422	69.225	18.599	18.599	0.782
5400	16.087	91.036	70.829	19.445	19.445	0.802
5500	16.107	91.681	72.434	20.297	20.297	0.821
5600	16.045	92.366	74.041	21.145	21.145	0.840
5700	16.041	93.005	75.643	21.993	21.993	0.858
5800	16.034	93.688	77.246	22.842	22.842	0.876
5900	16.024	94.404	78.848	23.688	23.688	0.893
6000	16.013	95.111	80.451	24.530	24.530	0.909
6100	16.013	95.804	82.054	25.374	25.374	0.924

Dec. 31, 1969

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	1
[10000]	3
17287	1

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹
(3000) (1)
1403 (1)
1182 (1)

Bond Distance: C-H = 1.121 Å C-F = 1.314 Å

Bond Angle: H-C-F = 101.6°

Product of the Moments of Inertia: $I_A I_B I_C = 1.0217 \times 10^{-117} \text{ g}^3 \text{ cm}^6$ $\sigma = 1$

Heat of Formation

The heat of formation can be estimated as the average of those of the CH₂ and CF₂ radicals, which gives $\Delta H_f^\circ(\text{CHF}, g) = 25 \pm 20 \text{ kcal/mol}$. A better value for the heat of formation can be obtained by considering the bond energies CHF = CH + F and CHF = CF + H. When $\Delta H_f^\circ(\text{CHF}, g) = 25 \text{ kcal/mol}$ is substituted into the above equations it gives D_{C-F} = 136 kcal and D_{C-H} = 86 kcal. These are not unreasonable values but are probably close to the upper and lower limits respectively. A value of $\Delta H_f^\circ(\text{CHF}, g) = 30 \text{ kcal/mol}$ gives D_{C-F} = 131 kcal and D_{C-H} = 81 kcal which are more probable since both fall within the bounds of normal bond strengths. The strongest established C-F bond is 135 kcal in CF₃ and the weakest established C-H bond is 80 kcal in CH. We adopt $\Delta H_f^\circ(\text{CHF}, g) = 30 \pm 7 \text{ kcal/mol}$.

Heat Capacity and Entropy

The structure and electronic levels of the molecule have been established by Merer and Travis (1) from an analysis of the rotational structure of the visible absorption bands. The estimated triplet state is based on the electronic levels of CF₂ and CH₂ as given in these tables. The vibrational levels are from Merer and Travis (1) and Jacox and Milligan (2), the latter investigated the infrared spectrum of matrix-isolated HCF and also estimated the missing frequency.

The individual moments of inertia are $I_A = 2.2979 \times 10^{-39} \text{ g cm}^2$, $I_B = 1.795 \times 10^{-40} \text{ g cm}^2$, and $I_C = 2.4774 \times 10^{-39} \text{ g cm}^2$.

References

1. A. J. Merer and D. N. Travis, Can. J. Phys., **44**, 1541 (1966).
2. M. E. Jacox and D. E. Milligan, J. Chem. Phys., **50**, 3752 (1969).

Formyl Fluoride (CHFO)

(Ideal Gas) Mol. Wt. = 48.019

CHFO

MOL. WT. = 48.019

(IDEAL GAS)

FORMYL FLUORIDE (CHFO)

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF ⁰	Log K _p
100	7.069	49.944	INFINITE	2.494	89.139	89.139	INFINITE
200	8.474	55.371	59.803	.866	89.442	89.442	164.642
298	9.659	58.961	58.961	.000	89.697	89.697	96.810
300	9.685	59.020	58.961	.018	90.006	87.982	64.498
400	11.078	61.968	59.357	1.056	90.301	87.261	44.092
500	12.352	64.610	60.152	2.229	90.566	86.471	37.794
600	13.432	66.961	61.094	3.320	90.796	85.430	31.189
700	14.370	69.105	62.008	4.400	90.997	84.151	26.459
800	15.197	71.078	62.895	5.460	91.170	82.751	22.535
900	15.901	72.878	63.761	6.501	91.318	82.224	20.135
1000	16.523	74.560	64.602	7.518	91.442	81.584	17.917
1100	16.662	76.127	65.399	8.509	91.549	81.034	16.099
1200	17.034	77.593	66.167	9.486	91.639	80.072	14.582
1300	17.321	78.961	66.911	10.446	91.700	78.131	13.169
1400	17.521	80.266	67.611	11.387	91.760	76.131	11.794
1500	17.653	81.489	68.229	12.311	91.854	74.153	10.464
1600	18.053	82.648	70.219	13.226	91.913	72.213	9.173
1700	18.226	83.748	72.191	14.126	91.967	70.219	7.915
1800	18.378	84.791	74.141	15.011	92.009	68.211	6.675
1900	18.509	85.791	76.056	15.881	92.040	66.211	5.452
2000	18.625	86.744	77.936	16.737	92.116	64.211	4.257
2100	18.728	87.655	79.788	17.580	92.167	62.143	3.099
2200	18.819	88.529	81.608	18.409	92.210	60.099	1.974
2300	18.901	89.371	83.397	19.226	92.246	58.044	0.875
2400	18.971	90.173	85.161	20.031	92.275	56.000	0.200
2500	19.036	90.948	86.895	20.826	92.303	54.000	0.000
2600	19.094	91.696	88.604	21.611	92.328	52.000	0.000
2700	19.146	92.418	90.287	22.386	92.350	50.000	0.000
2800	19.193	93.115	91.941	23.151	92.369	48.000	0.000
2900	19.237	93.789	93.568	23.906	92.386	46.000	0.000
3000	19.276	94.442	95.139	24.651	92.401	44.000	0.000
3100	19.312	95.075	96.666	25.386	92.414	42.000	0.000
3200	19.344	95.688	98.159	26.111	92.425	40.000	0.000
3300	19.372	96.279	99.611	26.826	92.434	38.000	0.000
3400	19.400	96.853	101.031	27.531	92.441	36.000	0.000
3500	19.427	97.426	102.411	28.226	92.446	34.000	0.000
3600	19.450	97.973	103.751	28.911	92.449	32.000	0.000
3700	19.472	98.506	105.051	29.586	92.451	30.000	0.000
3800	19.493	99.026	106.311	30.251	92.452	28.000	0.000
3900	19.510	99.533	107.531	30.906	92.453	26.000	0.000
4000	19.528	100.027	108.711	31.551	92.454	24.000	0.000
4100	19.544	100.509	109.851	32.186	92.455	22.000	0.000
4200	19.559	100.980	110.951	32.811	92.456	20.000	0.000
4300	19.573	101.441	112.011	33.426	92.457	18.000	0.000
4400	19.586	101.891	113.031	34.031	92.458	16.000	0.000
4500	19.598	102.331	114.011	34.626	92.459	14.000	0.000
4600	19.609	102.762	114.951	35.201	92.460	12.000	0.000
4700	19.620	103.184	115.851	35.766	92.461	10.000	0.000
4800	19.630	103.599	116.711	36.321	92.462	8.000	0.000
4900	19.640	104.002	117.531	36.866	92.463	6.000	0.000
5000	19.649	104.396	118.311	37.391	92.464	4.000	0.000
5100	19.657	104.788	119.051	37.896	92.465	2.000	0.000
5200	19.665	105.170	119.751	38.381	92.466	0.000	0.000
5300	19.673	105.543	120.411	38.846	92.467	0.000	0.000
5400	19.681	105.906	121.031	39.291	92.468	0.000	0.000
5500	19.687	106.273	121.611	39.716	92.469	0.000	0.000
5600	19.693	106.628	122.151	40.126	92.470	0.000	0.000
5700	19.700	106.977	122.651	40.521	92.471	0.000	0.000
5800	19.706	107.316	123.111	40.896	92.472	0.000	0.000
5900	19.711	107.645	123.531	41.251	92.473	0.000	0.000
6000	19.715	107.968	123.911	41.586	92.474	0.000	0.000

June 30, 1961

 $\Delta H_{f, 298}^0 = [-92] \text{ kcal. mole}^{-1}$ Point Group C_1 $\Delta H_{f, 298}^0 = [-90] \text{ kcal. mole}^{-1}$ $S_{298}^0 = 58.96 \pm 0.2 \text{ cal. deg}^{-1} \text{ mole}^{-1}$

Vibrational Levels and Multiplicities

ω cm. ⁻¹	ω cm. ⁻¹
2981 (1)	1064.8 (1)
1836.9 (1)	662.5 (1)
1342.5 (1)	[1030] (1)

Bond Lengths and Angles C-F = 1.31 ± 0.02 Å C-O = 1.183 ± 0.003 Å C-H = 1.10 ± 0.02 Å

 $\chi_{\text{HCO}} = 109 \pm 3^\circ$ $\chi_{\text{HCO}} = 129 \pm 3^\circ$ Moments of Inertia $I_A = 0.92052 \times 10^{-39} \text{ g. cm}^2$ $I_B = 7.13510 \times 10^{-39} \text{ g. cm}^2$ $I_C = 8.07064 \times 10^{-39} \text{ g. cm}^2$ $r = 1$

Heat of Formation

 ΔH_f for III was estimated to be the average of the ΔH_f 's of I and II.(I) $\text{CH}_2\text{O(g)} = \text{CO(g)} + 2\text{H(g)}$ 106 kcal.(II) $\text{CF}_2\text{O(g)} = \text{CO(g)} + 2\text{F(g)}$ 162 kcal.(III) $\text{CHFO(g)} = \text{CO(g)} + \text{F(g)} + \text{H(g)}$ [134] kcal.The auxiliary ΔH_f 298.15 of $\text{CH}_2\text{O} = -28$, $\text{H} = 52$, $\text{F} = 19$, $\text{CO} = -26$, $\text{CF}_2\text{O} = -150$ kcal. mole⁻¹ was used. See the respective sheets for details. The estimated heat of formation is consistent with the instability of CHFO(g) at room temperature.

Heat Capacities and Entropies

The molecular structural parameters were obtained by O. H. LeBlanc, V. W. Laurie and W. D. Ormrod, J. Chem. Phys. 33, 598 (1960), from combining the results of microwave measurements with those of electron diffraction determined by M. E. Jones, K. Hedberg, and V. Schomaker, J. Am. Chem. Soc. 77, 5278 (1955). Agreement within the assigned uncertainties was obtained by R. P. Stratton and A. H. Nielsen, J. Mol. Spect. 3, 373 (1960), on the basis of infrared measurements.

Five of the fundamental were observed by Stratton and Nielsen, loc. cit. in agreement with those obtained by H. W. Morgan, P. A. Staats and J. H. Goldstein, J. Chem. Phys. 25, 337 (1956). The estimated frequency was based upon the observed value of 857.4 cm.⁻¹ for the fundamental in the infrared spectrum of the deuterated compound and the application of the Teller-Redlich isotope rule.

CHFO

Trifluoromethane (CHF₃)

GFW = 70.01432

(Ideal Gas)

Point Group C_{3v} $\Delta H_f^\circ = -164.9 \pm 0.8 \text{ kcal/mol}$ $S^\circ_{298.15} = 62.032 \pm 0.08 \text{ gibbs/mol}$ $\Delta H_f^\circ_{298.15} = -166.6 \pm 0.8 \text{ kcal/mol}$

Ground State Quantum Weight = 1

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	Log Kp
100	8.000	51.000	INF	2.162	INF
200	9.853	57.667	43.071	1.081	163.635
298	12.199	62.032	0.000	0.000	175.923
300	12.244	62.108	0.233	166.609	116.069
400	14.579	65.956	1.366	167.014	115.336
500	16.537	68.530	2.728	167.332	64.977
600	18.128	70.593	4.264	167.575	60.690
700	19.359	72.593	4.664	167.571	54.492
800	20.331	74.484	6.341	167.746	49.267
900	21.109	76.135	8.927	167.871	39.218
1000	21.742	77.606	10.600	167.955	34.122
1100	22.262	78.931	12.144	168.004	30.043
1200	22.694	80.155	13.585	168.027	26.704
1300	23.057	81.319	14.945	168.027	23.922
1400	23.368	82.433	17.193	168.027	21.546
1500	23.624	83.506	19.481	168.014	19.568
1600	23.847	84.542	21.812	167.990	17.902
1700	24.040	85.542	24.152	167.950	16.274
1800	24.207	86.504	26.526	167.906	14.924
1900	24.352	87.435	28.921	167.858	13.726
2000	24.480	88.335	31.333	167.806	12.658
2100	24.592	89.200	33.763	167.749	11.688
2200	24.691	90.035	36.212	167.689	10.817
2300	24.778	90.842	38.677	167.630	10.024
2400	24.853	91.619	41.121	167.572	9.300
2500	24.918	92.366	43.546	167.513	8.647
2600	24.972	93.082	45.956	167.450	8.067
2700	25.019	93.768	48.346	167.402	7.464
2800	25.059	94.427	50.712	167.349	6.801
2900	25.093	95.060	53.056	167.298	6.093
3000	25.118	95.668	55.364	167.249	5.350
3100	25.137	96.251	57.641	167.194	4.629
3200	25.152	96.809	59.887	167.142	3.951
3300	25.163	97.346	62.107	167.093	3.361
3400	25.170	97.864	64.297	167.046	2.807
3500	25.175	98.364	66.456	166.998	2.287
3600	25.178	98.846	68.587	166.955	1.806
3700	25.179	99.311	70.694	166.913	1.366
3800	25.179	99.761	72.773	166.874	0.966
3900	25.178	100.196	74.827	166.836	0.606
4000	25.176	100.616	76.859	166.798	0.286
4100	25.173	101.021	78.870	166.764	0.006
4200	25.169	101.412	80.861	166.730	-0.286
4300	25.164	101.789	82.833	166.698	-0.606
4400	25.158	102.153	84.786	166.668	-0.966
4500	25.151	102.506	86.721	166.638	-1.366
4600	25.143	102.848	88.637	166.609	-1.806
4700	25.134	103.179	90.534	166.581	-2.286
4800	25.124	103.500	92.412	166.554	-2.806
4900	25.113	103.811	94.271	166.528	-3.366
5000	25.101	104.112	96.112	166.503	-3.966
5100	25.088	104.403	97.935	166.478	-4.606
5200	25.074	104.684	99.749	166.454	-5.286
5300	25.059	104.955	101.544	166.430	-5.966
5400	25.043	105.216	103.321	166.407	-6.686
5500	25.026	105.467	105.081	166.384	-7.446
5600	25.008	105.708	106.816	166.362	-8.246
5700	24.989	105.939	108.531	166.340	-9.086
5800	24.969	106.160	110.226	166.318	-9.966
5900	24.948	106.371	111.901	166.297	-10.886
6000	24.926	106.572	113.556	166.276	-11.846

Dec. 31, 1950; Dec. 31, 1963; June 30, 1969

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}
----------------------------	----------------------------

3035 (1)	1376 (2)
----------	----------

1137 (1)	1152 (2)
----------	----------

700 (1)	508 (2)
---------	---------

Bond Distance: C-F = 1.333 Å C-H = 1.098 Å

Bond Angle: F-C-F = 108.6 ± 0.5° F-C-H = 110.33°

Product of the Moments of Inertia: $I_A I_B I_C = 9.7204 \times 10^{-115} \text{ g}^3 \text{ cm}^6$ $\sigma = 3$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₃X (X = H, Cl, Br, I, CF₃) and C₂F₆. Details of the input data and the adjustment are given in (1). Trifluoromethane is linked to HF(21.5 H₂O) by calorimetric data, to CHF₃(g) and CF₃I(g) by equilibrium data, and to CF₃(g) by kinetic data. Heugebauer (2) reported calorimetric data for CHF₃(g) + 0.5 O₂(g) + CO₂(g) + 3 HF(21.5 H₂O), where CF₃(g) was also formed in a competing reaction. Recalculation of the original data with $\Delta H_f^\circ(298.15 \text{ CF}_4, \text{g}) = -223.0 \text{ kcal/mol}$ yields the mean value of $\Delta H_f^\circ(298.15) = -90.35 \pm 0.7 \text{ kcal/mol}$, but the individual values of ΔH_f° show a disturbing trend with the amount of competing reaction. Possible causes for the trend include corrosion and error in the analysis of the reaction products. Calibration was done in the presence of HF in an attempt to eliminate the heat due to corrosion. Because of this unexplained trend, we increase the uncertainty to ± 1.0 kcal/mol. Goy (3) and Coomber (4) determined equilibrium data for CHF₃(g) + X₂(g) = CF₃X(g) + HX(g) where X = I and Br. Kinetic data pertinent to CHF₃ are noted on the table for CF₃(g).

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction data by Thornton (5) and from microwave data by Ghosh (6). The results are in close agreement and average values are adopted. Vibrational frequencies are from the assignment of Long (7) who reviewed the spectral data and gave force-constant calculations. Preference has been given to the gas-phase spectra, particularly the Raman data of Claassen (8). Shimanouchi (9) assigned $\nu_2 = 1117$ rather than 1137 cm^{-1} , but he apparently did not consider the gas-phase data of (8, 10). Principal moments of inertia are $I_A = 14.786 \times 10^{-39}$ and $I_B = I_C = 8.108 \times 10^{-39} \text{ g cm}^2$.

Valentine (11) used low-temperature calorimetric data to derive the ideal gas entropy at the normal boiling point of 190.97°K. The experimental value of 57.18 gibbs/mol is in good agreement with 57.216 gibbs/mol obtained from this table. Schwing (12) measured C_p for CHF₃ vapor (25-100°C) and confirmed that the vibrational assignment is adequate. Uncertainty in C_p and S° increases at higher temperatures due to neglect of anharmonicity in the calculations. Discussions of anharmonic contributions are given on the tables for CF₄(g) and CClF₃(g). The error probably does not exceed 0.3 gibbs/mol in S° at 1000°K. C_p° is consistent with C_p° measured at 300°K by the wire-ribbon method (13).

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFRL Contract Nr. F04611-67-C-0009, Dow Chemical Co., July, 1969.
2. C. A. Neugebauer and J. L. Margrave, J. Phys. Chem. **62**, 1043 (1958).
3. C. A. Goy, A. Lord and H. O. Pritchard, J. Phys. Chem. **71**, 1086 (1967).
4. J. W. Coomber and E. Whittle, Trans. Faraday Soc. **63**, 608 (1967).
5. C. G. Thornton, Dissertation Abstracts **14**, 604 (1954); R. L. Livingston, Ann. Rev. Phys. Chem. **5**, 397 (1954).
6. S. N. Ghosh, R. Tambarulo and W. Gordy, J. Chem. Phys. **20**, 605 (1952); C. A. Burrus and W. Gordy, *ibid.* **28**, 391 (1957); M. Jen and D. R. Lide, *ibid.* **36**, 2525 (1962).
7. D. A. Long, R. B. Grevener and D. T. L. Jones, Trans. Faraday Soc. **60**, 1509 (1964).
8. H. H. Claassen and J. R. Nielsen, J. Opt. Soc. Amer. **43**, 352 (1953).
9. T. Shimanouchi, U. S. Nat. Bur. Stand. NBS-RS 17, 17 (1967).
10. W. F. Edgall and C. May, J. Chem. Phys. **21**, 1301 (1953); **22**, 1808 (1954).
11. R. H. Valentine, G. E. Brodale and W. F. Glauque, J. Phys. Chem. **66**, 392 (1962).
12. R. C. Schwing, Dissertation Abstracts **23**, 2404 (1964).
13. W. N. Vanderkooi and T. DeVries, J. Phys. Chem. **60**, 636 (1956).

Point Group $C_{\infty v}$

$$\Delta H_f^\circ = 32.39 \pm 2.0 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 32.3 \pm 2.0 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 48.21 \pm 0.01 \text{ gibbs/mol}$$

Ground State Quantum Weight = 1

Hydrogen Cyanide (HCN)

(Ideal Gas)

$$GFW = 27.02582$$

T, °K	Cp°	S°	(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-2.207	32.393	32.393	INFINITE
100	6.561	40.093	45.143	-1.713	32.387	32.387	21.877
200	6.570	40.100	45.143	-1.713	32.387	32.387	21.877
298	6.570	48.212	48.212	-1.000	32.300	29.606	21.849
300	6.567	48.265	48.212	-.016	32.299	29.791	21.702
400	6.376	50.649	48.550	.916	32.258	29.961	15.823
500	6.974	53.008	49.239	1.895	32.206	29.182	12.301
600	10.470	54.871	50.026	2.907	32.145	27.335	9.957
700	10.909	56.519	50.638	3.976	32.074	26.539	8.286
800	11.309	58.002	51.642	5.088	32.002	25.754	7.036
900	11.674	59.355	52.425	6.237	31.929	24.976	6.045
1000	12.005	60.603	53.181	7.421	31.861	24.207	5.290
1100	12.305	61.761	53.909	8.637	31.797	23.444	4.650
1200	12.574	62.843	54.609	9.881	31.737	22.689	4.132
1300	12.815	63.860	55.282	11.151	31.680	21.936	3.688
1400	13.031	64.817	55.929	12.443	31.629	21.180	3.308
1500	13.224	65.723	56.552	13.756	31.581	20.446	2.979
1600	13.396	66.582	57.152	15.087	31.535	19.704	2.691
1700	13.551	67.399	57.731	16.435	31.493	18.966	2.438
1800	13.689	68.177	58.290	17.797	31.454	18.230	2.213
1900	13.813	68.921	58.830	19.172	31.417	17.498	2.013
2000	13.925	69.632	59.353	20.559	31.383	16.766	1.832
2100	14.027	70.314	59.859	21.957	31.350	16.037	1.669
2200	14.118	70.969	60.349	23.364	31.318	15.306	1.521
2300	14.202	71.598	60.824	24.780	31.288	14.581	1.385
2400	14.278	72.204	61.286	26.204	31.258	13.856	1.262
2500	14.347	72.789	61.734	27.636	31.228	13.129	1.148
2600	14.411	73.353	62.171	29.074	31.199	12.407	1.043
2700	14.470	73.898	62.595	30.518	31.170	11.683	.946
2800	14.523	74.425	63.008	31.967	31.141	10.962	.852
2900	14.573	74.936	63.411	33.422	31.112	10.244	.772
3000	14.620	75.430	63.803	34.882	31.082	9.524	.694
3100	14.662	75.910	64.186	36.346	31.054	8.805	.621
3200	14.702	76.377	64.560	37.814	31.023	8.088	.552
3300	14.739	76.830	64.925	39.286	30.990	7.371	.488
3400	14.774	77.270	65.281	40.762	30.959	6.657	.428
3500	14.806	77.699	65.630	42.241	30.924	5.940	.371
3600	14.836	78.116	65.971	43.723	30.889	5.227	.317
3700	14.864	78.523	66.305	45.208	30.851	4.516	.267
3800	14.890	78.920	66.631	46.696	30.813	3.807	.219
3900	14.914	79.307	66.952	48.186	30.772	3.098	.174
4000	14.937	79.685	67.265	49.679	30.730	2.388	.130
4100	14.959	80.054	67.573	51.173	30.685	1.678	.089
4200	14.979	80.415	67.874	52.670	30.637	.974	.051
4300	14.998	80.767	68.170	54.169	30.588	.267	.014
4400	15.015	81.112	68.460	55.670	30.536	-.439	.022
4500	15.031	81.450	68.745	57.172	30.481	-1.145	.056
4600	15.046	81.781	69.025	58.676	30.424	-1.843	.080
4700	15.060	82.104	69.300	60.181	30.364	-2.544	.110
4800	15.073	82.421	69.570	61.688	30.300	-3.242	.146
4900	15.085	82.732	69.835	63.196	30.234	-3.942	.176
5000	15.096	83.037	70.096	64.705	30.165	-4.636	.203
5100	15.107	83.336	70.353	66.215	30.092	-5.339	.229
5200	15.116	83.630	70.605	67.726	30.017	-6.030	.253
5300	15.124	83.918	70.854	69.238	29.938	-6.720	.277
5400	15.131	84.200	71.099	70.751	29.856	-7.412	.300
5500	15.137	84.478	71.339	72.264	29.769	-8.109	.322
5600	15.143	84.751	71.576	73.778	29.679	-8.790	.343
5700	15.148	85.019	71.810	75.293	29.585	-9.477	.363
5800	15.152	85.283	72.040	76.808	29.487	-10.161	.383
5900	15.155	85.542	72.264	78.323	29.384	-10.841	.402
6000	15.157	85.796	72.490	79.839	29.280	-11.527	.420

Dec. 31, 1960; Mar. 31, 1961; June 30, 1969; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

$$\omega, \text{ cm}^{-1}$$

$$2096.3 (1)$$

$$713.5 (2)$$

$$3311.5 (1)$$

$$C-N = 1.153 \text{ \AA}$$

$$H-C-N = 180^\circ$$

$$\sigma = 1$$

$$\text{Rotational Constant: } B_0 = 1.4782 \text{ cm}^{-1}$$

$$\text{Bond Distances: } C-H = 1.066 \text{ \AA}$$

$$\text{Spectroscopic constants used in calculating corrections to the rigid-rotator harmonic oscillator approximation (cm}^{-1}\text{):}$$

$$c_1 = 10.10 \times 10^{-3}$$

$$-x_{11} = 7.07$$

$$-x_{12} = 2.53$$

$$c_2 = -3.61 \times 10^{-3}$$

$$-x_{22} = 2.65$$

$$-x_{23} = 19.01$$

$$c_3 = 10.42 \times 10^{-3}$$

$$-x_{33} = 52.49$$

$$-x_{34} = 10.44$$

$$g_{22} = 5.16$$

$$\text{Heat of Formation}$$

$$\text{The value adopted is from reference 1. The data of Thomsen (2) who measured both } C_2H_2 \text{ and HCN and Berthelot (3) were used in conjunction with the well established value for } C_2H_2 \text{ to derive the adopted value (4).}$$

$$\text{Badger (5) studied the equilibrium } NH_3(g) + C(c) = HCN(g) + H_2(g) \text{ from both sides; we obtain a 3rd law } \Delta H_f^\circ = 46 \pm 0.9 \text{ kcal and a 2nd law } \Delta H_f^\circ = 30.5 \pm 1.9 \text{ kcal, the 3rd law drift is } 14 \pm 24 \text{ eu. The 3rd law value leads to } \Delta H_f^\circ(\text{HCN}, g) = 35 \pm 1 \text{ kcal/mol.}$$

$$\text{Horvath et al. (6) studied the equilibrium } 2 \text{ CO}(g) + NH_3(g) = HCN(g) + CO_2(g) + H_2(g). \text{ We obtain } \Delta H_f^\circ = 1.1 \pm 0.5 \text{ kcal from a 3rd law analysis with a drift of } -2 \pm 3 \text{ eu, and a 2nd law value of } 2.9 \pm 2.6 \text{ kcal. The 3rd law value leads to } \Delta H_f^\circ(\text{HCN}, g) = 31.35 \pm 0.6 \text{ kcal/mol. The two sets of equilibrium data are self-consistent but disagree with each other and the direct combustions. We adopt an uncertainty of } 2.0 \text{ kcal/mol to draw attention to this unsatisfactory situation.}$$

$$\text{Heat Capacity and Entropy}$$

$$\text{McBride et al. (7) used the constants listed above to calculate the adopted table which includes first and second corrections for anharmonicity, vibration-rotation interaction and centrifugal stretching. The bond lengths and molecular constants are those listed by Rank et al. (8). A more extensive set of anharmonic constants has recently been determined by Nakagawa and Morino (9), they are in generally good agreement with the values used.}$$

$$\text{References}$$

$$1. \text{ U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.}$$

$$2. \text{ J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1886.}$$

$$3. \text{ M. Berthelot, Ann. Chim. Phys. 23, 252 (1881).}$$

$$4. \text{ W. H. Evans, Nat. Bur. Std., private communication, May 1969.}$$

$$5. \text{ R. M. Badger, J. Amer. Chem. Soc. 46, 2166 (1924).}$$

$$6. \text{ J. Horvath, T. Yano, and K. Kanai, Shokubai 7, 6 (1951); CA. 49 6553e.}$$

$$7. \text{ B. J. McBride, S. Heisel, J. G. Ehlers, and S. Gordon, NASA SP 3001 (1963).}$$

$$8. \text{ D. H. Rank, G. Skorinko, D. P. Eastman, and T. A. Wiggins, J. Opt. Soc. 50, 421 (1960).}$$

$$9. \text{ T. Nakagawa and Y. Morino, Bull. Chem. Soc. Japan 42, 2212 (1969).}$$

Isocyanic Acid (HNCO)

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 43.027

(Ideal Gas)

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	8.000	INFINITE	-2.615	-27.179	-27.179	INFINITE
100	9.000	57.933	-1.875	-27.179	-27.179	26.896
200	10.000	56.909	.000	-27.900	-28.681	16.053
298	10.724	56.909	.000	-27.900	-28.681	16.053
300	10.732	56.975	.020	-27.904	-28.667	16.698
400	12.085	57.348	1.165	-28.055	-28.897	13.602
500	13.114	58.071	2.427	-28.179	-29.093	10.531
600	13.934	58.537	3.781	-28.287	-29.266	8.474
700	14.613	58.738	5.209	-28.387	-29.421	7.000
800	15.191	59.728	6.133	-28.479	-29.561	5.690
900	15.690	71.546	8.244	-28.563	-29.691	5.024
1000	16.125	73.222	9.387	-28.639	-29.814	4.330
1100	16.507	74.778	11.468	-28.705	-29.927	3.760
1200	16.842	76.259	13.136	-28.764	-30.036	3.285
1300	17.136	77.589	14.835	-28.818	-30.140	2.881
1400	17.394	78.868	16.561	-28.867	-30.239	2.535
1500	17.622	80.076	18.313	-28.915	-30.336	2.234
1600	17.823	81.220	20.087	-28.964	-30.430	1.971
1700	18.001	82.306	21.876	-29.003	-30.520	1.738
1800	18.159	83.339	23.685	-29.039	-30.608	1.531
1900	18.299	84.325	25.500	-29.075	-30.694	1.354
2000	18.424	85.267	27.334	-29.109	-30.778	1.178
2100	18.535	86.168	29.192	-29.144	-30.861	1.026
2200	18.635	87.033	31.050	-29.180	-30.942	.888
2300	18.725	87.863	32.918	-29.218	-31.021	.762
2400	18.805	88.662	34.795	-29.256	-31.098	.666
2500	18.878	89.431	36.679	-29.291	-31.174	.580
2600	18.944	90.173	38.570	-29.346	-31.249	.511
2700	19.004	90.889	40.468	-29.393	-31.321	.441
2800	19.059	91.581	42.371	-29.442	-31.390	.380
2900	19.108	92.251	44.279	-29.494	-31.458	.326
3000	19.154	92.899	46.193	-29.549	-31.526	.278
3100	19.195	93.528	48.110	-29.607	-31.592	.235
3200	19.234	94.138	50.032	-29.668	-31.658	.198
3300	19.269	94.731	51.957	-29.732	-31.724	.166
3400	19.301	95.306	53.885	-29.800	-31.790	.138
3500	19.331	95.866	55.817	-29.872	-31.856	.114
3600	19.359	96.411	57.751	-29.949	-31.922	.092
3700	19.384	96.942	59.688	-30.029	-31.989	.072
3800	19.408	97.459	61.628	-30.112	-32.057	.054
3900	19.430	97.964	63.570	-30.201	-32.125	.038
4000	19.451	98.456	65.514	-30.294	-32.194	.024
4100	19.470	98.936	67.463	-30.391	-32.263	.012
4200	19.488	99.406	69.408	-30.492	-32.333	.002
4300	19.505	99.865	71.358	-30.597	-32.404	.000
4400	19.521	100.313	73.309	-30.706	-32.476	.000
4500	19.536	100.752	75.262	-30.820	-32.549	.000
4600	19.550	101.182	77.216	-30.937	-32.623	.000
4700	19.563	101.602	79.172	-31.058	-32.698	.000
4800	19.575	102.014	81.129	-31.184	-32.774	.000
4900	19.586	102.418	83.087	-31.313	-32.851	.000
5000	19.597	102.814	85.046	-31.446	-32.929	.000
5100	19.608	103.202	87.006	-31.584	-33.008	.000
5200	19.617	103.583	88.968	-31.725	-33.089	.000
5300	19.627	103.956	90.930	-31.870	-33.172	.000
5400	19.635	104.323	92.893	-32.019	-33.257	.000
5500	19.644	104.684	94.857	-32.172	-33.343	.000
5600	19.652	105.038	96.822	-32.328	-33.430	.000
5700	19.659	105.386	98.787	-32.488	-33.518	.000
5800	19.666	105.728	100.753	-32.653	-33.607	.000
5900	19.673	106.064	102.720	-32.823	-33.697	.000
6000	19.679	106.395	104.688	-33.000	-33.788	.000

December 31, 1960.

CHNO

Moments of Inertia: $I_A = 7.7276 \times 10^{-39}$ g. cm.², $I_B = 7.636 \times 10^{-39}$ g. cm.², $I_C = 0.03157 \times 10^{-39}$ g. cm.²
 $\sigma = 1$.

Data from J. S. Gordon, Thiokol Chemical Corp., Reaction Motors Division, Denville, N. J., "Thermodynamic Data for Combustion Products", January, 1960.

Mol. Wt. = 43.027

 $\Delta H_f^\circ 298.15 = -27.9$ kcal. mole⁻¹ $S^\circ 298.15 = 56.909$ cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω cm. ⁻¹
572 (1)
670 (1)
787 (1)
1327 (1)
2274 (1)
3531 (1)

Formyl (HCO)

(Ideal Gas) Mol. Wt. = 29.019

CHO

MOL. WT. = 29.019

(IDEAL GAS)

FORMYL (HCO)

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	0.000	INFINITE	INFINITE	2.387	2.986	2.986	INFINITE	INFINITE
100	7.849	44.930	40.855	2.941	2.941	2.941	4.118	6.968
200	7.849	50.147	42.849	2.941	2.941	2.941	5.114	7.968
298	8.204	53.683	43.683	2.900	2.900	2.900	6.353	8.786
300	8.271	53.734	43.683	.015	2.902	6.356	4.783	8.783
400	8.703	56.171	44.012	.563	3.002	7.773	4.247	8.247
500	9.184	58.164	44.649	1.758	3.142	8.950	3.912	7.912
600	9.640	59.881	45.381	2.700	3.305	10.097	3.678	7.678
700	10.108	61.404	46.135	3.481	3.481	11.214	3.501	7.501
800	10.518	62.781	46.881	4.720	3.661	12.307	3.362	7.362
900	10.888	64.042	47.607	5.791	3.840	13.378	3.248	7.248
1000	11.216	65.206	48.310	6.896	4.013	14.428	3.153	7.153
1100	11.505	66.289	48.986	8.033	4.182	15.462	3.072	7.072
1200	11.758	67.301	49.638	9.196	4.346	16.479	3.001	6.938
1300	11.979	68.251	50.264	10.383	4.508	17.484	2.939	6.876
1400	12.172	69.146	50.867	11.591	4.665	18.475	2.884	6.835
1500	12.341	69.992	51.447	12.817	4.822	19.456	2.835	6.790
1600	12.489	70.793	52.007	14.059	4.978	20.429	2.790	6.750
1700	12.618	71.554	52.546	15.314	5.131	21.386	2.750	6.712
1800	12.732	72.279	53.067	16.582	5.285	22.341	2.712	6.678
1900	12.832	72.970	53.570	17.860	5.440	23.283	2.678	6.646
2000	12.921	73.630	54.057	19.148	5.594	24.219	2.646	6.616
2100	13.000	74.263	54.528	20.444	5.750	25.145	2.617	6.584
2200	13.071	74.869	54.984	21.747	5.909	26.067	2.589	6.553
2300	13.133	75.452	55.427	23.058	6.068	26.978	2.563	6.523
2400	13.190	76.012	55.856	24.374	6.232	27.883	2.539	6.493
2500	13.240	76.551	56.273	25.695	6.398	28.784	2.516	6.463
2600	13.286	77.071	56.678	27.022	6.566	29.675	2.494	6.434
2700	13.327	77.574	57.073	28.353	6.736	30.562	2.474	6.404
2800	13.365	78.059	57.458	29.687	6.912	31.440	2.454	6.374
2900	13.399	78.529	57.830	31.025	7.091	32.311	2.435	6.345
3000	13.430	78.983	58.194	32.367	7.273	33.179	2.417	6.317
3100	13.458	79.428	58.550	33.711	7.457	34.039	2.400	6.290
3200	13.484	79.865	58.896	35.058	7.646	34.894	2.383	6.263
3300	13.508	80.287	59.234	36.408	7.839	35.744	2.367	6.237
3400	13.530	80.671	59.565	37.760	8.035	36.586	2.352	6.212
3500	13.550	81.063	59.888	39.114	8.235	37.425	2.337	6.187
3600	13.569	81.445	70.208	40.470	8.439	38.255	2.322	6.162
3700	13.586	81.817	70.513	41.828	8.648	39.080	2.308	6.137
3800	13.602	82.180	70.815	43.187	8.859	39.897	2.294	6.112
3900	13.617	82.533	71.111	44.548	9.075	40.711	2.281	6.087
4000	13.631	82.878	71.401	45.911	9.294	41.520	2.268	6.062
4100	13.644	83.215	71.685	47.275	9.510	42.325	2.256	6.037
4200	13.656	83.544	71.963	48.640	9.746	43.119	2.244	6.012
4300	13.667	83.866	72.236	50.006	9.978	43.912	2.232	5.987
4400	13.678	84.180	72.504	51.373	10.214	44.700	2.220	5.962
4500	13.688	84.487	72.767	52.741	10.454	45.484	2.209	5.937
4600	13.697	84.788	73.025	54.111	10.698	46.255	2.198	5.912
4700	13.706	85.083	73.279	55.481	10.946	47.025	2.187	5.887
4800	13.714	85.372	73.527	56.852	11.198	47.789	2.176	5.862
4900	13.722	85.654	73.772	58.224	11.453	48.551	2.165	5.837
5000	13.729	85.932	74.013	59.596	11.712	49.306	2.155	5.812
5100	13.736	86.204	74.249	60.969	11.977	50.057	2.145	5.787
5200	13.742	86.470	74.481	62.343	12.244	50.802	2.135	5.762
5300	13.749	86.732	74.710	63.718	12.515	51.535	2.125	5.737
5400	13.754	86.989	74.935	65.093	12.791	52.272	2.115	5.712
5500	13.760	87.242	75.157	66.469	13.070	52.999	2.106	5.687
5600	13.765	87.490	75.375	67.845	13.353	53.725	2.097	5.662
5700	13.770	87.733	75.586	69.222	13.640	54.446	2.087	5.637
5800	13.775	87.973	75.801	70.599	13.932	55.158	2.078	5.612
5900	13.779	88.208	76.009	71.977	14.226	55.862	2.069	5.587
6000	13.784	88.440	76.214	73.355	14.525	56.570	2.060	5.562

March 31, 1961

HC bond length = $1.08 \pm 0.005 \text{ \AA}$ CO bond length = $1.198 \pm 0.005 \text{ \AA}$ HCO angle = $119^\circ 30' \pm 1^\circ$

Product of Moments of Inertia = $I_A I_B I_C = 4.73 \times 10^{-118} \text{ g.}^3 \text{ cm.}^6$ $\sigma = 1$

Heat of Formation

Calculated from $\Delta H_0^\circ = 75.1 \pm 2.3 \text{ kcal.}$ for the reaction $\text{H}_2\text{CO(g)} \rightarrow \text{HCO(g)} + \text{H(g)}$, reported by J. C. D. Brand and R. T. Reed, J. Chem. Soc. 2386 (1957).

Heat Capacity and Entropy

The vibrational levels and multiplicities are from G. E. Ewing, W. E. Thompson, and G. C. Pimentel, J. Chem. Phys. 32, 927 (1960), while the ground state multiplicity and structural data are from G. Herzberg and D. A. Ramsay, Proc. Roy. Soc. A233, 34 (1955).

Vibrational Levels and Multiplicities

ω , cm. ⁻¹	[3000] (1)
1860 (1)	
1085 (1)	

$\Delta H_0^\circ = -3.0 \pm 3 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -2.9 \pm 3 \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [53.683] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Point Group C_a
 Ground State Multiplicity = [2]

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ^o ₂₉₈)/T	H ^o - H ^o ₂₉₈	cent/mol ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	9.617	48.344	4.000	204.400	200.862	- 1.47236
300						
350	9.636	48.397	48.344	204.408	200.859	- 1.46311
400	9.693	48.992	48.493	204.400	200.832	- 1.46038
500	9.942	53.150	48.374	205.291	198.212	- 1.46638
600	10.385	55.002	50.162	205.700	196.757	- 1.46699
700	10.777	56.633	50.972	206.059	195.235	- 1.46955
800	11.125	58.053	51.750	206.283	193.655	- 1.47305
900	11.472	59.250	52.550	206.389	192.034	- 1.47763
1000	11.781	60.253	53.300	206.230	190.367	- 1.48305
1100	12.064	61.189	54.021	207.614	188.663	- 1.48884
1200	12.320	62.050	54.713	208.003	186.924	- 1.49444
1300	12.550	62.843	55.376	208.392	185.151	- 1.50000
1400	12.760	63.578	56.016	208.782	183.349	- 1.50562
1500	12.946	64.260	56.630	209.192	181.518	- 1.51138
1600	13.113	64.891	57.222	209.594	179.657	- 1.51726
1700	13.265	65.473	57.792	210.009	177.767	- 1.52326
1800	13.405	66.007	58.342	210.439	175.855	- 1.52938
1900	13.535	66.496	58.873	210.819	173.939	- 1.53562
2000	13.622	66.946	59.387	211.230	171.986	- 1.54200
2100	13.718	67.363	59.885	211.684	170.014	- 1.54854
2200	13.822	67.748	60.364	212.171	168.021	- 1.55524
2300	13.938	68.100	60.834	212.684	166.012	- 1.56208
2400	14.065	68.420	61.287	213.222	164.000	- 1.56906
2500	14.201	68.710	61.728	213.781	161.975	- 1.57618
2600	14.345	68.973	62.156	214.360	159.944	- 1.58344
2700	14.495	69.210	62.571	214.956	157.907	- 1.59084
2800	14.650	69.423	62.978	215.576	155.873	- 1.59838
2900	14.810	69.612	63.372	216.216	153.840	- 1.60606
3000	14.975	69.778	63.757	216.874	151.807	- 1.61388
3100	15.145	69.923	64.133	217.558	149.774	- 1.62184
3200	15.320	70.048	64.500	218.266	147.741	- 1.62994
3300	15.500	70.154	64.857	218.996	145.707	- 1.63818
3400	15.685	70.242	65.206	219.746	143.674	- 1.64656
3500	15.875	70.313	65.548	220.516	141.641	- 1.65508
3600	16.070	70.368	65.882	221.306	139.608	- 1.66374
3700	16.270	70.408	66.209	222.116	137.575	- 1.67254
3800	16.475	70.434	66.529	222.946	135.542	- 1.68148
3900	16.685	70.447	66.842	223.796	133.509	- 1.69056
4000	16.900	70.448	67.149	224.666	131.476	- 1.69978
4100	17.120	70.437	67.450	225.556	129.443	- 1.70914
4200	17.345	70.414	67.746	226.466	127.410	- 1.71864
4300	17.575	70.379	68.034	227.396	125.377	- 1.72828
4400	17.810	70.334	68.318	228.346	123.344	- 1.73806
4500	18.050	70.279	68.597	229.316	121.311	- 1.74798
4600	18.295	70.214	68.870	230.306	119.278	- 1.75804
4700	18.545	70.139	69.139	231.316	117.245	- 1.76824
4800	18.800	70.054	69.403	232.346	115.212	- 1.77858
4900	19.060	70.000	69.662	233.396	113.179	- 1.78906
5000	19.325	70.000	69.917	234.466	111.146	- 1.79968
5100	19.595	70.000	70.168	235.556	109.113	- 1.81044
5200	19.870	70.000	70.414	236.666	107.080	- 1.82134
5300	20.150	70.000	70.657	237.796	105.047	- 1.83238
5400	20.435	70.000	70.896	238.946	103.014	- 1.84356
5500	20.725	70.000	71.131	240.116	100.981	- 1.85488
5600	21.020	70.000	71.363	241.306	98.948	- 1.86634
5700	21.320	70.000	71.595	242.516	96.915	- 1.87794
5800	21.625	70.000	71.827	243.746	94.882	- 1.88968
5900	21.935	70.000	72.059	245.006	92.849	- 1.90156
6000	22.250	70.000	72.291	246.286	90.816	- 1.91358

June 30, 1966

$$\Delta H_{298}^{\circ} = 203.0 \pm 10 \text{ kcal/mol}$$

$$\Delta H_{298,15}^{\circ} = 204.4 \pm 10 \text{ kcal/mol}$$

Point Group [C_{∞v}]

$$S_{298,15}^{\circ} = [48.3] \text{ gibbs/mol}$$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$$\frac{\omega_e}{\text{cm}^{-1}}$$

$$[2310](1)$$

$$[700](2)$$

$$[3540](1)$$

$$\text{Bond Distance: C-H} = [1.029] \text{ \AA}$$

$$\text{Bond Angle: H-C-O} = [180^{\circ}]$$

$$\text{Rotational Constant: } B_0 = [1.56015] \text{ cm}^{-1}$$

Heat of Formation.

The selected heat of formation, ΔH_{298}° (HCO⁺, g) = 203 kcal/mol was obtained from electron impact studies on cis- and trans-HCOOH by F. M. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957. A higher value, $\Delta H_{298}^{\circ} = 220$ kcal/mol, has also been reported from appearance potential measurements on CH₃CHO by J. R. Major, C. R. Patrick and J. C. Robb, Trans-Paraday Soc. 57, 14 (1961). Generally, errors in the heat of formation derived from electron impact studies are such as to cause the quantities to be high because of unaccounted excitations or residual kinetic energy in the fragments; therefore, the value of 203 kcal/mol is preferable, assuming the same reliability of the experiments.

Heat Capacity and Entropy.

Since the molecule HCO⁺(g) has the same number of valence electrons as HCN(g), a linear molecular configuration is assumed for HCO⁺(g) in the tabulation. The bond distances H-C and C-O were estimated by comparison with those in similar molecules by D. G. Clifton, J. Chem. Phys. 41, 3656 (1964). The vibrational frequencies were calculated by the valence force method from the estimated stretching and bending force constants of Clifton. The principal moment of inertia is 1.7941 X 10⁻³⁹ g cm².

Point Group $C_{\infty v}$ $\Delta H_f^\circ = [39.9 \pm 15] \text{ kcal/mol}$

Methinophosphide (HCP)

(Ideal Gas) GFW = 43.99292

CH-

 $\Delta H_f^\circ = [40 \pm 15] \text{ kcal/mol}$

T, K	Cp*	S*	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH*	Log Kp
0	6.000	0.000	INFIMITE	2.235	39.891	INFIMITE
100	6.978	43.067	58.470	1.540	40.101	-81.266
200	7.714	48.070	52.152	0.814	40.130	-37.411
298	8.683	51.375	51.375	0.000	40.000	-22.991
300	8.694	51.430	51.375	0.016	39.997	-22.810
400	9.902	54.134	51.737	0.959	39.613	-15.541
500	10.658	56.428	52.452	1.988	39.603	-11.200
600	11.236	58.428	53.284	3.084	39.370	-8.323
700	11.672	60.152	54.231	4.291	39.104	-6.223
800	12.042	61.779	55.004	5.420	38.802	-4.739
900	12.415	63.222	55.838	6.646	38.469	-3.751
1000	12.707	64.545	56.643	7.902	38.101	-3.106
1100	12.967	65.767	57.418	9.186	37.756	-2.777
1200	13.207	66.922	58.152	10.500	37.442	-2.526
1300	13.407	67.972	58.876	11.825	37.166	-2.336
1400	13.592	68.973	59.562	13.175	36.928	-2.198
1500	13.759	69.916	60.221	14.543	36.719	-2.099
1600	13.909	70.809	60.855	15.926	36.536	-2.026
1700	14.048	71.653	61.463	17.325	36.378	-1.968
1800	14.178	72.453	62.054	18.735	36.244	-1.922
1900	14.279	73.232	62.623	20.157	36.132	-1.886
2000	14.341	73.967	63.172	21.590	36.040	-1.858
2100	14.375	74.671	63.703	23.033	35.965	-1.835
2200	14.387	75.346	64.217	24.485	35.904	-1.816
2300	14.369	75.995	64.715	25.945	35.854	-1.800
2400	14.315	76.620	65.198	27.413	35.819	-1.786
2500	14.233	77.222	65.667	28.888	35.796	-1.773
2600	14.120	77.803	66.122	30.370	35.782	-1.761
2700	14.000	78.364	66.567	31.851	35.778	-1.750
2800	13.868	78.908	67.000	33.331	35.784	-1.740
2900	13.723	79.434	67.416	34.811	35.799	-1.731
3000	13.566	79.944	67.826	36.296	35.832	-1.723
3100	13.400	80.430	68.229	37.786	35.880	-1.716
3200	13.225	80.894	68.616	39.281	35.941	-1.710
3300	13.042	81.339	68.984	40.781	36.014	-1.704
3400	12.852	81.764	69.335	42.287	36.100	-1.698
3500	12.658	82.178	69.678	43.798	36.198	-1.692
3600	12.460	82.570	70.003	45.313	36.308	-1.686
3700	12.258	82.942	70.311	46.833	36.430	-1.680
3800	12.053	83.295	70.700	48.358	36.564	-1.674
3900	11.845	83.637	71.103	50.129	36.712	-1.668
4000	11.634	83.957	71.429	51.685	36.874	-1.662
4100	11.420	84.258	71.749	53.247	37.050	-1.656
4200	11.203	84.542	72.053	54.815	37.240	-1.650
4300	10.984	84.811	72.341	56.388	37.444	-1.644
4400	10.762	85.065	72.613	57.966	37.662	-1.638
4500	10.538	85.304	72.970	59.556	37.894	-1.632
4600	10.312	85.528	73.261	61.150	38.140	-1.626
4700	10.084	85.738	73.580	62.750	38.400	-1.620
4800	9.854	85.934	73.830	64.356	38.674	-1.614
4900	9.622	86.117	74.107	65.979	38.962	-1.608
5000	9.388	86.284	74.379	67.606	39.264	-1.602
5100	9.152	86.438	74.648	69.241	39.580	-1.596
5200	8.914	86.580	74.912	70.883	39.910	-1.590
5300	8.674	86.709	75.172	72.534	40.254	-1.584
5400	8.432	86.825	75.428	74.200	40.612	-1.578
5500	8.188	86.929	75.681	75.887	40.984	-1.572
5600	7.942	87.022	75.930	77.576	41.370	-1.566
5700	7.694	87.105	76.178	79.277	41.770	-1.560
5800	7.444	87.178	76.418	80.991	42.184	-1.554
5900	7.192	87.241	76.657	82.717	42.612	-1.548
6000	6.938	87.290	76.893	84.457	43.054	-1.542

Dec. 31, 1969

Electronic Levels and Quantum Weights

State	$\epsilon_i, \text{cm}^{-1}$	g_i
$X^1\Sigma^+$	0	1
$a^3\Sigma^+$	24440	3
$b^3\Pi$	30430	6
$c^3\Sigma^-$	31024	3
A^1A''	34746	1
$B^1\Pi$	35927	2
$d^3\Pi$	35976	6
C^1A'	40248	1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}
3216.9 (1)
674.7 (2)
1278.4 (1)

Spectroscopic constants used in calculating corrections to the rigid-rotor harmonic oscillator model (cm^{-1}):

$$\begin{aligned}\sigma_1 &= 3.4 \times 10^{-3} & -\chi_{11} &= \{3.7\} & -\chi_{12} &= \{1.9\} \\ \sigma_2 &= -3.4 \times 10^{-4} & -\chi_{22} &= \{2.4\} & -\chi_{23} &= \{18.0\} \\ \sigma_3 &= 3.1 \times 10^{-3} & -\chi_{23} &= \{51.0\} & -\chi_{13} &= \{6.0\}\end{aligned}$$

Bond Distances: C-H = 1.0667 Å C-P = 1.5421 Å

Bond Angle: H-C-P = 180°

Rotational Constant: $B_0 = 0.56633 \text{ cm}^{-1}$ $\sigma = 1$

Heat of Formation

The bonding in HCP and HCN is very similar, as evidenced by the bond lengths and vibrational frequencies. We assume that the C-H bond strength is thus the same in these two molecules. For the reaction $\text{HCN} \rightarrow \text{H} + \text{CN}$ we derive $\Delta H^\circ = 123.8 \text{ kcal}$ from $\Delta H_f^\circ(\text{HCN}) = 32.3$, $\Delta H_f^\circ(\text{H}) = 52.1$ and $\Delta H_f^\circ(\text{CN}) = 104 \text{ kcal/mol}$. Applying this to the reaction $\text{HCP} \rightarrow \text{H} + \text{CP}$, we obtain $\Delta H_f^\circ(\text{HCP}) = 40 \pm 15 \text{ kcal/mol}$, from $\Delta H_f^\circ(\text{CP}) = 111.7 \text{ kcal/mol}$.

Heat Capacity and Entropy

The molecular configuration was first reported by Gier (1), and later the bond lengths were determined by Tyler (2) using microwave spectroscopy. The vibrational frequencies and electronic levels were obtained from an analysis of the ultraviolet spectrum by Johns et al. (3). Since the first excited state is above 24000 cm^{-1} and the first nonlinear state at $34,000 \text{ cm}^{-1}$, there is negligible error introduced by assuming ground state molecular constants for all excited states. The anharmonic constants were estimated from those of HCN by Gordon (4) and the adopted table includes these corrections and the electronic contributions.

References

1. T. E. Gier, J. Amer. Chem. Soc. **83**, 1769 (1961).
2. J. K. Tyler, J. Chem. Phys. **40**, 1170 (1964).
3. J. W. C. Johns, H. F. Shurvell and J. K. Tyler, Can. J. Phys. **47**, 893 (1969).
4. J. S. Gordon, Atlantic Research Corp., Alexandria, Va., private communication, Jan. 12, 1970.

Methylene (CH₂)

(Ideal Gas)

GFW = 14.02709

Point Group D_{∞h}

$$\Delta H_f^\circ = 92.25 \pm 1.0 \text{ kcal/mol}$$

$$S^\circ_{298.15} = 43.27 \pm 0.5 \text{ gibbs/mol}$$

$$\Delta H_f^\circ_{298.15} = 92.07 \pm 1.0 \text{ kcal/mol}$$



Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
$X^3\Sigma^-$	0
a^3A_1	1
b^3B_1	1
c^3A_1	1

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹
(2960) (1)
(1114) (2)
(3200) (1)

$$\text{Bond Distance: C-H} = 1.029 \text{ \AA}$$

$$\text{Bond Angle: H-C-H} = 180^\circ$$

$$\text{Rotational Constant: } B_0 = 7.8974 \text{ cm}^{-1}$$

$$\sigma = 2$$

Heat of Formation

Chupka and Livshitz (1) have recently obtained the photoionization threshold for the production of CH₂⁺ from CH₃ as 15.09 ± 0.03 eV. In conjunction with the spectroscopic ionization potential determined by Herzberg (2), they report D₀(CH₃-H) = 4.694 ± 0.033 eV (108.25 ± 0.77 kcal). Use of ΔH₀⁰(CH₃, g) = 35.62 kcal/mol from these tables yields ΔH₀⁰(CH₂, g) = 92.25 ± 1.0 kcal/mol, which is adopted.

Chupka (3) and Dibeler et al. (4) have determined the photoionization threshold for the production of CH₂⁺ from CH₄. If the latter value is corrected for rotational energy effects as suggested by Chupka the two values are identical and yield ΔH₀⁰(CH₂, g) = 94.6 kcal/mol. However, Chupka indicates that this is a maximum value since the process of H₂ elimination is likely to occur with excess energy in the products at the threshold. Chupka et al. (14) have obtained the appearance threshold of CH₂⁺ from C₂H₄(g) by photoionization and obtained a maximum value of ΔH₀⁰(CH₂, g) = 95.5 kcal/mol.

Dibeler and Liston (5) have also reported the photoionization threshold for the process CH₃CH + CH₂⁺ + HCN as 14.94 eV (344.55 kcal). Using auxiliary data from (2) and (13) we obtain ΔH₀⁰(CH₂, g) = 95 kcal/mol, however the above process is also likely to occur with excess energy and so this is a maximum value.

The older electron impact data of Langer et al. (6) contained several inconsistencies with presently accepted values and was reanalysed by Prophet (7) to give ΔH₀⁰(CH₂, g) = 95 ± 5 kcal/mol. Chupka et al. (8) have also reported a heat of formation, from chemical equilibria measured in a mass spectrometer, as 86.8 ± 6 kcal/mol.

Heat Capacity and Entropy

The ground state configuration, bond length and angle are from Herzberg (9). The excited electronic states are from the calculations of Goldberg and Riter (10) who have tried to allow for correlation energy effects in the different states. The separation between the a₁ and b₁ states is established as 7100 cm⁻¹. The degenerate bending frequency was listed as a possible fundamental of CH₂ by Milligan and Pimentel (11). There is considerable uncertainty that it is in fact the ground state bending frequency, excited state bending frequencies of 1363 and 557 cm⁻¹ have been reported. The symmetric stretch was estimated to be that listed by Herzberg (12) for a bent molecule. The asymmetric stretch was estimated using the valence force field approximation.

The uncertainty in the entropy reflects the possible errors in the vibrational frequencies and the uncertain position of the low lying electronic levels and their varying geometries.

References:

- W. A. Chupka and C. Livshitz, J. Chem. Phys. **48**, 1109 (1968).
- G. Herzberg, Proc. Roy. Soc. (London) **A182**, 291 (1961).
- V. H. Dibeler, M. Kraus, J. Chem. Phys. **42**, 1031 (1965).
- V. H. Dibeler and S. K. Liston, J. Chem. Phys. **42**, 3791 (1965).
- V. H. Dibeler and D. P. Stevenson, J. Chem. Phys. **22**, 1836 (1954).
- A. Langer, J. A. Hipple and D. P. Stevenson, J. Chem. Phys. **38**, 2345 (1963).
- H. Prophet, J. Chem. Phys. **38**, 2345 (1963).
- W. A. Chupka, J. Berkowitz and D. J. Nesich, "Advances in Mass Spectrometry," R. M. Elliott, Ed. Pergamon Press, Ltd., Oxford, 1968.
- G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
- M. C. Goldberg and J. R. Riter, J. Chem. Phys. **50**, 547 (1969).
- D. E. Milligan and G. Pimentel, J. Chem. Phys. **23**, 1405 (1958).
- G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945.
- U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
- W. A. Chupka, J. Berkowitz and K. H. A. Refaey, J. Chem. Phys. **50**, 1938 (1969).

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1962; June 30, 1969

T, °K	Cp	S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	4.000	INFINITE	-	92.250	92.250	INFINITE
100	35.000	35.000	-2.006	92.250	92.250	96.031
200	7.040	40.383	-7.710	92.182	89.963	96.296
298	7.492	43.266	-7.000	92.070	88.680	65.151
300	7.504	43.312	-7.014	92.067	88.680	64.735
400	8.172	45.561	-1.797	91.910	87.815	67.980
500	8.620	47.435	-1.647	91.742	86.510	37.944
600	9.007	49.116	-2.559	91.576	85.836	31.267
700	9.497	50.607	-3.527	91.417	84.896	26.506
800	10.451	51.969	-4.547	91.272	83.974	22.941
900	10.919	53.227	-5.616	91.142	83.069	20.172
1000	11.349	54.400	-6.730	91.032	82.178	17.960
1100	11.738	55.500	-7.885	90.938	81.297	16.152
1200	12.087	56.537	-9.076	90.859	80.425	14.647
1300	12.397	57.517	-10.301	90.791	79.556	13.375
1400	12.671	58.446	-11.554	90.734	78.697	12.265
1500	12.912	59.328	-12.834	90.684	77.840	11.331
1600	13.125	60.169	-14.136	90.638	76.982	10.515
1700	13.312	60.970	-15.458	90.599	76.132	9.787
1800	13.478	61.736	-16.798	90.563	75.281	9.140
1900	13.625	62.469	-18.153	90.530	74.437	8.562
2000	13.755	63.171	-19.522	90.499	73.597	8.041
2100	13.872	63.845	-20.903	90.469	72.744	7.571
2200	13.976	64.493	-22.296	90.439	71.888	7.142
2300	14.070	65.116	-23.698	90.410	71.058	6.752
2400	14.155	65.719	-25.106	90.382	70.246	6.397
2500	14.231	66.296	-26.529	90.348	69.474	6.065
2600	14.301	66.855	-27.955	90.315	68.740	5.761
2700	14.364	67.396	-29.389	90.282	68.041	5.480
2800	14.422	67.920	-30.828	90.247	67.376	5.219
2900	14.475	68.430	-32.270	90.213	66.746	4.975
3000	14.524	68.918	-33.723	90.171	66.146	4.750
3100	14.569	69.395	-35.178	90.132	65.576	4.538
3200	14.610	69.859	-36.637	90.089	65.037	4.339
3300	14.648	70.316	-38.100	90.043	64.526	4.152
3400	14.683	70.767	-39.566	90.000	64.040	3.975
3500	14.716	71.173	-41.036	89.943	63.582	3.812
3600	14.746	71.588	-42.509	89.889	63.155	3.656
3700	14.774	71.992	-43.985	89.830	62.757	3.509
3800	14.800	72.376	-45.464	89.770	62.387	3.367
3900	14.824	72.746	-46.945	89.704	62.043	3.229
4000	14.846	73.147	-48.429	89.636	61.724	3.112
4100	14.867	73.514	-49.914	89.563	61.430	3.002
4200	14.886	73.872	-51.402	89.486	61.160	2.897
4300	14.903	74.212	-52.892	89.405	60.913	2.797
4400	14.921	74.555	-54.382	89.320	60.680	2.700
4500	14.936	74.901	-55.876	89.230	60.460	2.596
4600	14.951	75.229	-57.370	89.136	60.257	2.474
4700	14.964	75.551	-58.866	89.038	60.073	2.364
4800	14.976	75.863	-60.363	88.936	59.907	2.261
4900	14.987	76.175	-61.862	88.830	59.757	2.165
5000	15.000	76.478	-63.361	88.717	59.622	2.136
5100	15.010	76.775	-64.861	88.601	59.500	2.060
5200	15.020	77.067	-66.363	88.479	59.389	1.997
5300	15.029	77.353	-67.865	88.353	59.289	1.943
5400	15.037	77.633	-69.368	88.223	59.197	1.890
5500	15.045	77.910	-70.873	88.087	59.113	1.785
5600	15.053	78.181	-72.377	87.946	59.035	1.722
5700	15.060	78.448	-73.883	87.801	58.962	1.662
5800	15.067	78.711	-75.389	87.650	58.894	1.604
5900	15.073	78.967	-76.896	87.495	58.831	1.549
6000	15.079	79.221	-78.404	87.336	58.772	1.494



Chlorofluoromethane (CH₂ClF)

(Ideal Gas)

GFw = 68.4785

T, °K	Cp°	S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔG° _f	Log Kp
0	0.000	INFINITE	2.689	60.861	60.861	INFINITE
100	8.195	53.043	71.942	61.530	61.530	138.311
200	9.858	59.077	64.138	62.047	58.444	63.865
298	11.242	63.171	0.000	62.600	56.558	41.958
300	11.279	63.240	0.021	62.611	56.521	41.176
400	13.281	66.761	1.249	63.122	54.411	29.729
500	15.072	69.423	6.583	63.550	52.163	22.809
600	16.561	72.407	4.254	63.894	49.876	18.167
700	17.866	75.092	6.516	64.166	47.535	14.535
800	18.960	77.493	7.802	64.366	45.156	11.771
900	19.860	80.164	9.728	64.534	42.767	9.131
1000	20.386	82.274	11.732	64.644	40.277	8.603
1100	21.005	84.246	13.802	64.717	37.837	7.517
1200	21.595	85.940	15.917	64.777	35.492	6.536
1300	22.159	87.440	18.107	64.822	33.242	5.733
1400	22.387	89.684	20.326	64.773	31.042	4.760
1500	22.729	91.441	22.582	64.755	28.842	4.066
1600	23.026	92.517	24.870	64.727	25.599	3.497
1700	23.252	93.254	27.156	64.688	22.154	2.916
1800	23.512	94.554	29.556	64.582	18.272	2.102
1900	23.712	94.536	31.868	64.582	18.272	2.102
2000	23.888	97.756	80.222	64.523	15.836	1.730
2100	24.045	98.226	81.466	64.400	13.403	1.395
2200	24.195	101.125	85.086	64.350	10.975	1.090
2300	24.308	103.162	83.855	64.265	8.121	0.557
2400	24.419	104.162	83.855	64.265	6.121	0.324
2500	24.519	103.161	84.607	64.202	3.703	0.108
2600	24.609	104.125	85.340	64.138	1.282	0.08
2700	24.760	105.923	87.923	64.077	1.137	0.092
2800	24.830	106.824	87.923	63.961	5.942	0.449
3000	24.891	107.667	88.086	63.744	63.908	0.610
3100	24.947	108.484	88.731	61.236	63.857	10.777
3200	25.005	109.267	89.350	63.611	13.164	0.900
3300	25.065	110.023	90.577	63.731	17.994	1.152
3400	25.088	110.795	90.577	63.731	17.994	1.152
3500	25.128	111.523	91.165	63.700	20.396	1.274
3600	25.165	112.232	91.749	63.671	22.799	1.384
3700	25.200	112.922	92.555	63.650	25.202	1.489
3800	25.236	113.582	93.295	63.621	30.006	1.581
3900	25.259	114.250	93.395	63.621	30.006	1.581
4000	25.286	114.890	93.925	63.615	32.407	1.771
4100	25.312	115.514	94.444	63.614	34.804	1.855
4200	25.335	116.124	95.053	63.620	37.209	1.936
4300	25.357	116.724	95.653	63.622	39.615	2.015
4400	25.378	117.304	95.942	63.627	42.007	2.087
4500	25.397	117.875	96.532	63.671	44.403	2.157
4600	25.415	118.433	96.999	63.698	46.810	2.224
4700	25.432	118.970	97.360	63.712	49.215	2.288
4800	25.448	119.440	98.264	63.816	54.025	2.410
4900	25.464	120.040	106.705	63.816	54.025	2.410
5000	25.478	120.555	98.704	63.867	56.427	2.466
5100	25.491	121.060	99.138	63.924	58.831	2.521
5200	25.516	121.545	99.584	63.965	61.241	2.574
5300	25.538	122.018	100.045	64.005	63.645	2.625
5400	25.527	122.518	100.397	64.126	66.059	2.675
5500	25.538	122.986	100.803	64.206	68.473	2.721
5600	25.546	123.446	101.203	64.290	70.883	2.766
5700	25.559	123.843	101.546	64.382	73.296	2.810
5800	25.576	124.780	102.369	64.500	78.113	2.893
5900	25.584	125.210	102.746	64.668	80.547	2.934
6000	25.584	125.210	102.746	64.668	80.547	2.934

Dec. 31, 1960; Sept. 30, 1964; June 30, 1970

CHLOROFUOROMETHANE (CH₂ClF)

(IDEAL GAS)

GFw = 68.4785

Point Group C_s

ΔH_f° = [-60.9 ± 3] kcal/mol

S°_{298.15} = 63.17 ± 0.1 gibbs/mol

ΔH_f°_{298.15} = [-62.6 ± 3] kcal/mol

CH₂ClF

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
2993 (1)	1086 (1)	3046 (1)
1470 (1)	780 (1)	1236 (1)
1351 (1)	385 (1)	1004 (1)

Bond Distance: C-H = 1.078 Å C-Cl = 1.759 Å C-F = 1.378 Å

Bond Angle: H-C-H = 111°54' F-C-Cl = 110° H-C-Cl = 109°06'

σ = 1

Product of the Moments of Inertia: I_AI_BI_C = 4.8154 × 10⁻¹¹⁵ g³ cm⁶

Heat of Formation

The change in heat of atomization by successive replacement of F by Cl, in the CF₄ to CCl₄ series and CHF₃ to CHCl₃ series, follows a regular pattern (see CCl₂F₂ and CHCl₂F Tables). We make the assumption that this same regular variation occurs also in the CH₂F₂ to CH₂Cl₂ series. Thus, the difference between the atomization energies of CH₂F₂ and CH₂Cl₂ is divided into two unequal parts which fall into the pattern established in the CF₄ and CHF₃ sequences. We adopt a heat of atomization of 385.5 kcal which corresponds to a ΔH_f°₂₉₈(CH₂ClF, g) = -62.6 kcal/mol. The changes, in kcal, in the heat of atomization by successive replacement of F by Cl are tabulated, below for all three series.

CF ₄	43.8	CHF ₃	33.0	CH ₂ F ₂	35.0
CF ₃ Cl	41.4	CHCl ₃	29.7	CH ₂ Cl ₂	33.0
CF ₂ Cl ₂	37.3	CHCl ₂ F	33.0	CHCl ₂ F	33.0
CFCl ₃	36.0	CHCl ₂ F	33.0	CHCl ₂ F	33.0
CCl ₄	33.0	CHCl ₂ F	33.0	CHCl ₂ F	33.0

Heat Capacity and Entropy

Plyler and Benedict (1) assigned the vibrational frequencies from the infrared and Raman data for the liquid. The molecular structure was obtained from the microwave measurements of Muller (2). The individual moments of inertia are I_A = 2.008 × 10⁻³⁹ g cm², I_B = 16.241 × 10⁻³⁹ g cm², and I_C = 14.766 × 10⁻³⁹ g cm².

References

1. E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std. **57**, 202 (1951).
2. N. Muller, J. Amer. Chem. Soc. **75**, 800 (1953).

CH₂ClF

Dichloromethane (CH₂Cl₂)

(Ideal Gas) GFW = 84.9331

Point Group C_{2v} $\Delta H_f^\circ = -21.19 \pm 0.3$ kcal/mol $\Delta H_f^\circ = 84.574 \pm 0.01$ gibbs/mol $\Delta H_f^\circ = -22.83 \pm 0.3$ kcal/mol

Ground State Quantum Weight = 1

T, °K	Cp°	S° -(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf° kcal/mol	ΔGf°	Log Kp
0	∞	INFINITE	-2.630	-21.190	-21.190	INFINITE
100	6.547	53.781	21.091	-20.253	-18.461	20.195
200	10.126	60.160	65.619	-22.328	-16.485	12.084
298	12.164	64.574	1.092	-22.630	-16.485	11.991
300	12.204	64.650	0.033	-22.839	-16.485	11.991
400	14.237	68.446	65.078	-23.285	-17.783	5.220
500	15.933	71.811	66.095	-23.645	-11.941	3.487
600	17.296	74.841	4.522	-23.928	-9.573	2.236
700	18.403	77.593	6.309	-24.166	-7.102	1.551
800	19.316	80.133	10.114	-24.327	-5.195	1.043
900	20.095	82.438	12.212	-24.501	-	-
1000	20.755	84.566	72.375	-24.501	-	-
1100	21.322	86.592	14.316	-24.543	-2.667	-0.530
1200	21.809	88.469	16.474	-24.555	-1.133	-0.937
1300	22.216	90.133	20.916	-24.520	-0.092	-1.575
1400	22.550	91.692	23.194	-24.480	-12.563	-1.630
1500	22.913	93.162	25.499	-24.431	-15.078	-2.053
1600	23.190	94.550	27.830	-24.370	-17.486	-2.249
1700	23.431	95.763	29.778	-24.299	-19.814	-2.578
1800	23.631	96.892	32.558	-24.220	-22.144	-2.717
1900	23.831	97.946	34.950	-24.152	-24.666	-2.717
2000	23.996	100.219	82.748	-24.071	-27.315	-2.843
2100	24.143	101.393	83.604	-23.991	-29.758	-2.956
2200	24.274	102.520	84.439	-23.901	-31.931	-3.094
2300	24.395	103.602	85.256	-23.806	-33.846	-3.159
2400	24.495	104.642	86.056	-23.707	-35.611	-3.159
2500	24.569	105.644	86.799	-23.747	-37.072	-3.241
2600	24.674	106.610	87.543	-23.668	-39.506	-3.321
2700	24.751	107.542	88.266	-23.591	-41.931	-3.394
2800	24.811	108.443	88.974	-23.506	-44.346	-3.466
2900	24.863	109.316	89.658	-23.448	-46.742	-3.522
3000	24.941	110.160	90.327	-23.381	-49.200	-3.588
3100	24.994	110.979	90.980	-23.318	-51.619	-3.639
3200	25.042	111.763	91.618	-23.250	-54.035	-3.690
3300	25.082	112.519	92.241	-23.179	-56.446	-3.740
3400	25.127	113.294	92.848	-23.106	-58.844	-3.788
3500	25.165	114.023	93.443	-23.116	-61.272	-3.826
3600	25.199	114.732	94.025	-23.078	-63.684	-3.866
3700	25.241	115.497	94.594	-23.020	-66.095	-3.906
3800	25.269	116.216	95.151	-22.956	-68.505	-3.946
3900	25.289	116.753	95.696	-22.900	-70.915	-3.974
4000	25.315	117.394	96.231	-22.986	-73.323	-4.006
4100	25.338	118.019	96.754	-22.976	-75.727	-4.037
4200	25.362	118.627	97.259	-22.967	-78.137	-4.066
4300	25.381	119.211	97.755	-22.957	-80.544	-4.095
4400	25.401	119.811	98.266	-22.945	-82.951	-4.120
4500	25.420	120.382	98.751	-23.000	-85.352	-4.145
4600	25.437	120.941	99.228	-23.018	-87.766	-4.170
4700	25.456	121.484	99.696	-23.034	-90.177	-4.195
4800	25.468	122.028	100.155	-23.072	-92.584	-4.213
4900	25.482	122.549	100.607	-23.107	-94.997	-4.237
5000	25.496	123.064	101.051	-23.166	-97.404	-4.258
5100	25.509	123.569	101.487	-23.018	-99.816	-4.277
5200	25.529	124.064	101.919	-23.024	-102.228	-4.296
5300	25.532	124.551	102.339	-23.294	-104.644	-4.315
5400	25.543	125.028	102.755	-23.353	-107.056	-4.333
5500	25.553	125.497	103.164	-23.417	-109.474	-4.350
5600	25.569	125.957	103.567	-23.465	-111.887	-4.367
5700	25.581	126.405	103.955	-23.638	-114.293	-4.386
5800	25.591	126.855	104.350	-23.721	-116.723	-4.403
5900	25.599	127.292	104.740	-23.721	-119.146	-4.413
6000	25.597	127.722	105.119	-23.609	-121.563	-4.428

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1968

Vibrational Frequencies and Degeneracies
 $\omega_{cm^{-1}}$ $\omega_{cm^{-1}}$ $\omega_{cm^{-1}}$

2939 (1) 282 (1) 898 (1)

1467 (1) 1153 (1) 1268 (1)

717 (1) 3040 (1) 758 (1)

Bond Distances: C-H = 1.066 Å C-Cl = 1.7724 Å

Bond Angles: H-C-H = 112° Cl-C-Cl = 111.8°

Product of the Moments of Inertia: $I_{AB}I_C = 1.6686 \times 10^{-114}$ g cm⁶

Heat of Formation

Hu and Sinks (1) have measured the heat of combustion of CH₂Cl₂(l) in the rotating bomb calorimeter, using As₂O₃ solution as the reducing agent. They reported $\Delta H_c^\circ = -144.00$ kcal/mole for CH₂Cl₂(l) + O₂(g) → CO₂(g) + 2HCl(600H₂O, aq) which leads to $\Delta H_f^\circ(\text{CH}_2\text{Cl}_2, l) = -79.70$ kcal/mol, using $\Delta H_f^\circ = -94.051$ and -39.823 kcal/mol for CO₂(g) and HCl(600H₂O, aq), respectively (2). The standard deviation of five combustion runs was 0.12 kcal/mol. Employing the heat of vaporization of CH₂Cl₂(l) at 298°K as 6.87 kcal/mol (3), we obtain $\Delta H_f^\circ(\text{CH}_2\text{Cl}_2, g) = -22.83$ kcal/mol which is adopted in the tabulation.

L. Smith et al. (4), based on the combustion data of E. Efring (5), re-evaluated the heat of combustion of dichloromethane at 18.7°C as $\Delta H_c^\circ = -1701.4$ cal/g for CH₂Cl₂(l) + O₂(g) + 2HCl(600H₂O, aq). This value needs to be further corrected for a change in the heat of oxidation of As₂O₃(g) and calculated to 25°C to give $\Delta H_c^\circ = \Delta H_c^\circ - 144.89$ kcal/mol, $\Delta H_f^\circ(\text{CH}_2\text{Cl}_2, l) = -28.80$ kcal/mol and $\Delta H_f^\circ(\text{CH}_2\text{Cl}_2, g) = -21.93$ kcal/mol.

J. Lacher et al. (7) have measured the heat of hydrogenation of dichloromethane to methane and hydrogen chloride at 250°C as -40.07 kcal/mol. Correction to 298°K gives $\Delta H_f^\circ(\text{CH}_2\text{Cl}_2, g) = -23.05$ kcal/mol which is in good agreement with the value adopted.

Heat Capacity and Entropy

The bond distances and angles have been determined from the microwave spectra by R. J. Myers and W. D. Gwinn (6). The three principal moments of inertia are $I_A = 2.630 \times 10^{-39}$, $I_B = 2.5623 \times 10^{-38}$ and $I_C = 2.7727 \times 10^{-38}$ g cm².

The assigned fundamental vibrational frequencies are obtained from Shimanouchi's selection (9), based on infrared and Raman spectra by Shimanouchi and Suzuki (10), Palma et al. (11), and Welsh et al. (12).

References

- (1) A. T. Hu and G. C. Sinks, presented at the 13rd Calorimetry Conference, Midland, Mich., 1966.
- (2) U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
- (3) J. H. Mathews, J. Am. Chem. Soc. **88**, 562 (1926).
- (4) L. Smith, L. Bjellerup, S. Krook and H. Westermarck, Acta Chem. Scand. **17**, 65 (1963).
- (5) E. Efring, Ph. D. Dissertation, University of Lund, Lund, Sweden, 1938.
- (6) S. Sunner and S. Thoren, Acta Chem. Scand. **18**, 1528 (1964).
- (7) J. R. Lacher, A. Amador and J. D. Park, Trans. Faraday Soc. **63**, 1608 (1967).
- (8) R. J. Myers and W. D. Gwinn, J. Chem. Phys. **20**, 1420 (1952).
- (9) T. Shimanouchi, U. S. Natl. Bur. Std. NBS-RS-NBS6, 1967.
- (10) T. Shimanouchi and I. Suzuki, J. Mol. Spectry. **8**, 222 (1962).
- (11) F. E. Palma, E. A. Piotrowski, S. Sundram and F. F. Cleveland, J. Mol. Spectry. **13**, 119 (1964).
- (12) H. L. Welsh, M. F. Crawford, T. R. Thomas and C. R. Love, Can. J. Phys. **30**, 577 (1952).

Difluoromethane (CH₂F₂)

(Ideal Gas)

GFW = 52.0239

DIFLUOROMETHANE (CH₂F₂)

(IDEAL GAS)

GFW = 52.0239

Point Group C_{2v}

$\Delta H_f^\circ = -105.9 \pm 0.4$ kcal/mol

$S_{298.15}^\circ = 58.93 \pm 0.01$ gibbs/mol

$\Delta H_f^\circ = -107.7 \pm 0.4$ kcal/mol

Ground State Quantum Weight = 1



T, °K	C _p ^a	S ^b	-(C _p ^a - H ^c)/T	H ^c - H ^c ₂₉₈	ΔH ^d	ΔG ^e
0	8.000	∞	2.555	-105.879	∞	105.879
100	8.005	49.445	67.038	-104.967	104.967	103.180
200	8.066	55.182	59.816	-104.108	104.108	101.127
298	10.243	58.935	58.935	-107.710	107.710	101.127
300	10.277	58.998	58.935	-107.722	107.722	101.087
400	12.216	62.217	58.361	-106.309	106.309	96.303
500	14.095	65.149	60.278	-104.816	104.816	90.403
600	15.719	67.864	61.628	-103.233	103.233	83.600
700	17.079	70.394	62.402	-101.569	101.569	77.789
800	18.215	72.751	63.550	-99.634	99.634	72.072
900	19.169	74.953	64.896	-97.432	97.432	66.566
1000	19.975	77.016	66.526	-95.000	95.000	61.206
1100	20.659	78.953	68.432	-92.323	92.323	56.000
1200	21.241	80.776	70.611	-89.415	89.415	51.000
1300	21.740	82.496	73.057	-86.276	86.276	46.190
1400	22.169	84.124	75.749	-82.916	82.916	41.575
1500	22.538	85.666	78.733	-79.249	79.249	37.157
1600	22.858	87.131	82.005	-75.281	75.281	32.930
1700	23.137	88.525	85.557	-71.013	71.013	28.898
1800	23.381	89.855	89.295	-66.455	66.455	25.062
1900	23.594	91.125	93.219	-61.607	61.607	21.422
2000	23.782	92.340	97.240	-56.473	56.473	17.980
2100	23.949	93.504	101.369	-51.053	51.053	14.730
2200	24.097	94.622	105.607	-45.355	45.355	11.670
2300	24.228	95.696	109.953	-39.387	39.387	8.790
2400	24.346	96.730	114.407	-33.149	33.149	6.090
2500	24.452	97.726	118.976	-26.631	26.631	3.660
2600	24.547	98.687	123.659	-20.835	20.835	1.490
2700	24.633	99.615	128.455	-14.851	14.851	-0.420
2800	24.711	100.512	133.363	-8.677	8.677	-2.410
2900	24.781	101.380	138.382	-2.313	2.313	-4.560
3000	24.846	102.222	143.521	4.149	4.149	-6.870
3100	24.904	103.037	148.780	10.307	10.307	-9.340
3200	24.958	103.829	154.159	16.283	16.283	-11.970
3300	25.007	104.598	159.657	22.077	22.077	-14.760
3400	25.053	105.345	165.276	27.689	27.689	-17.700
3500	25.094	106.072	171.015	33.119	33.119	-20.790
3600	25.133	106.770	176.874	38.367	38.367	-23.930
3700	25.169	107.448	182.843	43.433	43.433	-27.130
3800	25.202	108.100	188.922	48.317	48.317	-30.390
3900	25.232	108.795	195.111	53.019	53.019	-33.710
4000	25.261	109.434	201.410	57.539	57.539	-37.090
4100	25.287	110.058	207.819	61.867	61.867	-40.530
4200	25.312	110.668	214.337	66.003	66.003	-44.030
4300	25.335	111.264	90.196	69.947	69.947	-47.590
4400	25.357	111.846	90.681	73.695	73.695	-51.210
4500	25.377	112.417	91.158	77.245	77.245	-54.890
4600	25.394	112.974	91.626	80.600	80.600	-58.630
4700	25.416	113.521	92.086	83.761	83.761	-62.430
4800	25.431	114.056	92.538	86.727	86.727	-66.290
4900	25.447	114.581	92.983	89.498	89.498	-70.210
5000	25.462	115.095	93.420	92.073	92.073	-74.190
5100	25.476	115.599	93.850	94.452	94.452	-78.230
5200	25.489	116.094	94.271	96.635	96.635	-82.330
5300	25.502	116.580	94.686	98.621	98.621	-86.490
5400	25.513	117.056	95.089	100.410	100.410	-90.710
5500	25.525	117.525	95.483	102.001	102.001	-95.000
5600	25.535	117.985	95.869	103.494	103.494	-99.350
5700	25.546	118.437	96.247	104.890	104.890	-103.770
5800	25.555	118.881	96.617	106.189	106.189	-108.260
5900	25.564	119.318	96.982	107.391	107.391	-112.810
6000	25.573	119.748	97.333	108.497	108.497	-117.420

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
2949 (1)	529 (1)	1176 (1)
1508 (1)	1262 (1)	1435 (1)
1116 (1)	3013 (1)	1090 (1)

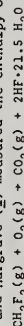
Bond Distances: C-F = 1.358 ± 0.001 Å C-H = 1.092 ± 0.003 Å

Bond Angles: F-C-F = 108° 17' ± 6' H-C-H = 111° 52' ± 25' σ = 2

Product of the Moments of Inertia: I_AI_BI_C = 1.2272 × 10⁻¹¹⁵ g³ cm⁶

Heat of Formation

Nugebauer and Margrave (1) measured the enthalpy of combustion of CH₂F₂. Their result for the combustion reaction



was $\Delta H_{298}^\circ = -139.84 \pm 0.22$ kcal/mole. Using ΔH_{298}° (HF-21.5 H₂O) = -76.75 ± 0.1 kcal/mol (2), obtained with dilution data compiled by Parker (3), we derive,

ΔH_{298}° (CH₂F₂, g) = -107.7 ± 0.4 kcal/mol,

from Margrave's data.

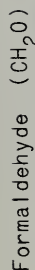
Heat Capacity and Entropy

The vibrational frequencies are average values from the infrared studies of Stewart and Nielsen (4) and Plyler and Benedict (5). Individual moments of inertia are calculated from the rotational constants reported by Lide (6) with the result I_A = 1.7082 × 10⁻³⁹ g cm², I_B = 7.9160 × 10⁻³⁹ g cm², and I_C = 9.0794 × 10⁻³⁹ g cm². The molecular structure data are from the microwave studies of Lide (6) and are in excellent agreement with electron-diffraction studies of Brockway, Thornton, and Bartell whose results are reported in the Annual Review of Physical Chemistry (7).

References

1. C. A. Nugebauer and J. L. Margrave, *J. Phys. Chem.*, **52**, 1043 (1958).
2. JANAF Table for HF(g), 12-31-58.
3. V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965.
4. H. B. Stewart and H. H. Nielsen, *Phys. Rev.*, **75**, 840 (1949).
5. E. K. Plyler and W. S. Benedict, *J. Research Nat. Bur. Standards*, **47**, 202 (1951).
6. D. R. Lide, Jr., *J. Amer. Chem. Soc.*, **74**, 3548 (1952).
7. R. L. Livingston, *Annual Review of Phys. Chem.*, **5**, 397 (1954).





(Ideal Gas) Mol. Wt. = 30.027

MOL. WT. = 30.027

(IDEAL GAS)

FORMALDEHYDE (CH₂O)

T, K. C_p S° - (F° - H₂₉₈°)/T H° - H₂₉₈° ΔH_f° ΔF_f° Log K_p

T, K.	C _p	S°	-(F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	7.000	48.000	INFINITE	2.395	26.782	26.782	INFINITE
100	7.000	48.000	INFINITE	1.800	27.381	27.381	INFINITE
200	6.907	48.596	53.016	1.604	27.700	27.700	28.141
300	6.761	49.261	52.261	1.500	27.700	27.700	28.141
400	6.475	52.313	52.261	1.016	27.706	26.258	19.128
500	6.385	54.669	52.603	1.006	28.113	25.713	18.546
600	6.307	57.077	52.871	1.006	28.505	25.308	18.157
700	6.244	59.079	54.083	2.998	28.860	24.347	0.868
800	6.193	60.931	54.931	4.200	29.174	23.588	7.358
900	6.150	62.459	55.790	5.495	29.459	22.789	6.214
1000	6.114	63.686	56.646	6.782	29.692	21.928	5.219
1100	6.083	64.606	57.485	8.062	29.880	21.024	4.395
1200	6.056	65.307	58.307	9.333	30.017	20.134	3.690
1300	6.032	65.806	59.110	10.598	30.116	19.228	3.092
1400	6.010	66.141	59.890	11.857	30.186	18.314	2.579
1500	6.000	66.341	60.649	13.100	30.236	17.381	2.135
1600	6.000	66.416	61.386	14.346	30.267	16.461	1.758
1700	6.000	66.466	62.102	15.592	30.286	15.531	1.431
1800	6.000	66.498	62.798	16.839	30.296	14.592	1.156
1900	6.000	66.514	63.473	18.083	30.300	13.652	0.921
2000	6.000	66.519	64.129	19.321	30.300	12.707	0.721
2100	6.000	66.521	64.767	20.553	30.300	11.761	0.551
2200	6.000	66.521	65.387	21.779	30.300	10.811	0.401
2300	6.000	66.521	65.990	22.999	30.300	9.862	0.261
2400	6.000	66.521	66.577	24.214	30.300	8.917	0.131
2500	6.000	66.521	67.146	25.424	30.300	7.977	0.011
2600	6.000	66.521	67.698	26.629	30.300	7.042	0.001
2700	6.000	66.521	68.234	27.829	30.300	6.112	0.000
2800	6.000	66.521	68.746	29.024	30.300	5.187	0.000
2900	6.000	66.521	69.234	30.214	30.300	4.262	0.000
3000	6.000	66.521	69.698	31.399	30.300	3.337	0.000
3100	6.000	66.521	70.146	32.579	30.300	2.412	0.000
3200	6.000	66.521	70.579	33.754	30.300	1.487	0.000
3300	6.000	66.521	71.000	34.924	30.300	0.562	0.000
3400	6.000	66.521	71.400	36.089	30.300	-0.363	0.000
3500	6.000	66.521	71.781	37.249	30.300	-1.288	0.000
3600	6.000	66.521	72.146	38.404	30.300	-2.213	0.000
3700	6.000	66.521	72.498	39.554	30.300	-3.138	0.000
3800	6.000	66.521	72.837	40.700	30.300	-4.063	0.000
3900	6.000	66.521	73.164	41.841	30.300	-4.988	0.000
4000	6.000	66.521	73.481	42.977	30.300	-5.913	0.000
4100	6.000	66.521	73.789	44.109	30.300	-6.838	0.000
4200	6.000	66.521	74.088	45.237	30.300	-7.763	0.000
4300	6.000	66.521	74.379	46.361	30.300	-8.688	0.000
4400	6.000	66.521	74.654	47.481	30.300	-9.613	0.000
4500	6.000	66.521	74.914	48.599	30.300	-10.538	0.000
4600	6.000	66.521	75.160	49.714	30.300	-11.463	0.000
4700	6.000	66.521	75.393	50.824	30.300	-12.388	0.000
4800	6.000	66.521	75.614	51.929	30.300	-13.313	0.000
4900	6.000	66.521	75.824	53.029	30.300	-14.238	0.000
5000	6.000	66.521	76.024	54.124	30.300	-15.163	0.000
5100	6.000	66.521	76.214	55.214	30.300	-16.088	0.000
5200	6.000	66.521	76.394	56.300	30.300	-17.013	0.000
5300	6.000	66.521	76.564	57.381	30.300	-17.938	0.000
5400	6.000	66.521	76.724	58.457	30.300	-18.863	0.000
5500	6.000	66.521	76.874	59.529	30.300	-19.788	0.000
5600	6.000	66.521	77.014	60.596	30.300	-20.713	0.000
5700	6.000	66.521	77.144	61.659	30.300	-21.638	0.000
5800	6.000	66.521	77.264	62.719	30.300	-22.563	0.000
5900	6.000	66.521	77.374	63.774	30.300	-23.488	0.000
6000	6.000	66.521	77.474	64.824	30.300	-24.413	0.000

March 31, 1961

Vibrational Levels and Multiplicities

ω, cm ⁻¹	ω, cm ⁻¹
2766.4 (1)	2843.4 (1)
1746.07 (1)	1247.4 (1)
1500.6 (1)	1163.5 (1)

Bond Lengths and Angles C-H = 1.12 ± 0.01 Å C-O = 1.21 ± 0.01 Å H-C-H = 118 ± 2°

Moments of Inertia I_A = 2.975 X 10⁻⁴⁰ g. cm.² I_B = 2.161 X 10⁻³⁹ g. cm.² I_C = 2.468 X 10⁻³⁹ g. cm.²

σ = 2

Heats of Formation

M. Delepine and M. Badoche, Compt. rend. 214, 777 (1942), measured the heat of combustion of a formaldehyde polymer. Their value is revised to ΔH_f 298.15 = -25.0 kcal. mole⁻¹ based on the following thermochemical cycle:

I C_(c) + 1/2 O₂(g) + H₂O(l) = 1/2 (CH₂O)_n(c) -42.3 kcal.

2.4

14.9

III CH₂O(g) = CH₂O(aq)

Equation I and II are based upon data listed by Delepine and Badoche. For reaction III Delepine and Badoche obtained 15 kcal. mole⁻¹. Whereas, P. Walker, J. Am. Chem. Soc. 55, 2821 (1933) obtained 14.8 kcal. mole⁻¹. A value of -27.7 kcal. mole⁻¹ is obtained from the combustion experiments of H. von Wartenberg and B. Lerner-Steinberg, Z. anorg. Chem. 39, 591 (1925). Corrections of -0.6 and 0.1 kcal. mole⁻¹ were applied to obtain a heat of reaction at constant pressure and at 298.15°K.

Equilibrium constant determinations of reaction (IV) by R. H. Newton and B. F. Dodge, J. Am. Chem. Soc. 55, 4747 (1933), lead to a ΔH_f 298.15 = -29.0 kcal. mole⁻¹.

IV H₂(g) + CO(g) = H₂CO(g)

The value obtained from the measurements of Wartenberg and Lerner-Steinberg is believed to be the most reliable.

Heat Capacities and Entropies

Frequencies were measured by H. H. Blau and H. H. Nielsen, J. Molec. Spect. 1, 124 (1957) in the I. R. Microwave determinations of R. B. Lawrence and M. F. W. Strandberg, Phys. Rev. 82, 365 (1951), and those of G. Eriandson, J. Chem. Phys. 25, 579 (1956) are in essential agreement.



Methyl Chloride (CH₃Cl)

(Ideal Gas) Mol. Wt. = 50.492

METHYL CHLORIDE (CH₃Cl) (IDEAL GAS)

MOL. WT. = 50.492

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.955	46.811	2.489	18.764	18.764	INFINITE
200	8.399	52.409	1.694	18.774	18.774	39.806
298	8.726	55.987	0.000	20.005	18.711	18.326
300	8.756	56.047	0.018	20.673	15.046	11.029
400	11.496	59.050	1.080	21.313	15.012	10.935
500	13.167	61.838	2.315	21.872	13.026	7.117
600	14.639	64.372	3.707	22.343	10.888	4.759
700	15.917	66.727	5.230	22.731	8.646	3.149
800	17.031	68.927	6.921	23.043	6.330	1.976
900	18.005	70.990	8.637	23.290	3.666	1.093
1000	18.857	72.932	10.481	23.476	1.566	0.380
1100	19.603	74.765	12.405	23.613	0.857	-0.187
1200	20.253	76.500	14.399	23.708	3.298	-0.655
1300	20.822	78.144	16.453	23.768	8.749	-1.047
1400	21.318	79.705	18.669	23.799	16.605	-1.379
1500	21.752	81.191	20.715	23.811	25.669	-1.665
1600	22.133	82.607	22.909	23.808	35.430	-1.913
1700	22.467	83.959	25.140	23.786	45.927	-2.121
1800	22.761	85.252	27.401	23.755	57.134	-2.301
1900	23.021	86.490	29.691	23.712	68.957	-2.461
2000	23.251	87.677	32.005	23.663	81.393	-2.603
2100	23.456	88.816	34.340	23.608	94.436	-2.729
2200	23.638	89.912	36.695	23.551	108.081	-2.842
2300	23.802	90.966	39.067	23.489	122.322	-2.943
2400	23.948	91.982	41.455	23.428	137.154	-3.033
2500	24.080	92.962	43.856	23.367	152.577	-3.115
2600	24.199	93.909	46.270	23.304	168.590	-3.189
2700	24.307	94.825	48.696	23.243	185.193	-3.257
2800	24.404	95.710	51.131	23.184	202.393	-3.319
2900	24.493	96.568	53.576	23.126	220.193	-3.376
3000	24.574	97.400	56.030	23.072	238.590	-3.428
3100	24.648	98.207	58.491	23.018	257.587	-3.476
3200	24.716	98.991	60.959	22.970	277.181	-3.519
3300	24.779	99.752	63.434	22.926	297.370	-3.557
3400	24.836	100.493	65.915	22.884	318.151	-3.590
3500	24.889	101.214	68.400	22.850	339.521	-3.618
3600	24.938	101.915	70.892	22.819	361.480	-3.642
3700	24.983	102.599	73.389	22.795	384.026	-3.662
3800	25.025	103.266	75.889	22.773	407.159	-3.678
3900	25.064	103.917	78.394	22.760	430.870	-3.691
4000	25.101	104.552	80.902	22.752	455.157	-3.700
4100	25.134	105.172	83.414	22.749	480.020	-3.706
4200	25.166	105.778	85.939	22.753	505.456	-3.709
4300	25.196	106.371	88.447	22.763	531.464	-3.709
4400	25.223	106.950	90.968	22.778	558.041	-3.706
4500	25.249	107.517	93.491	22.801	585.184	-3.699
4600	25.273	108.072	96.017	22.828	612.890	-3.688
4700	25.296	108.616	98.546	22.862	641.154	-3.672
4800	25.318	109.149	101.077	22.902	670.000	-3.652
4900	25.338	109.671	103.609	22.947	700.426	-3.628
5000	25.357	110.183	106.144	22.998	732.431	-3.599
5100	25.375	110.686	108.681	23.057	766.014	-3.565
5200	25.392	111.179	111.219	23.119	801.173	-3.526
5300	25.408	111.662	113.759	23.189	837.900	-3.482
5400	25.423	112.137	116.301	23.265	876.200	-3.434
5500	25.436	112.604	118.844	23.347	916.173	-3.381
5600	25.445	113.063	121.388	23.434	957.814	-3.323
5700	25.453	113.513	123.934	23.528	1001.120	-3.260
5800	25.457	113.956	126.481	23.629	1046.190	-3.192
5900	25.469	114.392	129.030	23.735	1093.020	-3.119
6000	25.480	114.820	131.579	23.847	1141.614	-3.052

Dec. 31, 1960; Sept. 30, 1964

Point Group C_{3v}

$$\Delta H_f^o = -18.76 \pm 0.17 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = -20.66 \pm 0.17 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 55.99 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
2928 (1)	3047 (2)
1355 (1)	1460 (2)
732 (1)	1020 (2)

Bond Distance: C-H = 1.0959 Å C-Cl = 1.7812 Å

Bond Angle: H-C-H = 108° H-C-Cl = 110°54'

Product of the Moments of Inertia: $I_A I_B I_C = 21.460 \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

$$\sigma = 3$$

Heat of Formation

The heat of formation was measured using hydrogenation to give methane and hydrogen chloride, by J. R. Lacher, E. Emery, E. Bohmalk and J. D. Park, J. Phys. Chem. **60**, 492 (1956). The value adopted was recalculated using JANAF auxiliary data for methane and HCl.

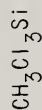
Heat Capacity and Entropy

The vibrational frequencies were tabulated by E. K. Plyler and W. S. Benedict, J. Research Natl. Bur. Standards **47**, 202 (1951). C. C. Costain, J. Chem. Phys. **29**, 864 (1958) has calculated the bond distances and angles based on an isotopic substitution method. From these the individual moments of inertia were calculated to be $I_A = 0.5262 \times 10^{-39} \text{ g. cm.}^2$ and $I_B = I_C = 6.3863 \times 10^{-39} \text{ g. cm.}^2$.



Trichloromethylsilane (Si(CH₃)Cl₃)
(Ideal Gas) Mol. Wt. = 149.496 **INTERIM TABLE**

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
200	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
300	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
400	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
500	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
600	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
700	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
800	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
900	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
1000	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
1100	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
1200	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
1300	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
1400	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
1500	24.470	83.900	83.900	.000	-126.400	-111.098	82.020

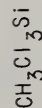


Trichloromethylsilane (Si(CH₃)Cl₃) (Ideal gas)

Mol. Wt. = 149.496
ΔH_f^o 298.15 = [-126.4] kcal. mole⁻¹
S_{298.15}^o = 83.9 cal. deg.⁻¹ mole⁻¹
Point Group C_{3v}

Heat of Formation. ΔH_f^o 298.15 was estimated.

Heat Capacity and Entropy. Cp and S_{298.15} were taken from G. J. Janz, Y. Mikawa, and P. Behnke, private communication, March 16, 1960.



Fluoromethane (CH₃F)

(Ideal Gas) Mol. Wt. 34.035

FLUOROMETHANE (CH₃F)

(IDEAL GAS)

MOL. WT. = 34.035

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞	∞
100	44.362	60.636	-2.422	-54.079	-54.079	116.094
200	8.085	54.036	-1.629	-53.457	-53.457	56.867
298	8.993	53.252	-0.000	-50.000	-50.000	36.864
300	8.988	53.308	0.017	-50.014	-50.258	36.611
400	10.556	56.099	2.132	-56.712	-46.038	26.351
500	12.256	58.638	4.375	-57.342	-43.726	15.926
600	14.832	61.015	5.285	-57.880	-43.726	10.620
700	16.447	63.569	6.772	-58.265	-43.726	8.834
800	17.512	65.369	8.284	-58.989	-43.726	7.399
900	18.440	66.263	9.975	-59.216	-43.726	6.221
1000	19.246	67.059	11.860	-59.398	-43.726	5.298
1100	19.952	67.774	13.847	-59.503	-43.726	4.464
1200	20.597	68.416	15.926	-59.531	-43.726	3.685
1300	21.087	68.992	18.129	-59.662	-43.726	3.064
1400	21.550	69.523	20.462	-59.698	-43.726	2.521
1500	21.993	69.999	22.937	-59.717	-43.726	2.041
1600	22.418	70.430	25.455	-59.707	-43.726	1.612
1700	22.818	70.826	28.017	-59.683	-43.726	1.228
1800	23.195	71.187	30.623	-59.652	-43.726	0.884
1900	23.552	71.514	33.269	-59.616	-43.726	0.579
2000	23.891	71.807	35.944	-59.575	-43.726	0.308
2100	24.214	72.066	38.647	-59.531	-43.726	0.069
2200	24.523	72.292	41.376	-59.487	-43.726	-0.145
2300	24.816	72.486	44.131	-59.442	-43.726	-0.352
2400	25.094	72.648	46.904	-59.396	-43.726	-0.552
2500	25.357	72.780	49.694	-59.350	-43.726	-0.745
2600	25.606	72.884	52.500	-59.304	-43.726	-0.931
2700	25.842	72.962	55.322	-59.258	-43.726	-1.111
2800	26.066	73.017	58.159	-59.212	-43.726	-1.284
2900	26.278	73.052	61.011	-59.166	-43.726	-1.451
3000	26.479	73.069	63.876	-59.120	-43.726	-1.612
3100	26.669	73.068	66.754	-59.074	-43.726	-1.768
3200	26.848	73.050	69.644	-59.028	-43.726	-1.919
3300	27.016	73.017	72.546	-58.982	-43.726	-2.065
3400	27.174	72.970	75.460	-58.936	-43.726	-2.206
3500	27.321	72.910	78.386	-58.890	-43.726	-2.342
3600	27.458	72.838	81.324	-58.844	-43.726	-2.473
3700	27.585	72.755	84.274	-58.798	-43.726	-2.600
3800	27.702	72.661	87.236	-58.752	-43.726	-2.723
3900	27.809	72.557	90.210	-58.706	-43.726	-2.842
4000	27.907	72.443	93.196	-58.660	-43.726	-2.957
4100	28.000	72.319	96.194	-58.614	-43.726	-3.069
4200	28.087	72.186	99.204	-58.568	-43.726	-3.177
4300	28.169	72.044	102.226	-58.522	-43.726	-3.281
4400	28.246	71.893	105.259	-58.476	-43.726	-3.381
4500	28.319	71.734	108.304	-58.430	-43.726	-3.477
4600	28.387	71.567	111.360	-58.384	-43.726	-3.570
4700	28.451	71.393	114.426	-58.338	-43.726	-3.659
4800	28.511	71.212	117.501	-58.292	-43.726	-3.744
4900	28.567	71.024	120.584	-58.246	-43.726	-3.825
5000	28.620	70.830	123.674	-58.200	-43.726	-3.902
5100	28.670	70.630	126.771	-58.154	-43.726	-3.975
5200	28.717	70.424	129.874	-58.108	-43.726	-4.044
5300	28.761	70.212	132.982	-58.062	-43.726	-4.109
5400	28.802	70.000	136.094	-58.016	-43.726	-4.170
5500	28.840	69.787	139.210	-57.970	-43.726	-4.228
5600	28.875	69.570	142.329	-57.924	-43.726	-4.283
5700	28.908	69.352	145.450	-57.878	-43.726	-4.335
5800	28.939	69.133	148.573	-57.832	-43.726	-4.384
5900	28.967	68.912	151.698	-57.786	-43.726	-4.430
6000	28.993	68.690	154.824	-57.740	-43.726	-4.473

Dec. 31, 1960; Dec. 31, 1963

Point Group = C_{3v}
 $\Delta H_f^0 = -54 \pm 8$ kcal. mole⁻¹
 $S_{298.15}^0 = 53.25$ cal. deg.⁻¹ mole⁻¹
 ΔH_f^0 298.15 = -56 ± 7 kcal. mole⁻¹
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies
 ω , cm.⁻¹ ω , cm.⁻¹

2985 (1) 3008 (2)
 1464 (1) 1467 (2)
 1049 (1) 1182 (2)

Bond Distances: C-F = 1.391 ± 0.005 Å C-H = 1.095 ± 0.010 Å

Bond Angles: H-C-H = 109.5° ± 2° $G^- = 3$

Product of the Moments of Inertia: $I_A I_B I_C = 5.96 \times 10^{-117}$ g.³ cm.⁶

Heat of Formation.

Appearance potentials for CH₃⁺ from CH₄⁺ and CH₃P reported by P. P. Lossing, K. V. Ingold, and I. H. S. Henderson, J. Chem. Phys. 22, 1489 (1954), the heats of dissociation of hydrogen (104.20 kcal.) and fluorine (37.72 kcal.), and the heat of formation of Methane (-17.90 kcal.) were used to calculate the heat of formation of gaseous CH₃P. These authors measured an appearance potential for CH₃⁺ from CH₃P of 14.6 ± 0.6 e.v., which would give an uncertainty of about ±15 kcal. mole⁻¹ in the heat of formation of methyl fluoride. However, a correlation of the heats of formation from the atoms of the methyl fluorides and methyl chlorides indicates that the uncertainty can be reduced to ± 7 kcal. mole⁻¹.

Heat Capacity and Entropy.

Fundamental vibrational frequencies were taken from the summary reported by W. L. Smith and I. M. Mills, J. Mol. Spect. 11, 11 (1963). Moments of inertia from the microwave results of O. R. Gilliam, H. D. Edwards, and W. Gordy, Phys. Rev. 75, 1014 (1949) are: $I_A = 5.52 \times 10^{-40}$ g. cm.², $I_B = I_C = 32.854 \times 10^{-40}$ g. cm.². Bond parameters are the values of L. O. Brockway, C. O. Thornton, and L. S. Bartell, whose electron diffraction results are given in the Annual Review of Physical Chemistry 5, 397 (1954). These values are in close agreement with the microwave parameters reported by Gilliam, Edwards, and Gordy (loc. cit.).





Trifluoromethylsilane (Si(CH₃)F₃)
(Ideal Gas) Mol. Wt. = 100.125

INTERIM TABLE

T. °K.	C _p ^o	S ^o - (F ^o -H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg ⁻¹	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100							
200							
298	21.720	75.070	75.070	.000	-294.625	-279.656	204.984
300	21.790	75.205	75.070	.040	-294.638	-279.564	203.652
400	25.140	81.653	75.948	5.745	-295.235	-274.485	149.942
500	27.640	87.667	77.768	5.049	-295.767	-269.191	117.658
600	29.950	93.136	79.699	7.944	-296.062	-263.853	96.104
700	31.640	97.885	81.135	11.025	-296.325	-258.462	80.692
800	32.850	102.205	84.378	14.262	-296.507	-253.041	69.124
900	34.210	106.165	87.171	17.626	-296.625	-247.598	60.122
1000	35.200	109.623	89.725	21.098	-296.690	-242.149	52.919
1100	36.060	113.219	90.799	24.662	-296.706	-236.694	47.024
1200	36.760	116.369	92.601	28.305	-296.684	-231.237	42.112
1300	37.310	119.356	94.731	32.015	-296.633	-225.765	37.656
1400	37.610	122.171	96.581	35.785	-296.557	-220.338	34.395
1500	38.460	124.767	98.133	39.606	-296.465	-214.895	31.309

Trifluoromethylsilane (Si(CH₃)F₃) (Ideal gas)

Mol. Wt. = 100.125

ΔH_f^o 298.15 = [-294.625] kcal. mole⁻¹

S_{298.15}^o = 75.07 cal. deg⁻¹ mole⁻¹

Heat of Formation. ΔH_f^o 298.15 was estimated.

Heat Capacity and Entropy. C_p and S_{298.15} were taken from O. Janz, Y. Mikawa, and P. Behnke, private communication, March 16, 1960.



(Ideal Gas) Mol. Wt. = 16.043

(IDEAL GAS)

METHANE (CH₄)

MOL. WT. = 16.043

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
100	7.000	35.706	INFINITE	2.396	15.991	15.991	INFINITE
200	7.001	31.716	16.228	1.401	13.400	13.400	33.656
298	6.001	21.222	45.287	0.805	17.816	15.188	15.188
300	6.518	44.490	0.000	17.095	12.145	6.902	6.902
300	8.535	44.503	0.016	17.009	12.110	6.922	6.922
400	9.680	47.144	44.637	0.233	16.636	10.066	5.500
500	11.076	49.453	45.533	1.860	19.316	7.845	3.429
600	12.483	51.597	46.367	3.138	19.916	5.493	2.001
700	13.813	53.622	47.250	4.454	20.429	3.046	0.951
800	15.084	55.568	48.078	5.718	20.869	0.514	0.493
900	16.317	57.385	49.006	7.000	21.207	2.020	-1.493
1000	17.510	59.141	50.016	8.125	21.482	4.625	-1.011
1100	18.682	60.819	50.922	9.082	21.696	7.247	-1.440
1200	19.842	62.440	51.745	10.000	21.874	9.897	-1.867
1300	20.992	64.013	52.494	10.882	22.026	12.574	-2.291
1400	20.130	65.541	53.167	11.733	22.155	15.195	-2.712
1500	20.688	66.840	54.387	12.579	22.250	17.659	-2.602
1600	21.161	68.191	55.208	13.414	22.337	20.320	-2.803
1700	21.597	69.594	55.794	14.240	22.418	23.054	-3.139
1800	21.997	70.790	56.730	15.060	22.494	25.822	-3.291
1900	22.273	71.926	57.559	15.879	22.569	28.622	-3.408
2000	22.562	73.076	58.306	16.690	22.649	31.467	-3.466
2100	22.820	74.183	59.036	17.499	22.665	34.351	-3.523
2200	23.050	75.259	59.745	18.303	22.626	37.271	-3.587
2300	23.264	76.304	60.437	19.103	22.582	40.231	-3.652
2400	23.461	77.273	61.171	19.899	22.535	43.233	-3.666
2500	23.608	78.233	61.791	20.691	22.488	46.277	-3.689
2600	23.788	79.182	62.441	21.479	22.439	49.361	-3.692
2700	23.904	80.078	63.130	22.264	22.390	52.481	-3.694
2800	24.053	80.927	63.790	23.046	22.341	55.641	-3.696
2900	24.131	81.778	64.399	23.823	22.292	58.842	-3.697
3000	24.233	82.597	64.905	24.600	22.243	62.083	-3.698
3100	24.327	83.394	65.488	25.379	22.194	65.363	-3.699
3200	24.453	84.160	66.050	26.156	22.145	68.683	-3.700
3300	24.565	84.900	66.590	26.930	22.096	72.043	-3.701
3400	24.633	85.652	67.169	27.702	22.047	75.443	-3.702
3500	24.695	86.365	67.707	28.474	21.998	78.883	-3.703
3600	24.695	87.060	68.235	29.246	21.949	82.363	-3.704
3700	24.626	87.726	68.690	30.010	21.899	85.783	-3.705
3800	24.586	88.376	69.122	30.774	21.849	89.243	-3.706
3900	24.655	89.043	69.741	31.538	21.799	92.743	-3.707
4000	24.901	89.673	70.251	32.302	21.749	96.283	-3.708
4100	24.944	90.288	70.732	33.066	21.699	99.863	-3.709
4200	24.984	90.878	71.256	33.830	21.649	103.483	-3.710
4300	25.022	91.444	71.766	34.594	21.599	107.143	-3.711
4400	25.057	92.054	72.126	35.358	21.549	110.843	-3.712
4500	25.090	92.617	72.575	36.122	21.499	114.583	-3.713
4600	25.121	93.169	73.017	36.886	21.449	118.363	-3.714
4700	25.157	93.700	73.456	37.650	21.399	122.183	-3.715
4800	25.197	94.240	73.896	38.414	21.349	126.043	-3.716
4900	25.203	94.759	74.300	39.178	21.299	129.943	-3.717
5000	25.227	95.268	74.718	39.942	21.249	133.883	-3.718
5100	25.250	95.768	75.122	40.706	21.199	137.863	-3.719
5200	25.262	96.240	75.520	41.470	21.149	141.883	-3.720
5300	25.272	96.694	75.900	42.234	21.099	145.943	-3.721
5400	25.311	97.213	76.310	43.000	21.049	149.943	-3.722
5500	25.330	97.678	76.684	43.764	20.999	153.983	-3.723
5600	25.347	98.134	77.073	44.528	20.949	158.063	-3.724
5700	25.364	98.578	77.444	45.292	20.899	162.183	-3.725
5800	25.379	99.048	77.818	46.056	20.849	166.343	-3.726
5900	25.394	99.458	78.178	46.820	20.799	170.543	-3.727
6000	25.409	99.885	78.536	47.584	20.749	174.783	-3.728

March 31, 1961

$\Delta H_{f0}^{\circ} = -15.99 \pm 0.08$ kcal. mole⁻¹
 $\Delta H_f^{\circ} 298.15 = -17.895 \pm 0.08$ kcal. mole⁻¹
Point Group T_d
 $S_{298.15} = 44.48 \pm 0.01$ cal. deg⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω , cm ⁻¹
2916.5 (1)
1534.0 (2)
3018.7 (3)
1306 (3)

Bond Lengths and Angles $\angle$ H-C-H = 109° 28' C-H = 1.091 ± 0.002 ÅMoments of Inertia $I_A = I_B = I_C = 5.313 \times 10^{-40}$ g. cm²

Heat of Formation

P. D. Rossini, J. Research Nat. Bur. Standards 5, 37 (1951) measured the heat of combustion of methane gas. His value at 298.15°K was corrected to the presently accepted molecular weight of water. The heat of formation was calculated using -68.3174 and -94.0540 kcal. mole⁻¹ for the heat of formation of H₂O(l) and CO₂(g) respectively.

Heat Capacities and Entropies

D. P. Stevenson and J. A. Ibers, J. Chem. Phys. 33, 762 (1960), calculated the bond distance from an analysis of available spectroscopic data. Vibrational frequencies listed by L. H. Jones and R. S. McDowell, J. Mol. Spect. 3, 632 (1959), are consistent with their results of a force constant calculation.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	- 4.145	- 28.284	INFINITE
100	13.261	11.762	45.884	- 3.412	- 26.720	58.397
200	15.972	28.186	31.094	- 1.562	- 25.358	27.710
298	15.868	30.340	0.000	0.000	- 24.359	17.077
300	15.866	30.638	30.540	0.029	- 24.372	17.755
400	15.850	35.198	31.162	1.614	- 23.390	12.780
500	15.859	38.736	32.336	3.200	- 22.400	9.791
600	15.868	41.628	33.451	4.786	- 21.439	7.800
700	15.878	44.075	34.070	6.373	- 20.496	6.399
800	15.887	46.196	36.244	7.962	- 19.562	5.344
900	15.897	48.068	37.655	9.551	- 18.633	4.525
1000	15.906	49.743	38.602	11.141	- 17.703	3.869
1100	15.915	51.250	39.485	12.732	- 16.764	3.128
1200	15.925	52.645	40.708	14.324	- 15.829	2.368
1300	15.934	53.920	41.676	15.917	- 14.873	1.727
1400	15.944	55.101	42.593	17.511	- 13.901	1.179
1500	15.953	56.201	43.464	19.106	- 12.916	0.705
1600	15.962	57.231	44.293	20.702	- 11.918	0.292
1700	15.972	58.199	45.082	22.298	- 10.916	0.072
1800	15.981	59.112	45.837	23.896	- 9.912	0.394
1900	15.991	59.977	46.558	25.494	- 8.932	0.682
2000	16.000	60.797	47.250	27.094	- 7.964	0.941

June 30, 1962; Mar. 31, 1966

$\Delta H_f^0 = 30.54 \pm 0.25$ cal. deg.⁻¹ mole⁻¹
 $T_f = 168.3 \pm 0.1^\circ\text{K.}$
 $T_m = 895 \pm 2^\circ\text{K.}$
 $\Delta H_f^0 = -28.28 \pm 0.2$ kcal. mole⁻¹
 $\Delta H_f^0 = -27.12 \pm 0.2$ kcal. mole⁻¹
 $\Delta H_f^0 = 0.279$ kcal. mole⁻¹
 $\Delta H_m^0 = 3.5$ kcal. mole⁻¹
 $\Delta H_g^0 = 298.15$ (to dimer) = 52 ± 10 kcal. mole⁻¹
 $\Delta H_g^0 = 298.15$ (to monomer) = 46 ± 5 kcal. mole⁻¹

Heat of Formation.

The enthalpy change, $\Delta H_f^0 = 2.80 \pm 0.10$ kcal. mole⁻¹, for the reaction $\text{KCN(c)} \rightarrow \text{KCN(g)}$ was reported by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, National Bureau of Standards, April 1, 1965. Incorporating this data with the heat of formation for $\text{K}^+(\infty \text{H}_2\text{O})$ and $\text{CN}^-(\infty \text{H}_2\text{O})$, reported by D. D. Wagman, M. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Part 1, Technical Note 270-1, October 1, 1965, National Bureau of Standards, the value of $\Delta H_f^0 = 298.15$ for KCN(c) was evaluated to be -27.12 ± 0.2 kcal. mole⁻¹.

Heat Capacity and Entropy.

The heat capacity for KCN(c) has been measured with a heat conduction method by C. E. Measer and W. T. Ziegler, J. Am. Chem. Soc. 63, 2703 (1941), 101.6-345.8°K., and adiabatically by H. Suga, T. Matsumoto and S. Seki, Bull. Chem. Soc. Japan, 38, 1115 (1965), 14.23-308.5°K. The data of Suga, Matsumoto and Seki were adopted after correction for curvature. The anomalous region between 50-105°K. has been treated as second order by inclusion of the enthalpy in the heat capacity. The C_p values above 310°K. were estimated by graphical extrapolation. The value of $\Delta H_f^0 = 298.15$ was evaluated based on $S_{15}^0 = 0.193$ cal. deg.⁻¹ mole⁻¹. This extrapolated value appears more reasonable than the value, $S_{15}^0 = 0.307$ cal. deg.⁻¹ mole⁻¹ reported by Suga, Matsumoto and Seki.

Transition Data.

T_f was taken from Suga, Matsumoto and Seki, loc. cit. ΔH_f^0 was calculated as the difference between the total enthalpy change, $H_{173.80}^0 - H_{159.02}^0 = 0.533$ kcal. mole⁻¹ obtained from C_p values measured by Measer and Ziegler, loc. cit., and the enthalpy change, 0.254 kcal. mole⁻¹, calculated from the arbitrarily smoothed C_p curve. Suga, et al. reported $\Delta H_f^0 = 0.339$ kcal. mole⁻¹; however, their C_p data do not adequately define the total enthalpy change through the transition region. The values of T_f and ΔH_f^0 reported by Measer and Ziegler, loc. cit., were $168.3 \pm 0.4^\circ\text{K.}$ and 0.30 kcal. mole⁻¹, respectively. The lower transition, $T = 82.9 \pm 0.2^\circ\text{K.}$ and $\Delta H_f^0 = 0.095 \pm 0.001$ kcal. mole⁻¹ reported by Suga, et al., was treated as second order by inclusion of the enthalpy in the heat capacity.

Melting Data.

See KCN(1) table.

Heat of Sublimation.

The difference between $\Delta H_f^0 = 298.15$ for $(\text{KCN})_2(\text{g})$ and 2KCN(c) is $\Delta H_g^0 = 298.15$ (to dimer) and for KCN(g) and KCN(c) is $\Delta H_g^0 = 298.15$ (to monomer).

Potassium Cyanide (KCN)

(Liquid)

Mol. Wt. = 65.11985

CKN

MOL. WT. = 65.11985

(LIQUID)

POTASSIUM CYANIDE (KCN)

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	S° - (F°-H° ₂₉₈)/T	ΔH _f [°]	ΔF _f [°]	Log K _p
0							
200	18.000	32.104	32.104	0.000	-24.891	-22.626	16.592
298	18.000	32.104	32.104	0.000	-24.891	-22.626	16.592
300	18.000	32.215	32.215	-0.933	-24.891	-22.626	16.592
400	18.000	32.592	32.592	-1.833	-24.891	-22.626	16.592
500	18.000	33.144	33.144	-2.633	-24.891	-22.626	16.592
600	18.000	33.636	33.636	-3.433	-24.891	-22.626	16.592
700	18.000	34.067	34.067	-4.233	-24.891	-22.626	16.592
800	18.000	34.449	34.449	-5.033	-24.891	-22.626	16.592
900	18.000	34.776	34.776	-5.833	-24.891	-22.626	16.592
1000	18.000	35.054	35.054	-6.633	-24.891	-22.626	16.592
1100	18.000	35.287	35.287	-7.433	-24.891	-22.626	16.592
1200	18.000	35.479	35.479	-8.233	-24.891	-22.626	16.592
1300	18.000	35.633	35.633	-9.033	-24.891	-22.626	16.592
1400	18.000	35.753	35.753	-9.833	-24.891	-22.626	16.592
1500	18.000	35.840	35.840	-10.633	-24.891	-22.626	16.592
1600	18.000	35.897	35.897	-11.433	-24.891	-22.626	16.592
1700	18.000	35.927	35.927	-12.233	-24.891	-22.626	16.592
1800	18.000	35.936	35.936	-13.033	-24.891	-22.626	16.592
1900	18.000	35.927	35.927	-13.833	-24.891	-22.626	16.592
2000	18.000	35.897	35.897	-14.633	-24.891	-22.626	16.592
2100	18.000	35.840	35.840	-15.433	-24.891	-22.626	16.592
2200	18.000	35.753	35.753	-16.233	-24.891	-22.626	16.592
2300	18.000	35.633	35.633	-17.033	-24.891	-22.626	16.592
2400	18.000	35.479	35.479	-17.833	-24.891	-22.626	16.592
2500	18.000	35.287	35.287	-18.633	-24.891	-22.626	16.592
2600	18.000	35.054	35.054	-19.433	-24.891	-22.626	16.592
2700	18.000	34.776	34.776	-20.233	-24.891	-22.626	16.592
2800	18.000	34.449	34.449	-21.033	-24.891	-22.626	16.592
2900	18.000	34.067	34.067	-21.833	-24.891	-22.626	16.592
3000	18.000	33.636	33.636	-22.633	-24.891	-22.626	16.592

June 30, 1962; Mar. 31, 1966

CKN

POTASSIUM CYANIDE (KCN) (IDEAL GAS) MOL. WT. = 65.11985

T, °K	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _f
0	.0000	INFINITE	-2.977	19.004	19.004	INFINITE
100	6.223	48.562	70.691	-18.998	16.919	-36.976
200	11.406	55.760	61.569	-18.824	16.224	-16.224
298	12.135	60.477	.000	19.000	12.806	-9.387
300	12.164	60.552	.022	18.999	12.767	-9.301
400	12.520	64.104	60.959	1.258	10.811	-5.907
500	12.778	66.026	61.880	2.523	18.178	-8.948
600	13.015	69.277	62.022	3.813	18.008	-2.593
700	13.238	71.401	63.978	5.126	17.816	-1.640
800	13.443	73.082	65.007	6.460	17.607	-1.969
900	13.625	74.676	65.994	7.814	17.382	-1.802
1000	13.782	76.120	66.935	9.184	17.139	-1.018
1100	13.918	77.440	67.831	10.570	16.880	-1.116
1200	14.034	78.656	68.683	11.967	16.604	-1.082
1300	14.133	79.783	69.594	13.376	16.316	-1.053
1400	14.218	80.834	70.463	14.763	16.015	-1.027
1500	14.290	81.817	71.005	16.219	15.705	-1.005
1600	14.352	82.742	71.410	17.651	15.384	-1.016
1700	14.406	83.613	72.385	19.080	15.053	-1.034
1800	14.453	84.438	73.032	20.532	14.717	-1.051
1900	14.504	85.221	73.553	21.975	14.375	-1.066
2000	14.529	85.965	74.250	23.431	14.028	-1.080
2100	14.561	86.675	74.895	24.898	13.675	-1.093
2200	14.589	87.353	75.370	26.343	13.313	-1.106
2300	14.613	88.002	75.614	27.803	12.933	-1.117
2400	14.635	88.624	76.030	29.265	12.543	-1.128
2500	14.655	89.222	76.930	30.730	12.143	-1.138
2600	14.672	89.797	77.614	32.196	11.734	-1.148
2700	14.688	90.351	77.883	33.664	11.314	-1.157
2800	14.702	90.886	78.338	35.134	10.884	-1.166
2900	14.715	91.402	78.780	36.605	10.443	-1.175
3000	14.727	91.901	79.209	38.077	10.000	-1.183
3100	14.738	92.384	79.426	39.550	9.556	-1.192
3200	14.747	92.852	80.032	41.024	9.112	-1.200
3300	14.756	93.306	80.427	42.499	8.669	-1.207
3400	14.765	93.747	80.813	43.975	8.226	-1.215
3500	14.772	94.175	81.188	45.452	7.783	-1.222
3600	14.779	94.591	81.555	46.930	7.340	-1.229
3700	14.786	94.996	81.913	48.408	6.897	-1.237
3800	14.791	95.390	82.262	49.887	6.454	-1.244
3900	14.797	95.775	82.604	51.366	6.011	-1.251
4000	14.802	96.149	82.938	52.846	5.568	-1.259
4100	14.807	96.515	83.264	54.327	5.125	-1.266
4200	14.811	96.872	83.584	55.808	4.682	-1.274
4300	14.815	97.220	83.897	57.289	4.239	-1.281
4400	14.819	97.561	84.204	58.771	3.796	-1.289
4500	14.823	97.894	84.505	60.253	3.353	-1.296
4600	14.826	98.220	84.799	61.735	2.910	-1.304
4700	14.830	98.539	85.088	63.218	2.467	-1.313
4800	14.833	98.851	85.372	64.701	2.024	-1.321
4900	14.835	99.157	85.650	66.185	1.581	-1.330
5000	14.838	99.457	85.923	67.668	1.138	-1.338
5100	14.841	99.751	86.191	69.152	0.695	-1.347
5200	14.843	100.039	86.455	70.637	0.252	-1.357
5300	14.845	100.321	86.714	72.121	-0.191	-1.367
5400	14.847	100.599	86.968	73.606	-0.634	-1.377
5500	14.849	100.871	87.219	75.090	-1.077	-1.387
5600	14.851	101.139	87.465	76.575	-1.520	-1.398
5700	14.853	101.402	87.707	78.061	-1.963	-1.409
5800	14.855	101.660	87.945	79.546	-2.406	-1.421
5900	14.856	101.914	88.180	81.032	-2.849	-1.433
6000	14.858	102.164	88.411	82.517	-3.292	-1.446

June 30, 1962; Mar. 31, 1966

$$\Delta H_f^o = [19 \pm 5] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o 298.15 = [19 \pm 5] \text{ kcal. mole}^{-1}$$

Point Group C_{∞v}

$$S_{298.15}^o = [60.48] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

(J), cm.⁻¹

[370] (1)

207 (2)

2158 (1)

K-C = [2.294] Å

σ = 1

Bond Distance: C-N = 1.16 ± 0.01 Å

Bond Angle: K-C-N = 180°

Rotational Constant: B = 0.11891 cm.⁻¹

Heat of Formation.

The vapor pressure of KCN(g) at 870°C. was estimated to be 1-10 mm. Hg by D. S. Willars, J. Am. Chem. Soc. **53**, 405 (1931). Assuming the vapor pressure at this temperature to be 1 mm. Hg, the heat of vaporization ($\Delta H_v^o 298.15$) for KCN(l) was evaluated as 44 kcal. mole⁻¹. Based on $\Delta H_f^o 298.15 = -24.89$ kcal. mole⁻¹ for KCN(l), the value of $\Delta H_f^o 298.15$ for KCN(g) was calculated to be 19 ± 5 kcal. mole⁻¹.

Heat Capacity and Entropy.

The molecular structure of KCN(g) has not been determined. It was assumed to be linear by comparison with that for HCN(g). The C-N bond distance was determined by N. Elliott and J. Hastings, Acta Cryst. **1**, 1018 (1961) by use of neutron diffraction measurements. The K-C bond distance was taken from G. E. Leroy, Ph. D. Thesis, Harvard University, 1961, which was estimated. The vibrational frequencies, $2/2$ and $2/3$, were obtained from O. E. Leroy and W. Klemperer, J. Chem. Phys. **35**, 774 (1961). The value of $2/1$ was calculated by valence force method described by O. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is 2.3540×10^{-38} g. cm.²

Potassium Carbonate (K_2CO_3)

(Crystal) Mol. Wt. = 138. 21335

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _f
0	∞	∞	∞	-273.569	-273.569	INFINITE
100	17.300	12.690	58.810	-274.673	-267.991	585.693
200	23.695	27.012	39.557	-274.908	-261.183	585.407
298	27.351	37.170	0.000	-274.900	-254.444	186.513
300	27.414	37.339	0.051	-274.899	-254.317	186.270
400	30.625	45.675	38.285	-275.934	-247.254	135.093
500	33.473	52.821	40.494	-275.628	-240.115	104.954
600	36.010	59.152	43.086	-275.114	-233.056	84.891
700	38.356	64.881	45.796	-274.419	-226.009	70.591
800	40.641	70.152	48.515	-273.549	-219.255	59.698
900	42.905	75.070	51.196	-272.503	-212.530	51.609
1000	45.160	79.707	53.817	-271.288	-205.929	45.006
1100	47.400	84.117	56.273	-269.716	-197.613	39.222
1200	49.640	88.437	58.667	-267.906	-187.741	33.743
1300	51.880	92.699	61.006	-265.864	-177.714	29.876
1400	54.120	96.925	63.449	-263.418	-166.132	26.247
1500	56.360	100.136	65.955	-260.964	-153.736	23.128
1600	58.600	103.345	68.508	-258.436	-140.524	20.424
1700	60.840	106.554	71.107	-255.836	-126.598	18.046
1800	63.080	111.005	73.663	-253.170	-113.059	15.986
1900	65.320	115.476	76.183	-250.470	-100.009	14.149
2000	67.560	117.883	78.758	-247.746	-87.457	12.517

POTASSIUM CARBONATE (K_2CO_3)

(CRYSTAL)

MOL. WT. = 138.21335

$$\Delta H_f^o = -273.57 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -274.9 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^o = 6.6 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 37.17 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1174 \pm 1^\circ K.$$

Heat of Formation.

The heat of formation was obtained from the heat of solution $\Delta H_{sol}^o = -7.6 \pm 0.5 \text{ kcal. mole}^{-1}$ and the heats of formation for $K^+(aq)$ and $CO_3^{2-}(aq)$, -60.32 and $-161.84 \text{ kcal. mole}^{-1}$, respectively. The standard heat of solution, ΔH_{sol}^o , was calculated by extrapolation to infinite dilution of the calorimetric data of L. Benjamen, *J. Chem. Eng. Data* **7**, 239-40 (1962), using the methods suggested by J. P. Rupert, H. P. Hopkins, Jr., and C. A. Wulff, *J. Phys. Chem.* **69**, 3059-62 (1965). The equilibrium constant for the hydrolysis $CO_3^{2-}(\infty H_2O) + OH^-(\infty H_2O) \rightleftharpoons HCO_3^-(\infty H_2O) + H_2O(l)$ was taken as $K = 2.1 \times 10^{-4}$ based on the selected values of D. D. Wagman, V. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-1, October 1, 1965. The resulting extrapolations were not as consistent as those of Rupert et al. (loc. cit.) for Na_2CO_3 . The ionic heats of formation were taken from Wagman et al. (loc. cit.). This procedure was adopted even though it may involve an inconsistency between the extrapolations for ΔH_{sol}^o and $CO_3^{2-}(\infty H_2O)$. The alternative evaluation of $\Delta H_f^{298.15}$ for $K_2CO_3(\sim 1900 H_2O)$ from the heats of mixing given by J. A. Muller, *Ann. chim. phys.* (6), **15**, 517 (1888) and M. Berthelot, *Ann. chim. phys.* (4) **29**, 433 (1873) may be subject to significant error if dissolved CO_2 was not excluded from the solutions. Presumably, this path was used by D. D. Wagman, NBS Report 8628, January 1965, in the selection of $\Delta H_f^{298.15} = -274.3 \text{ kcal. mole}^{-1}$. This value is $0.6 \text{ kcal. mole}^{-1}$ less negative than the value adopted here.

Heat Capacity and Entropy.

The low temperature heat capacity, $14.0-315^\circ K$, was measured by P. L. Oetting, unpublished data, Thermal Research Laboratory, Dow Chemical Company, Midland, Michigan, 1963. G. I. Janz, E. Neuenschwander and P. J. Kelly, *Trans. Faraday Soc.* **59**, 841 (1963) measured the heat content by drop calorimetry in the temperature range $650-1250^\circ K$, and gave enthalpy and heat capacity equations based on their measurements. The above information was used in a Shomate analysis in order to smooth the enthalpy and calculate heat capacity above $298^\circ K$. The values from the low and high temperature sources join smoothly at $298^\circ K$. The heat capacity was graphically extrapolated above the melting point. The entropy at $14.0^\circ K$ was calculated from the extrapolated low temperature C_p data, using the cubic law. The value of $S_{14.0}^o = 0.109 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

T_m was obtained from A. Reisman, *J. Am. Chem. Soc.* **80**, 3558 (1958) and ΔH_m^o was taken from Janz et al. (loc. cit.).

CK₂O₃

Potassium Carbonate (K₂CO₃)

Mol. St. = 138. 21335

(Liquid)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f [°]	ΔF _f [°]	Log K _f
0						
100	27.331	40.719	0.000	-270.220	-250.822	183.858
200	27.414	40.868	0.051	-270.219	-250.702	182.636
300	30.625	49.224	2.956	-271.254	-243.094	133.312
400	33.473	56.370	6.164	-270.948	-237.209	103.684
500						
600	36.016	62.701	9.440	-270.434	-230.506	83.962
700	38.046	68.440	12.720	-268.720	-223.720	69.560
800	39.600	73.600	17.300	-268.869	-217.413	59.394
900	50.000	79.588	22.300	-267.001	-211.094	51.260
1000	50.000	84.856	27.300	-265.189	-204.879	44.708
1100	50.000	89.421	32.300	-261.245	-196.096	39.139
1200	50.000	93.972	37.300	-256.047	-186.210	34.139
1300	50.000	97.074	42.300	-249.475	-176.410	29.095
1400	50.000	101.676	47.300	-242.721	-166.384	26.442
1500	50.000	105.129	52.300	-235.866	-160.506	23.386
1600	50.000	108.384	57.300	-228.845	-151.771	20.781
1700	50.000	111.387	62.300	-221.595	-142.704	18.476
1800	50.000	114.245	67.300	-214.267	-134.688	16.393
1900	50.000	116.948	72.300	-206.891	-126.323	14.530
2000	50.000	119.513	80.858	-200.126	-118.068	12.902
2100	50.000	121.953	82.300	-193.075	-109.814	11.430
2200	50.000	124.276	84.593	-185.809	-101.861	10.119
2300	50.000	126.501	86.367	-178.044	-93.897	8.922
2400	50.000	128.629	88.084	-170.022	-86.020	7.833
2500	50.000	130.670	89.747	-162.040	-78.232	6.830

Dec. 31, 1961; Mar. 31, 1966

POTASSIUM CARBONATE (K₂CO₃)

(LIQUID)

MOL. WT. = 138.21335

S°_{298.15} = 40.719 ± 0.1 cal. deg.⁻¹ mole⁻¹ΔH_f[°] 298.15 = -270.22 ± 0.5 kcal. mole⁻¹ΔG_f[°] = 0.60 ± 0.1 kcal. mole⁻¹T_m = 1174 ± 1°K.

Heat of Formation.

The ΔH_f[°] 298.15 was obtained from ΔH_f[°] 298.15(c) by adding ΔH_m[°] and the difference between H_m[°] - H_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 800°K. The heat capacity below 800°K. was obtained from the heat capacity of the crystal. Above 800°K. the heat capacity was adopted as 50.0 cal. deg.⁻¹ mole⁻¹, based on the enthalpy measurements in the range 1189-1250°K. reported by O. J. Janz, E. Neuenchwander and P. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See K₂CO₃(c) table.

Lithium Carbonate (Li_2CO_3)

(Crystal) Mol. wt. = 73.88735

 Li_2O_3

T, °K.	C_p°	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	∞.000	∞.000	∞.000	-288.692	-288.692	∞.000
100	8.320	4.792	3.306	-288.693	-288.571	619.744
200	17.310	13.507	13.507	-288.693	-277.152	302.857
298	23.000	21.551	21.551	-288.693	-270.598	196.553
300	23.080	21.694	21.694	-288.693	-270.474	197.040
400	26.810	28.860	28.860	-288.693	-263.738	144.098
500	30.820	35.259	35.259	-288.693	-256.855	112.271
600	35.700	41.295	41.295	-288.693	-249.839	91.004
700	40.613	47.053	47.053	-288.693	-242.724	75.854
800	45.550	52.611	52.611	-288.693	-235.554	64.534
900	50.500	57.975	57.975	-288.693	-228.356	55.751
1000	55.460	63.140	63.140	-288.693	-221.130	48.752
1100	60.420	68.100	68.100	-288.693	-213.876	43.056
1200	65.380	72.850	72.850	-288.693	-206.592	38.571
1300	70.340	77.400	77.400	-288.693	-199.276	34.271
1400	75.300	81.750	81.750	-288.693	-191.928	30.145
1500	80.260	85.900	85.900	-288.693	-184.548	26.171
1600	85.220	89.850	89.850	-288.693	-177.127	22.346
1700	90.180	93.600	93.600	-288.693	-169.665	18.666
1800	95.140	97.150	97.150	-288.693	-162.162	15.131
1900	100.100	100.500	100.500	-288.693	-154.619	11.741
2000	105.060	103.650	103.650	-288.693	-147.046	8.491

LITHIUM CARBONATE (Li_2CO_3)

(CRYSTAL)

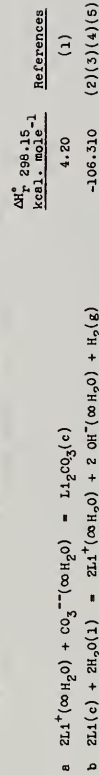
MOL. WT. = 73.88735

$$\begin{aligned} S_{298.15}^\circ &= 21.551 \pm 0.05 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \\ T_m &= 623^\circ\text{K.} \\ T_{1/2} &= 683 \pm 3^\circ\text{K.} \\ T_m &= 985 \pm 1^\circ\text{K.} \end{aligned}$$

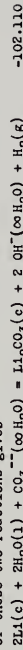
$$\begin{aligned} \Delta H_f^\circ &= -288.69 \pm 0.04 \text{ kcal. mole}^{-1} \\ \Delta H_f^\circ &= -290.64 \pm 0.04 \text{ kcal. mole}^{-1} \\ \Delta H_f^\circ &= [0.134] \text{ kcal. mole}^{-1} \\ \Delta H_f^\circ &= [0.535] \text{ kcal. mole}^{-1} \\ \Delta H_m^\circ &= 10.70 \pm 0.1 \text{ kcal. mole}^{-1} \end{aligned}$$

Heat of Formation.

The heat of formation was derived from the following reactions:



Summation of these two reactions gives

Using ΔH_f° of $\text{H}_2\text{O}(\text{l})$, $\text{CO}_3^{2-}(\infty \text{H}_2\text{O})$ and $\text{OH}^-(\infty \text{H}_2\text{O})$ from Ref. 6 yields $\Delta H_f^\circ \text{Li}_2\text{CO}_3 = -290.64 \text{ kcal. mole}^{-1}$.

References

- (1) O. L. I. Brown and W. M. Latimer, J. Am. Chem. Soc. 58, 2228(1936).
- (2) JANAP table for $\text{LiOH}(\text{c})$, March 31, 1966.
- (3) S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958). S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking-Bomb Solution Calorimeters," UCL-7992, Oct. 1964.
- (4) C. B. Messer, L. G. Fasolino and C. E. Thalhammer, J. Am. Chem. Soc. 77, 4524 (1955).
- (5) V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes" NSRDS-NBS 2 Natl. Bur. Std., April 1, 1965.
- (6) D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, October 1, 1965.

Heat Capacity and Entropy.

The low temperature heat capacity, $16.68\text{--}300^\circ\text{K.}$, was measured by O. L. I. Brown and W. M. Latimer, J. Am. Chem. Soc. 58, 2228 (1936). G. I. Janz, E. Nauenschwander and P. J. Kelly, Trans. Faraday Soc. 59, 841 (1963) measured the heat content by drop calorimetry in the temperature range $560\text{--}1150^\circ\text{K.}$, and gave enthalpy and heat capacity equations based on their measurement. The above information was used in a Shomate analysis in order to smoothly the enthalpy and calculate heat capacity. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was graphically extrapolated above the melting point. The entropy at 16.68°K. was calculated from the extrapolated low temperature C_p data, using the cubic law. The value of $S_{16.68}^\circ = 0.053 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Transition Data.

T_m were taken from A. Reisman, J. Am. Chem. Soc. 80, 3558 (1958). The enthalpies of transition were estimated from the relative areas of the transitions and the heat of fusion of the differential analysis curve reported by Reisman loc. cit.

Melting Data.

T_m was obtained from Reisman loc. cit. and ΔH_m° was taken from Janz et. al. (loc. cit.).

 Li_2O_3

LITHIUM CARBONATE (Li₂CO₃)

(LIQUID)

MOL. WT. = 73.88735

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100						
200						
298	23.000	30.423	30.423	0.00	-281.629	193.687
300	23.080	30.566	30.423	0.043	-281.632	192.415
400	26.810	37.732	31.376	2.543	-281.686	161.115
500	30.820	44.131	35.296	5.418	-283.063	110.271
600	35.700	50.167	35.608	8.736	-282.681	89.661
700	44.320	56.387	38.136	12.776	-281.633	74.976
800	44.320	62.305	40.785	17.208	-280.241	64.011
900	44.320	67.525	43.481	21.640	-278.999	55.524
1000	44.320	72.195	46.123	26.072	-277.585	48.767
1100	44.320	76.419	48.688	30.504	-276.319	43.264
1200	44.320	80.275	51.162	34.936	-275.071	38.699
1300	44.320	83.823	53.540	39.368	-273.845	34.854
1400	44.320	87.107	55.822	43.800	-272.635	31.572
1500	44.320	90.165	58.010	48.232	-271.440	28.741
1600	44.320	93.026	60.110	52.664	-270.255	26.275
1700	44.320	95.712	62.126	57.096	-269.174	23.766
1800	44.320	98.246	64.063	61.528	-268.068	21.349
1900	44.320	100.662	65.926	65.960	-266.882	19.196
2000	44.320	102.915	67.719	70.392	-265.634	17.267

Mer. 31, 1966

$S_{298.15}^o = 30.423 \pm 0.05 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 993.15 \pm 1^\circ\text{K.}$
 $\Delta H_f^{o, 298.15} = -281.63 \pm 0.04 \text{ kcal. mole}^{-1}$
 $\Delta H_m^{o, 298.15} = 10.7 \pm 0.1 \text{ kcal. mole}^{-1}$

Heat of Formation.

The $\Delta H_f^{o, 298.15}$ was obtained from $\Delta H_f^{o, 298.15(c)}$ by adding $\Delta H_m^{o, 298.15}$ and the difference between $H_m^{o, 298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 683.15°K. The heat capacity below 683.15°K. was obtained from the heat capacity of the crystal. Above 683.15°K. the heat capacity was adopted as $44.32 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, based on the enthalpy measurements in the range $996\text{--}1150^\circ\text{K.}$ reported by G. J. Janz, E. Neuenchwander and P. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See Li₂CO₃(c) table.

Magnesium Carbonate (MgCO_3)
(Crystal)

GFW = 84.32135

MgCO_3

MAGNESIUM CARBONATE (MgCO_3)

(CRYSTAL)

OPW = 84.32135

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal/mol ΔH°	ΔG°	Log Kp
0	4.000	4.000	INFINITE	- 2.704	- 263.933	- 263.933	INFINITE
100	5.899	2.576	28.648	- 2.607	- 264.956	- 256.756	565.510
200	13.760	9.356	17.274	- 1.584	- 265.616	- 252.371	275.778
298	18.215	15.740	15.740	0.000	- 265.700	- 245.742	180.134
300	18.284	15.852	15.740	0.034	- 265.701	- 245.618	178.933
400	21.476	21.571	16.498	2.029	- 265.632	- 238.930	130.555
500	23.915	26.631	18.058	4.301	- 265.417	- 232.276	101.528
600	26.040	31.187	19.848	6.803	- 265.098	- 225.678	82.293
700	27.760	35.137	21.766	9.466	- 264.615	- 219.138	68.218
800	29.220	39.142	23.706	12.349	- 264.011	- 212.641	58.419
900	30.500	42.660	25.619	15.337	- 263.696	- 206.251	50.095
1000	31.500	45.928	27.488	18.440	- 263.259	- 199.716	43.648

Heat of Formation:
 $S_{298.15}^\circ = 15.74 \text{ gibbs/mol}$
 $T_d = 675^\circ \text{K}$
 $\Delta H_f^\circ = -263.9 \pm 2 \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = -265.7 \pm 2 \text{ kcal/mol}$

The adopted $\Delta H_{298.15}^\circ = -265.7 \pm 2 \text{ kcal/mol}$ is the average value derived from the dissociation pressures of $\text{MgCO}_3(\text{c})$ in the temperature range $671\text{--}782^\circ \text{K}$ measured by Marc and from the $\Delta H_{923}^\circ = 25.9 \pm 0.6 \text{ kcal/mol}$ determined by Thomasson using a high temperature differential calorimeter. The decomposition of MgCO_3 has been studied in a bomb calorimeter by Roth; this yields $\Delta H_{293}^\circ = 23.8 \text{ kcal/mol}$ when corrected to constant pressure. The value is derived from the small difference between two large heats of combustion, so the uncertainty is probably large. Roth also reported $\Delta H_{365}^\circ = 26.15 \text{ kcal/mol}$ from calorimetric data on the heat of solution in HCl. Berthelot measured the heat of solution of $\text{MgSO}_4(\text{aq})$ with $\text{K}_2\text{CO}_3(\text{aq})$. Analyzing his data we find $\Delta H_{298.15}^\circ = -268.6 \text{ kcal/mol}$.

Discrepancies are apparent in the wide range of the calorimetric results and in the third law drift of the equilibrium data. Possible sources for the drift include lack of true equilibrium (e.g., excess surface energy for MgO) and uncertainty in the high temperature entropy of MgCO_3 (see entropy write-up). Non-standard state behavior of the crystal phases may also be a problem in the calorimetric studies. The data of Thomasson and Cunningham, based on a high temperature differential thermal analysis technique, are probably the most reliable of the calorimetric values; however, there are uncertainties in the absolute energy calibration. The first result of Roth may be dismissed as too discrepant and the remaining two calorimetric values are within $\pm 3 \text{ kcal}$ of the selected heat of formation.

Source: 1. Marc and A. Simek, Z. Anorg. Chem. 82, 17 (1913).
 2. C. V. Thomasson and D. A. Cunningham, J. Sci. Instr. 41, 308-10 (1964).
 3. W. A. Roth, J. Prakt. Chem. 158, 117 (1941).
 4. Berthelot, Ann. Chim. Phys. 5, 160-179 (1875).

Source	Method	Reaction	T, °K	(kcal/mol) $\Delta H_{298.15}^\circ$	eu	(kcal/mol) $\Delta H_{298.15}^\circ$
1. Marc	Kp	$\text{MgCO}_3(\text{c}) = \text{MgO}(\text{c}) + \text{CO}_2(\text{g})$	671-782	-	28.3 ± 0.9	-266.04
2. Thomasson	Calorimetric	$\text{MgCO}_3(\text{c}) = \text{MgO}(\text{c}) + \text{CO}_2(\text{g})$	923	25.9	27.7	-265.45
3. Roth	Calorimetric	$\text{MgCO}_3(\text{c}) = \text{MgO}(\text{c}) + \text{CO}_2(\text{g})$	293	23.8	23.8	-260.35
Roth	Calorimetric	$\text{MgCO}_3(\text{c}) = \text{MgO}(\text{c}) + \text{CO}_2(\text{g})$	363	26.15	26.10	-263.95
4. Berthelot	Calorimetric	$\text{K}_2\text{CO}_3(\sim.5\text{m}) + \text{MgSO}_4(\sim.5\text{m}) = \text{MgCO}_3(\text{c}) + \text{K}_2\text{SO}_4(\sim.5\text{m})$	288	1.05	1.35	-268.6

Source:

1. R. Marc and A. Simek, Z. Anorg. Chem. 82, 17 (1913).
2. C. V. Thomasson and D. A. Cunningham, J. Sci. Instr. 41, 308-10 (1964).
3. W. A. Roth, J. Prakt. Chem. 158, 117 (1941).
4. Berthelot, Ann. Chim. Phys. 5, 160-179 (1875).

Heat Capacity and Entropy.

Low temperature heat capacities ($56.3 - 291.0^\circ \text{K}$) were measured by C. T. Anderson, J. Am. Chem. Soc. 56, 849 (1934). The high temperature heat capacities are derived by a Shomate analysis of smoothed enthalpies reported by K. K. Kelley, Bulletin 584, p. 114, U.S. Bureau of Mines, Washington, D.C. 1960. Kelley obtained the smoothed values from unpublished high temperature ($400\text{--}743^\circ \text{K}$) enthalpy measurements by C. H. Shomate, Berkeley Thermodynamics Laboratory, Region II, Bureau of Mines, Berkeley, California. The data were joined smoothly at 298°K and extrapolated graphically above 743°K . The entropy was obtained from the heat capacities using $S_{56.2}^\circ = 0.57 \text{ eu}$.

Because of the drift in the decomposition pressure data, it is pertinent to assess the uncertainty in the functions. The greatest potential source for error is in the values above room temperature where the increment of entropy is about 20 eu between 298 and 700°K . Unfortunately, no evaluation of the unpublished enthalpies is possible, but an increase of 10% in the entropy increment would reduce the drift to a tolerable level.

Decomposition Data.

T_d is calculated as the temperature at which ΔG° equals zero for $\text{MgCO}_3(\text{c}) = \text{MgO}(\text{c}) + \text{CO}_2(\text{g})$.

Cyanide (CN)

(Ideal Gas)

GFW = 26.01785

Ground State Configuration $2\sigma^2$ $\Delta H_f^\circ = 103.2 \pm 2.5 \text{ kcal/mol}$ $S_{298.15}^\circ = 48.41 \pm 0.01 \text{ gibbs/mol}$ $\Delta H_f^\circ = 103.2 \pm 2.5 \text{ kcal/mol}$

CN

T, °K	Cp*	$S^\circ - (G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	kcal/mol	ΔG_f°	Log Kp
0	6.050	40.204	1.978	103.215	103.215	INFINITE	
100	6.957	45.626	1.683	103.618	103.618	104.331	
200	7.689	48.406	1.000	104.000	104.000	106.796	
300	8.259	48.440	0.13	104.002	104.002	106.751	
400	8.659	48.440	0.12	104.002	104.002	106.751	
500	7.155	52.041	49.199	104.195	104.195	106.863	
600	7.326	53.360	48.766	104.135	104.135	106.867	
700	7.510	54.503	50.380	104.088	104.088	106.867	
800	7.689	55.518	50.960	104.018	104.018	106.867	
900	7.862	56.428	51.502	103.928	103.928	106.867	
1000	8.022	57.248	52.016	103.828	103.828	106.867	
1100	8.123	58.036	52.561	103.717	103.717	106.867	
1200	8.235	58.748	53.048	103.598	103.598	106.867	
1300	8.337	59.411	53.512	103.473	103.473	106.867	
1400	8.432	60.038	53.968	103.343	103.343	106.867	
1500	8.522	60.617	54.380	103.214	103.214	106.867	
1600	8.612	61.170	54.768	103.082	103.082	106.867	
1700	8.702	61.695	55.179	102.953	102.953	106.867	
1800	8.794	62.195	55.575	102.824	102.824	106.867	
1900	8.889	62.675	55.955	102.694	102.694	106.867	
2000	8.989	63.131	56.266	102.579	102.579	106.867	
2100	9.090	63.572	56.404	102.465	102.465	106.867	
2200	9.195	63.998	56.530	102.356	102.356	106.867	
2300	9.302	64.407	56.646	102.254	102.254	106.867	
2400	9.410	64.800	56.756	102.158	102.158	106.867	
2500	9.519	65.193	56.851	102.072	102.072	106.867	
2600	9.628	65.589	56.941	101.992	101.992	106.867	
2700	9.735	65.934	57.023	101.921	101.921	106.867	
2800	9.842	66.235	57.095	101.851	101.851	106.867	
2900	9.949	66.497	57.158	101.784	101.784	106.867	
3000	10.040	66.676	57.227	101.734	101.734	106.867	
3100	10.135	67.307	58.482	101.713	101.713	106.867	
3200	10.225	67.630	59.732	101.699	101.699	106.867	
3300	10.310	67.955	60.975	101.691	101.691	106.867	
3400	10.390	68.255	62.215	101.684	101.684	106.867	
3500	10.464	68.557	63.449	101.614	101.614	106.867	
3600	10.534	68.853	64.678	101.603	101.603	106.867	
3700	10.598	69.142	65.903	101.596	101.596	106.867	
3800	10.659	69.423	67.125	101.595	101.595	106.867	
3900	10.710	69.703	68.346	101.595	101.595	106.867	
4000	10.758	69.975	69.562	101.600	101.600	106.867	
4100	10.802	70.241	70.778	101.606	101.606	106.867	
4200	10.841	70.502	71.988	101.615	101.615	106.867	
4300	10.876	70.758	73.198	101.624	101.624	106.867	
4400	10.906	71.008	74.408	101.634	101.634	106.867	
4500	10.933	71.253	75.618	101.647	101.647	106.867	
4600	10.956	71.494	76.828	101.659	101.659	106.867	
4700	10.975	71.730	78.038	101.672	101.672	106.867	
4800	11.005	72.188	79.248	101.685	101.685	106.867	
4900	11.016	72.410	80.458	101.702	101.702	106.867	
5000	11.024	72.628	81.668	101.709	101.709	106.867	
5100	11.031	72.843	82.878	101.716	101.716	106.867	
5200	11.038	73.058	84.088	101.723	101.723	106.867	
5300	11.039	73.268	85.298	101.722	101.722	106.867	
5400	11.039	73.468	86.508	101.720	101.720	106.867	
5500	11.039	73.660	87.718	101.720	101.720	106.867	
5600	11.039	73.852	88.928	101.714	101.714	106.867	
5700	11.038	74.044	90.138	101.714	101.714	106.867	
5800	11.038	74.236	91.348	101.714	101.714	106.867	
5900	11.038	74.428	92.558	101.714	101.714	106.867	
6000	11.038	74.620	93.768	101.714	101.714	106.867	

Dec. 31, 1980; June 30, 1961; Dec. 31, 1962; June 30, 1963

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	g_1	$\epsilon_2, \text{cm}^{-1}$	g_2
0	2	58960	2
9118	4	59683	4
25798	2	60939	4
53955	4	64782	4
$\omega_e X_e = 2068.61 \text{ cm}^{-1}$		$\omega_e X_e = 13,114 \text{ cm}^{-1}$	
$B_e = 1.9389 \text{ cm}^{-1}$		$r_e = 0.0172 \text{ cm}^{-1}$	
$r_e = 1.175 \text{ Å}$		$r_e = 1.175 \text{ Å}$	

Heat of Formation

The heat of formation of CN has been the subject of considerable uncertainty for many years. J. Berkowitz (1) has reviewed the earlier work and he concludes that $\Delta H_f^\circ(\text{CN}, g) = 109 \text{ kcal/mol}$. Since this review a considerable body of work has emerged which supports a value near 100 kcal/mol .

Tsang et al. (2) obtained $\Delta H_f^\circ(\text{CN}, g) = 100 \pm 4 \text{ kcal/mol}$ from shock tube studies of the decomposition of cyanogen. Dibeler and Liston (3, 4) have studied a series of cyanogen compounds and obtained their heats of dissociation from photoionization threshold measurements. The values below are obtained from the halogen ion threshold measurements using JANAF auxiliary data, except for HCN which is from the CN^+ threshold measurements. The value below is calculated using the ionization potential from CNCL measurements (3).

Davis and Okabe (5) employed a direct photodissociation technique to obtain dissociation energies for many of the same molecules. The method determines the disappearance threshold for fluorescence due to decay of excited molecules $\text{CN } B^2\Sigma^- - X^2\Sigma^+$. This corresponds to the energy needed to just break the bond and form excited cyanogen in the $B^2\Sigma^-$ state, whose energy above ground is well known.

Setser and Steadman (6) used metastable excited argon atoms with a maximum electronic energy of 270 kcal/mol to break the bonds in HCN and $(\text{CN})_2$. From the emission spectra of the excited $B^2\Sigma^-$ CN they were able to calculate the highest populated vibrational level and thus a maximum limit to the dissociation energy.

Berkowitz et al. (7) have recently examined the photoionization spectrum of HCN using the H^+ ion threshold. They also determined the threshold for the CN^+ ion which agrees exactly with that of Dibeler and Liston (4) when the latter is corrected for rotational energy contributions (0.7 kcal). Berkowitz et al. (7) suggest that the HCN limit of Setser and Steadman (6) should be ≤ 105 due to neglect of the significant vibrational population of the first harmonic of the bending mode. However, if the same allowance is made for the C_2N_2 data the limit is only ≤ 104 and this presumes significant occupation of the third harmonic of the bending mode of C_2N_2 .

It is apparent from the data that considerable scatter still exists and several sources of error are probable. HCN and the cyanogen halides all have significant uncertainties in their heats of formation, and the effects of rotational and vibrational contributions at 300°K are uncertain, but could be eliminated by using refrigerated gases. We choose to adopt a median value within the range of almost all determinations of $\Delta H_f^\circ(\text{CN}, g) = 103.2 \pm 2.5 \text{ kcal/mol}$.

X	Reference	2	3, 4	5	6	7
C1		99.23±0.5	99.86±1.2	103.5±2.0	104.1±2.5	103.5±2.0
Br		84.72±0.5	86.94±1.2	102.6±2.0	104.8±2.5	102.6±2.0
I		72.95±0.5	71.72±1.0	101.4±2.0	100.2±2.5	101.4±2.0
H		119.99±0.5	119.92±1.2	124.57±0.3	100.7±2.5	100.7±2.5
CN		125±8	129.61±1.2	100±4	101.5±0.8	105.3±2.5

Heat Capacity and Entropy

The thermodynamic functions are taken from Johnston et al. (8) calculated based on the direct summation of the energy levels. All the electronic levels and molecular constants listed above are from Carroll (9). Johnston et al. used only the first two excited electronic states but the contribution of the higher levels is negligible.

References

1. J. Berkowitz, J. Chem. Phys. **36**, 2533 (1962).
2. W. Tsang, S. H. Bauer and M. Cowperthwaite, J. Chem. Phys. **36**, 1768 (1962).
3. V. H. Dibeler and S. K. Liston, J. Chem. Phys. **47**, 4548 (1967).
4. V. H. Dibeler and S. K. Liston, J. Chem. Phys. **48**, 4765 (1968).
5. D. D. Davis and H. Okabe, J. Chem. Phys. **49**, 5526 (1968).
6. D. W. Setser and D. H. Steadman, J. Chem. Phys. **49**, 467 (1968).
7. J. Berkowitz, W. A. Chupka, and T. A. Walter, J. Chem. Phys. **50**, 1497 (1969).
8. H. L. Johnston, J. Belser, and L. S. Svedoff, "Thermodynamic Properties of CN between 1° and 6000° computed from spectroscopic data, NBS Monograph 225, 1953. [AD 13743].
9. P. K. Carroll, Can. J. Phys. **34**, 83 (1956).

CN

Cyano Unipositive Ion (CN⁺)

GFW = 26.01730

Ground State Configuration [1⁺]S_{298.15} = 50.98 ± 1.5 gibbs/mol $\Delta H_f^\circ = 428.6 \pm 3.0$ kcal/mol $\Delta H_f^\circ = 429.4 \pm 3.0$ kcal/molCN⁺

Electronic Levels and Degeneracies

ϵ_i , cm ⁻¹	g_i
0	(6)
(1500)	(1)
(6000)	(2)
(8000)	(3)
(15000)	(2)

 $\omega_e = (1580)$ cm⁻¹ $\omega_e x_e = (12.5)$ cm⁻¹ $\sigma = 1$ $B_e = (1.566)$ cm⁻¹ $\alpha_e = (0.017)$ cm⁻¹ $r_e = 1.29$ Å

Heat of Formation

Dibeler and Liston (1) have measured the photoionization thresholds for the processes:

ClCN + hv → Cl⁺ + CN + e⁻ $\Delta H_f^\circ = 399.44 \pm 0.5$ kcalClCN + hv → Cl + CN⁺ + e⁻ $\Delta H_f^\circ = 426.65 \pm 0.5$ kcal

By subtraction we obtain

Cl + CN⁺ + Cl⁺ + CN $\Delta H_f^\circ = -27.21 \pm 0.7$ kcalUsing JANAF values for Cl, Cl⁺ and CN we obtain $\Delta H_f^\circ(\text{CN}^+) = 430.6 \pm 3.0$ kcal/mol and the ionization potential of CN, g = 327.42 ± 0.7 kcal/mol.

Berkowitz et al. (2) have measured the photoionization thresholds for the processes:

HCN + hv → H⁺ + CN + e⁻ $\Delta H_f^\circ = 438.18 \pm 0.3$ kcalHCN + hv → H + CN⁺ $\Delta H_f^\circ = 448.09 \pm 0.3$ kcal

By subtraction we obtain

H + CN⁺ + H⁺ + CN $\Delta H_f^\circ = -9.91 \pm 0.4$ kcalUsing JANAF values for H, H⁺ and CN we obtain $\Delta H_f^\circ(\text{CN}^+) = 426.7 \pm 3.0$ kcal/mol, and the ionization potential of CN, g = 323.51 ± 0.4 kcal/mol.We adopt a median value for $\Delta H_f^\circ(\text{CN}^+) = 428.6 \pm 3.0$ kcal/mol and 325.4 ± 2 kcal/mol for the ionization potential of CN.

Heat Capacity and Entropy

The molecule has eight valence electrons and thus we expect that its molecular constants should fall between those for C₂ and BN. The ground electronic state is either $^1\Sigma$ or $^1\Pi$ and the two levels are likely to be very close. As a consequence the thermodynamic functions are dominated by the Π contribution and so we choose this to be the ground state. The other levels are estimated based on the values of Fougere and Nesbet (3) for C₂ and of Verhaegen et al. (4) for BN. The vibrational constants and bond length are estimated between those for the Π states of BN and C₂. The rotational constants B_e is obtained from the estimated bond length and α_e is calculated from the other constants assuming a Morse potential function. The enthalpy at 0°K is -2.076 kcal/mol.

References:

1. V. H. Dibeler and S. K. Liston, J. Chem. Phys. **47**, 4548 (1967).
2. J. Berkowitz, W. A. Chupka and T. A. Walter, J. Chem. Phys. **50**, 1497 (1969).
3. P. F. Fougere and R. K. Nesbet, J. Chem. Phys. **44**, 285 (1966).
4. G. Verhaegen, W. G. Richards and C. M. Moser, J. Chem. Phys. **46**, 160 (1967).

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ - (G^\circ - H_{298}^\circ)/T}$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG_f°	Log Kp
0					
100					
200					
298	7.034	50.986	1.000	429.400	-307.824
300	7.037	51.029	-0.13	429.412	-305.863
400	7.240	53.079	51.264	430.027	-227.625
500	7.514	54.723	1.463	430.591	-160.605
600	7.788	56.118	2.229	431.119	-109.218
700	8.027	57.337	3.023	431.617	-66.772
800	8.225	58.422	3.833	432.097	-26.356
900	8.385	59.400	4.664	432.558	109.918
1000	8.516	60.291	5.509	433.007	266.796
1100	8.624	61.108	6.366	433.444	394.813
1200	8.716	61.862	7.233	433.872	500.973
1300	8.797	62.563	8.109	434.289	587.094
1400	8.870	63.218	8.992	434.703	654.418
1500	8.937	63.832	9.883	435.112	704.235
1600	9.001	64.411	10.779	435.516	739.250
1700	9.061	64.958	11.683	435.923	761.209
1800	9.119	65.478	12.592	436.324	771.209
1900	9.175	65.972	13.506	436.727	770.095
2000	9.229	66.444	14.427	437.131	758.192
2100	9.281	66.896	15.352	437.535	735.681
2200	9.331	67.329	16.283	437.939	703.444
2300	9.379	67.745	17.218	438.344	661.500
2400	9.425	68.145	18.156	438.750	610.817
2500	9.469	68.530	19.103	439.159	552.218
2600	9.510	68.903	20.052	439.567	487.781
2700	9.550	69.262	21.005	439.976	418.434
2800	9.587	69.610	21.962	440.380	345.372
2900	9.622	69.947	22.923	440.783	268.509
3000	9.656	70.274	23.886	441.191	188.914
3100	9.687	70.591	24.854	441.600	107.466
3200	9.716	70.899	25.824	442.005	25.176
3300	9.743	71.199	26.797	442.410	-176.880
3400	9.769	71.490	27.772	442.816	-295.858
3500	9.793	71.773	28.750	443.222	-411.292
3600	9.815	72.050	29.731	443.628	-524.184
3700	9.835	72.319	30.713	444.035	-634.528
3800	9.854	72.581	31.698	444.441	-742.427
3900	9.872	72.838	32.684	444.848	-847.881
4000	9.888	73.088	33.672	445.253	-950.894
4100	9.903	73.332	34.662	445.658	-1051.462
4200	9.917	73.571	35.653	446.062	-1149.592
4300	9.930	73.804	36.645	446.465	-1245.286
4400	9.942	74.033	37.639	446.868	-1338.544
4500	9.953	74.256	38.633	447.270	-1429.366
4600	9.963	74.475	39.629	447.674	-1517.754
4700	9.972	74.690	40.626	448.078	-1603.799
4800	9.980	74.900	41.624	448.482	-1687.492
4900	9.988	75.106	42.622	448.886	-1768.834
5000	9.995	75.307	43.621	449.289	-1847.826
5100	10.001	75.505	44.621	449.692	-1924.462
5200	10.007	75.700	45.622	450.095	-1998.734
5300	10.012	75.890	46.622	450.497	-2070.642
5400	10.017	76.078	47.624	450.898	-2140.186
5500	10.022	76.264	48.626	451.298	-2207.362
5600	10.025	76.442	49.626	451.698	-2272.166
5700	10.029	76.619	50.626	452.098	-2334.594
5800	10.032	76.794	51.626	452.498	-2394.642
5900	10.035	76.965	52.626	452.898	-2452.306
6000	10.037	77.134	53.626	453.298	-2507.582

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o)/T	kcal/mol H ^o - H ^o 298	ΔG ^o	Log Kp
0					
100	6.963	46.613	46.613	10.756	7.686
200	6.963	46.613	46.613	10.726	7.614
298	6.963	46.613	46.613	10.726	7.614
300	6.963	46.613	46.613	10.726	7.614
400	6.963	46.613	46.613	10.726	7.614
500	6.963	46.613	46.613	10.726	7.614
600	7.240	51.791	48.168	5.944	2.165
700	7.406	52.069	48.778	4.542	1.418
800	7.575	53.669	49.353	3.420	0.860
900	7.735	54.770	49.905	2.470	0.478
1000	7.880	55.593	50.434	1.670	0.173
1100	8.008	56.350	50.937	1.066	
1200	8.120	57.052	51.418	0.631	
1300	8.218	57.706	51.877	0.404	
1400	8.303	58.318	52.315	0.364	
1500	8.377	58.893	52.735	0.364	
1600	8.442	59.436	53.137	0.364	
1700	8.498	59.950	53.523	0.364	
1800	8.548	60.437	53.893	0.364	
1900	8.592	60.900	54.250	0.364	
2000	8.631	61.342	54.594	0.364	
2100	8.666	61.764	54.925	0.364	
2200	8.698	62.168	55.245	0.364	
2300	8.726	62.555	55.555	0.364	
2400	8.752	62.927	55.854	0.364	
2500	8.775	63.285	56.144	0.364	
2600	8.794	63.629	56.426	0.364	
2700	8.816	63.962	56.699	0.364	
2800	8.834	64.283	56.964	0.364	
2900	8.850	64.593	57.222	0.364	
3000	8.866	64.893	57.472	0.364	
3100	8.880	65.184	57.716	0.364	
3200	8.894	65.466	57.954	0.364	
3300	8.906	65.740	58.186	0.364	
3400	8.918	66.006	58.412	0.364	
3500	8.929	66.265	58.633	0.364	
3600	8.940	66.517	58.848	0.364	
3700	8.950	66.762	59.059	0.364	
3800	8.960	67.001	59.265	0.364	
3900	8.969	67.233	59.466	0.364	
4000	8.978	67.461	59.663	0.364	
4100	8.986	67.682	59.856	0.364	
4200	8.994	67.899	60.045	0.364	
4300	9.002	68.111	60.230	0.364	
4400	9.009	68.318	60.412	0.364	
4500	9.017	68.520	60.589	0.364	
4600	9.024	68.719	60.764	0.364	
4700	9.030	68.913	60.935	0.364	
4800	9.037	69.103	61.104	0.364	
4900	9.043	69.289	61.269	0.364	
5000	9.050	69.472	61.431	0.364	
5100	9.056	69.651	61.590	0.364	
5200	9.062	69.827	61.747	0.364	
5300	9.067	70.000	61.901	0.364	
5400	9.073	70.169	62.053	0.364	
5500	9.079	70.336	62.202	0.364	
5600	9.084	70.500	62.349	0.364	
5700	9.090	70.660	62.493	0.364	
5800	9.095	70.819	62.635	0.364	
5900	9.100	70.975	62.775	0.364	
6000	9.105	71.127	62.913	0.364	

June 30, 1969

Electronic Levels and Degeneracies

ϵ_i , cm ⁻¹	g_i
0	[1]
[67000]	[2]

$\omega_e = [2250]$ cm ⁻¹	$\omega_e x_e = [13.8]$ cm ⁻¹	$\sigma = 1$
$B_e = [2.116]$ cm ⁻¹	$\alpha_e = [0.0177]$ cm ⁻¹	$r_e = [1.111]$ Å

Heat of Formation

Barkowitz et al. (1) have recently obtained 88 ± 0.5 kcal for the electron affinity of CN from the photoionization thresholds of the reactions $HCN + H^+ + CN^-$ and $HCN + H^+ + CN + e^-$.

Other values have been reported by Page (2), who reinterpreted his earlier data (3), to yield 73 ± 1 kcal/mol; Bakulina and Ionov (4) in conjunction with the data of Branscomb and Smith (5) reported 78 ± 5 kcal/mol and Inoue (6) who obtained 83 ± 7 kcal/mol.

We adopt the value given by Barkowitz et al. (1) as being the most well defined in terms of both the precision of measurements and the reactions being studied. This leads to $\Delta H_f^\circ(CN^-, g) = 15.2 \pm 3$ kcal/mol or $\Delta H_f^\circ(CN^-, g) = 16 \pm 3$ kcal/mol.

Heat Capacity and Entropy

The electronic structure and molecular constants are estimated by analogy with the isoelectronic species CO and N₂. The uncertainties in the constants are generally small since N₂ and CO are quite similar, thus the entropy has an uncertainty of only 0.5 eu. The enthalpy at 0°K is -2.072 kcal/mol.

References:

1. J. Barkowitz, W. A. Chupka, and T. A. Walter, J. Chem. Phys. **50**, 1497 (1969).
2. F. M. Page, J. Chem. Phys. **49**, 2466 (1968).
3. R. Lippert and F. M. Page, Trans. Faraday Soc. **59**, 1086 (1963).
4. I. N. Bakulina and H. I. Ionov, Russ. J. Phys. Chem. (Eng. Transl.) **33**, 286 (1959).
5. L. M. Branscomb and S. J. Smith, J. Chem. Phys. **25**, 598 (1956).
6. M. Inoue, J. Chim. Phys. **63**, 1061 (1966).

Sodium Cyanide (NaCN)

(Crystal) Mol. Wt. = 49.00765

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	11.000	0.000	INFINITE	INFINITE	4.642	-23.493	-23.493	INFINITE
100	11.320	8.450	47.821	47.821	3.742	-23.870	-21.814	47.674
200	11.520	16.315	28.315	28.315	2.000	-21.680	-19.227	42.652
298	10.415	28.315	28.315	28.315	0.000	-21.680	-19.227	42.652
300	16.390	28.416	28.315	0.300	-21.672	-19.211	13.995	
400	16.410	33.141	28.960	1.672	-21.969	-18.397	10.052	
500	16.432	36.805	30.176	3.315	-21.738	-17.531	7.663	
600	16.455	39.803	31.538	4.959	-21.549	-16.709	6.086	
700	16.478	42.341	32.905	6.506	-21.397	-15.915	4.969	
800	16.502	44.543	34.225	8.255	-21.273	-15.140	4.136	
900	16.526	46.488	35.482	9.906	-21.179	-14.380	3.492	
1000	16.550	48.231	36.671	11.560	-21.108	-13.629	2.979	
1100	16.576	49.809	37.795	13.216	-21.064	-12.885	2.560	
1200	16.602	51.253	38.857	14.875	-21.036	-12.158	2.128	
1300	16.628	52.582	39.862	16.536	-21.022	-11.447	1.685	
1400	16.653	53.816	40.815	18.200	-21.018	-10.750	1.238	
1500	16.678	54.965	41.721	19.867	-21.022	-10.067	0.785	
1600	16.703	56.043	42.583	21.536	-21.036	-9.396	0.329	
1700	16.728	57.056	43.404	23.208	-21.064	-8.744	-0.129	
1800	16.752	58.013	44.190	24.882	-21.108	-8.114	-0.579	
1900	16.776	58.919	44.941	26.558	-21.168	-7.504	-1.029	
2000	16.800	59.780	45.662	28.237	-21.240	-6.919	-1.479	

SODIUM CYANIDE (NaCN)

(CRYSTAL)

MOL. WT. = 49.00765

$S_{298.15}^{\circ} = [28.32 \pm 0.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 835^{\circ} \text{ K.}$
 $\Delta H_f^{\circ} 0 = -23.49 \pm 0.3 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = -21.68 \pm 0.3 \text{ kcal. mole}^{-1}$
 $\Delta H_m^{\circ} = [2.1] \text{ kcal. mole}^{-1}$
 $\Delta H_g^{\circ} 298.15 (\text{to dimer}) = [41.3] \text{ kcal. mole}^{-1}$
 $\Delta H_g^{\circ} 298.15 (\text{to monomer}) = 44.21 \text{ kcal. mole}^{-1}$

Heat of Formation.

The enthalpy change for the reaction $\text{NaCN}(c) \rightarrow \text{NaCN}(\infty \text{ H}_2\text{O})$ was reported to be $0.29 \pm 0.20 \text{ kcal. mole}^{-1}$ by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-RS-2, National Bureau of Standards, April 1, 1965. Incorporating this data with the heats of formation for $\text{Na}^+(\infty \text{ H}_2\text{O})$, -57.39 , and $\text{CN}^-(\infty \text{ H}_2\text{O})$, $36.0 \text{ kcal. mole}^{-1}$, reported by D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Part 1, Technical Note 270-1, October 1, 1965, National Bureau of Standards, the value of $\Delta H_f^{\circ} 298.15$ for $\text{NaCN}(c)$ was derived and adopted.

G. Lord and A. A. Woolf, J. Chem. Soc. 2546 (1954), determined the value, $\Delta H_f^{\circ} 298.15 (\text{NaCN}, c) = -21.4 \text{ kcal. mole}^{-1}$, by solution calorimetry. This value is in agreement with the adopted one.

Heat Capacity and Entropy.

The low temperature heat capacities, $101.6-345.8^{\circ} \text{ K.}$, were reported by C. E. Measer and W. T. Ziegler, J. Am. Chem. Soc. 63, 2703 (1941). The C_p values above 345.8° K. were estimated by graphical extrapolation. $S_{298.15}^{\circ}$ was derived from low temperature heat capacities, based on $S_{100}^{\circ} = 8.4 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ which was estimated by comparison with the $S_{298.15}^{\circ}$ values for NaCl, KCl, and KCN crystals.

Transition Data.

The transition temperatures, T_{t2} and T_{t1} , were determined by C. E. Measer and W. T. Ziegler, loc. cit. The corresponding enthalpies of transition were reported to be 0.15 and $0.70 \text{ kcal. mole}^{-1}$, respectively. However, these quantities were incorporated with C_p values used to evaluate $H^{\circ}-H_{298.15}^{\circ}$. Therefore ΔH_f° 's are not listed.

Citing Data.

see NaCN(1) table for details.

Heat Sublimation.

The difference between $\Delta H_f^{\circ} 298.15$ for $(\text{NaCN})_2(g)$ and $2\text{NaCN}(c)$ is $\Delta H_g^{\circ} 298.15$ (to dimer) and for $\text{NaCN}(g)$ and $\text{NaCN}(c)$ is $\Delta H_g^{\circ} 298.15$ (to monomer).

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(H°-H° ₂₉₈)/T	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _f
0						
100	16.415	29.996	29.996	0.000	- 20.160	- 18.208
200						13.347
300	16.390	30.097	29.996	0.030	- 20.152	- 18.196
400	16.410	30.822	30.641	1.072	- 20.449	- 17.549
500	16.432	38.486	31.857	3.315	- 20.218	- 16.852
600	19.000	41.484	33.219	4.759	- 20.029	- 16.197
700	19.000	44.413	36.614	6.959	- 19.624	- 15.592
800	19.000	46.930	38.003	8.759	- 19.249	- 15.041
900	19.000	49.188	37.345	10.550	- 18.906	- 14.537
1000	19.000	51.190	38.631	12.259	- 18.589	- 14.075
1100	19.000	53.001	39.856	14.459	- 18.302	- 13.633
1200	19.000	54.654	41.021	16.359	- 18.030	- 13.204
1300	19.000	56.179	42.129	18.259	- 40.830	- 10.404
1400	19.000	57.583	43.184	20.159	- 40.393	- 8.080
1500	19.000	58.894	44.188	22.059	- 39.969	- 5.787
1600	19.000	60.120	45.146	23.959	- 39.554	- 3.522
1700	19.000	61.272	46.061	25.859	- 39.145	- 1.282
1800	19.000	62.358	46.936	27.759	- 38.746	- 0.934
1900	19.000	63.385	47.775	29.659	- 38.351	- 0.590
2000	19.000	64.360	48.580	31.559	- 37.963	- 0.249
2100	19.000	65.287	49.354	33.459	- 37.578	- 0.093
2200	19.000	66.170	50.098	35.359	- 37.200	- 0.053
2300	19.000	67.015	50.816	37.259	- 36.825	- 0.009
2400	19.000	67.824	51.507	39.159	- 36.454	- 0.036
2500	19.000	68.599	52.176	41.059	- 36.087	- 0.069
2600	19.000	69.345	52.822	42.959	- 35.725	- 0.100
2700	19.000	70.062	53.447	44.859	- 35.367	- 0.129
2800	19.000	70.753	54.053	46.759	- 35.012	- 0.157
2900	19.000	71.419	54.640	48.659	- 34.662	- 0.183
3000	19.000	72.063	55.210	50.559	- 34.318	- 0.208

Dec. 31, 1960; Mar. 31, 1966

$$\Delta H_f^{298.15} = [29.996] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{298.15} = [-20.160] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{298.15} = [2.1] \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{298.15} = [35.39] \text{ kcal. mole}^{-1}$$

$$T_m = 835^\circ \text{ K.}$$

$$T_b = [1803]^\circ \text{ K.}$$

Heat of Formation.

$\Delta H_f^{298.15}(l)$ was obtained from $\Delta H_f^{298.15}(c)$ by adding $\Delta H_m^{298.15}$ and the difference between $H_{835}^{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with those for NaCN(c), KCN(c) and KCN(l). A glass transition temperature is assumed at 600°K. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting temperature was reported by M. Truthe, Z. anorg. Chem. 76, 129 (1912). $\Delta H_m^{298.15}$ was estimated such that the derived third law value for $\Delta H_v^{298.15}$ (NaCN, l) agrees with the second law value. See NaCN(g) table for details.

Vaporization Data.

T_b is the temperature at which the free energy change for the reaction $\text{NaCN}(l) = \text{NaCN}(g)$ becomes zero. The difference between $\Delta H_f^{298.15}$ for NaCN(g) and NaCN(l) at T_b is $\Delta H_v^{298.15}$.

Sodium Cyanide (NaCN)

(Ideal Gas)

Mol. Wt. = 49.00765

CNNA

MOL. WT. = 49.00765

(IDEAL GAS)

SODIUM CYANIDE (NaCN)

Point Group $C_{\infty v}$ $S_{298.15}^{\circ} = [59.14] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Group State Quantum Weight = 1

 $\Delta H_f^{\circ} = 22.46 \pm 0.50 \text{ kcal. mole}^{-1}$ $\Delta H_f^{\circ} 298.15 = 22.53 \pm 0.50 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

 $\omega_e, \text{ cm.}^{-1}$
 $\frac{\omega_e}{(400)(1)}$
239 (2)
2176 (1)Bond Distance: Na-C = $[1.992] \text{ \AA}$ C-N = $[1.16] \text{ \AA}$ Bond Angle: Na-C-N = $[180]^{\circ}$ Rotational Constant: $B = [0.18272] \text{ cm.}^{-1}$ $\sigma = 1$

Heat of Formation

The vapor pressures of NaCN(l) at temperatures 805-1353°K. were measured by C. K. Ingold, J. Chem. Soc. 123, 865 (1923). According to the investigation reported by R. P. Porter, J. Chem. Phys. 35, 318 (1961), the vapor consists of NaCN and (NaCN)₂. Based on his data the dimer/monomer ratios at temperatures 805-1353°K. (1078.2-1626.2°K.) were calculated to be 0.29-0.09. Hence the respective partial pressures for NaCN(g) and (NaCN)₂(g) were derived. By the second and third law methods, the values of $\Delta H_f^{\circ} 298.15$ (1 → monomer) were evaluated to be 43.43 and 42.69 kcal. mole⁻¹, respectively. The heat of formation ($\Delta H_f^{\circ} 298.15$) for NaCN(g) was calculated from $\Delta H_f^{\circ} 298.15$ (NaCN, c) and the third law value for ΔH_v° .

Heat Capacity and Entropy

The molecular structure of NaCN(g) has not been determined. It was assumed to be linear by comparison with that for HCN(g). The C-N bond distance was assumed to be the same as that in KCN(g) and the Na-C bond distance was taken from G. E. Lerol, Ph. D. Dissertation, Harvard University, 1961, which was calculated. The vibrational frequencies, ν_2 and ν_3 , were measured by G. E. Lerol and M. Klemperer, J. Chem. Phys. 35, 774 (1961) from infrared absorption spectra. The value of ν_1 was calculated by valence force method described by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is $1.53187 \times 10^{-38} \text{ g. cm.}^2$.

T. °K.	C_p°	S°	$-(F^{\circ}-H_{298}^{\circ})/T$	$H^{\circ}-H_{298}^{\circ}$	ΔH_f°	ΔF_f°	Log K _p
0	8.000	INFINITE	-	2.898	22.461	22.461	INFINITE
100	8.531	46.316	-	2.925	22.461	22.461	19.000
200	11.110	59.514	-	2.944	22.461	22.461	19.000
298	11.993	58.139	-	3.000	22.530	16.091	11.799
300	12.003	58.213	-	3.022	22.530	16.051	11.693
400	12.419	61.729	-	3.045	21.814	13.951	7.622
500	12.707	64.532	-	3.058	12.003	12.003	5.246
600	12.960	66.872	-	3.068	10.087	10.087	3.674
700	13.194	68.887	-	3.073	8.200	8.200	2.560
800	13.405	70.663	-	3.078	6.424	6.424	1.733
900	13.592	72.253	-	3.082	4.899	4.899	1.095
1000	13.754	73.694	-	3.084	3.641	3.641	0.590
1100	13.893	75.011	-	3.084	2.653	2.653	0.181
1200	14.012	76.225	-	3.082	1.919	1.919	0.072
1300	14.113	77.351	-	3.078	1.326	1.326	0.030
1400	14.200	78.400	-	3.073	0.871	0.871	0.008
1500	14.274	79.382	-	3.068	0.516	0.516	0.004
1600	14.338	80.306	-	3.062	0.256	0.256	0.001
1700	14.393	81.177	-	3.056	0.082	0.082	0.000
1800	14.441	82.001	-	3.050	0.000	0.000	0.000
1900	14.483	82.783	-	3.044	0.000	0.000	0.000
2000	14.520	83.527	-	3.037	0.000	0.000	0.000
2100	14.552	84.236	-	3.030	0.000	0.000	0.000
2200	14.580	84.914	-	3.023	0.000	0.000	0.000
2300	14.606	85.562	-	3.016	0.000	0.000	0.000
2400	14.628	86.184	-	3.009	0.000	0.000	0.000
2500	14.648	86.782	-	3.002	0.000	0.000	0.000
2600	14.666	87.357	-	2.995	0.000	0.000	0.000
2700	14.682	87.911	-	2.988	0.000	0.000	0.000
2800	14.697	88.445	-	2.981	0.000	0.000	0.000
2900	14.710	88.961	-	2.974	0.000	0.000	0.000
3000	14.722	89.460	-	2.967	0.000	0.000	0.000
3100	14.733	89.943	-	2.960	0.000	0.000	0.000
3200	14.743	90.411	-	2.953	0.000	0.000	0.000
3300	14.753	90.864	-	2.946	0.000	0.000	0.000
3400	14.761	91.305	-	2.939	0.000	0.000	0.000
3500	14.769	91.733	-	2.932	0.000	0.000	0.000
3600	14.776	92.149	-	2.925	0.000	0.000	0.000
3700	14.782	92.554	-	2.918	0.000	0.000	0.000
3800	14.789	92.948	-	2.911	0.000	0.000	0.000
3900	14.794	93.332	-	2.904	0.000	0.000	0.000
4000	14.799	93.707	-	2.897	0.000	0.000	0.000
4100	14.804	94.073	-	2.890	0.000	0.000	0.000
4200	14.809	94.429	-	2.883	0.000	0.000	0.000
4300	14.813	94.778	-	2.876	0.000	0.000	0.000
4400	14.817	95.118	-	2.869	0.000	0.000	0.000
4500	14.821	95.452	-	2.862	0.000	0.000	0.000
4600	14.824	95.777	-	2.855	0.000	0.000	0.000
4700	14.828	96.096	-	2.848	0.000	0.000	0.000
4800	14.831	96.408	-	2.841	0.000	0.000	0.000
4900	14.834	96.714	-	2.834	0.000	0.000	0.000
5000	14.836	97.014	-	2.827	0.000	0.000	0.000
5100	14.839	97.308	-	2.820	0.000	0.000	0.000
5200	14.841	97.596	-	2.813	0.000	0.000	0.000
5300	14.844	97.879	-	2.806	0.000	0.000	0.000
5400	14.846	98.156	-	2.799	0.000	0.000	0.000
5500	14.848	98.429	-	2.792	0.000	0.000	0.000
5600	14.850	98.696	-	2.785	0.000	0.000	0.000
5700	14.852	98.959	-	2.778	0.000	0.000	0.000
5800	14.853	99.217	-	2.771	0.000	0.000	0.000
5900	14.855	99.471	-	2.764	0.000	0.000	0.000
6000	14.857	99.721	-	2.757	0.000	0.000	0.000

Dec. 31, 1960; Mar. 31, 1966

CNNA

CNN Radical (CN₂)

GFW = 40.02455

(Ideal Gas)

T, °K	C _p ^o	S ^o	gibbs/mol -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	+0.00	INFINITE	-	2.479	139.545	139.545	INFINITE
100	7.403	45.837	63.598	-	139.541	138.795	-303.337
200	9.100	51.517	58.250	-	139.596	138.035	-150.838
298	10.105	55.354	55.354	+0.00	139.700	137.248	-100.605
300	10.120	55.617	55.355	-0.19	139.702	137.232	-99.973
400	10.803	58.427	55.760	1.407	139.807	136.593	-76.522
500	11.323	60.856	56.548	2.474	139.892	135.529	-59.240
600	11.745	62.999	57.452	3.328	139.956	134.650	-48.046
700	12.104	64.837	58.378	4.221	139.996	133.762	-41.762
800	12.419	66.417	59.299	5.057	139.996	132.861	-37.461
900	12.691	67.953	60.172	7.003	140.030	131.976	-32.648
1000	12.933	69.302	61.018	8.284	140.031	131.080	-28.648
1100	13.144	70.545	61.828	9.598	140.024	130.185	-25.865
1200	13.300	71.699	62.603	12.212	140.031	129.292	-23.547
1300	13.419	72.777	63.333	15.152	139.996	128.404	-21.648
1400	13.633	73.776	64.054	18.610	139.972	127.508	-19.905
1500	13.756	74.720	64.734	21.979	139.948	126.619	-18.448
1600	13.864	75.612	65.386	24.361	139.924	125.730	-17.174
1700	13.952	76.455	66.013	26.752	139.898	124.844	-16.050
1800	14.030	77.255	66.615	29.152	139.869	123.961	-15.051
1900	14.115	78.017	67.196	31.567	139.843	123.077	-14.157
2000	14.180	78.742	67.755	33.975	139.815	122.197	-13.353
2100	14.238	79.436	68.295	36.396	139.787	121.315	-12.625
2200	14.290	80.100	68.815	38.822	139.756	120.435	-11.964
2300	14.336	80.735	69.315	41.252	139.726	119.558	-11.360
2400	14.377	81.346	69.809	43.680	139.696	118.684	-10.808
2500	14.414	81.934	70.283	46.129	139.665	117.807	-10.299
2600	14.447	82.500	70.742	48.572	139.632	116.934	-9.829
2700	14.476	83.045	71.189	51.009	139.599	116.060	-9.394
2800	14.505	83.573	71.620	53.427	139.566	115.189	-8.994
2900	14.530	84.082	72.061	55.829	139.532	114.322	-8.616
3000	14.552	84.575	72.511	58.213	139.496	113.463	-8.265
3100	14.573	85.053	72.950	60.579	139.460	112.613	-7.937
3200	14.591	85.516	73.373	62.926	139.423	111.777	-7.630
3300	14.610	85.965	73.781	65.256	139.385	110.951	-7.341
3400	14.626	86.402	74.197	67.567	139.344	109.988	-7.070
3500	14.640	86.826	74.614	69.853	139.302	109.121	-6.814
3600	14.654	87.238	75.000	72.113	139.258	108.262	-6.572
3700	14.669	87.630	75.364	74.350	139.215	107.402	-6.344
3800	14.679	88.003	75.704	76.564	139.170	106.546	-6.129
3900	14.689	88.413	76.010	78.750	139.122	105.688	-5.923
4000	14.700	88.785	76.313	80.909	139.074	104.830	-5.728
4100	14.709	89.148	76.548	83.044	139.023	103.972	-5.542
4200	14.718	89.494	76.750	85.156	138.970	103.113	-5.366
4300	14.726	89.829	76.929	87.245	138.916	102.253	-5.200
4400	14.734	90.187	77.075	89.306	138.861	101.417	-5.037
4500	14.741	90.519	77.248	91.349	138.802	100.561	-4.884
4600	14.748	90.843	77.433	93.374	138.743	99.716	-4.738
4700	14.754	91.147	77.626	95.384	138.682	98.870	-4.593
4800	14.760	91.471	77.838	97.379	138.617	98.023	-4.463
4900	14.766	91.775	78.059	99.351	138.551	97.175	-4.334
5000	14.771	92.073	78.224	101.299	138.483	96.338	-4.211
5100	14.776	92.366	78.415	103.225	138.411	95.484	-4.092
5200	14.781	92.655	78.629	105.130	138.339	94.630	-3.978
5300	14.785	92.935	78.833	107.011	138.263	93.807	-3.868
5400	14.789	93.211	79.041	108.869	138.186	92.972	-3.763
5500	14.794	93.482	80.184	110.704	138.104	92.141	-3.661
5600	14.797	93.749	80.474	112.519	138.022	91.301	-3.563
5700	14.800	94.011	80.760	114.311	137.936	90.465	-3.469
5800	14.804	94.268	81.039	116.079	137.849	89.629	-3.378
5900	14.808	94.521	81.321	117.829	137.755	88.809	-3.290
6000	14.811	94.770	81.547	119.561	137.661	87.975	-3.204

June 30, 1966

 $\Delta H_f^{\circ} = [139.5 \pm 30] \text{ kcal/mol}$ $\Delta H_f^{\circ} = [139.7 \pm 30] \text{ kcal/mol}$ $S_{298}^{\circ} = 55.35 \text{ gibbs/mol}$

Round State Quantum Weight = 3

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹
1241 (1)
393 (2)
2847 (1)

Bond Distance: C-N = [1.15] Å

Bond Angle: C-N-N = 180°

Rotational Constant: $B_0 = [0.450368] \text{ cm}^{-1}$ $\sigma = 1$

Heat of Formation.

The heat of formation is calculated from the estimated heat of reaction $\Delta H_f^{\circ} = 255 \pm 30 \text{ kcal/mol}$ for $\text{CN}(\text{g}) \rightarrow \text{C}(\text{g}) + 2\text{N}(\text{g})$. Since CN radical can dissociate to give C + N₂ or CN + N, the molecule must have more energy than either CN or N₂. It is assumed that the extra bond will be quite weak, for this we estimate $30 \pm 30 \text{ kcal/mol}$ which gives $\Delta H_f^{\circ} = 255 \pm 30 \text{ kcal/mol}$ for the first path and $\Delta H_f^{\circ} = 204 \pm 30 \text{ kcal/mol}$ for the second. We adopt the former value.

Heat Capacity and Entropy.

D. E. Milligan and M. E. Jacox, J. Chem. Phys. 44, 2850 (1966), have measured three fundamental vibrational frequencies for CN radical (g) in the infrared and ultraviolet spectra by matrix-isolation, and proposed a linear molecular configuration with a $\sum$ ground state which has been confirmed by E. Weisserman, L. Barash and W. A. Yager, J. Am. Chem. Soc. 81, 2075 (1959), in the electron paramagnetic resonance observations. Also Milligan and Jacox suggested a "C≡N-N" bond structure, based on the agreement between the C-N and N-N stretching force constants (calculated from observed vibrational frequencies in the CN radical) and the typical C≡N and N-N stretching force constants. In addition, they estimated the bond distances $r_{\text{C-N}} = 1.15 \text{ Å}$ and $r_{\text{N-N}} = 1.25 \text{ Å}$ from the proposed structure. The principal moment of inertia is $6.2148 \times 10^{-39} \text{ g cm}^2$.

GFW = 40.02455

(Ideal Gas) (IDEAL GAS)

GFW = 40.02455

NCN Radical (CN₂)Point Group D_{∞h} $\Delta H_f^\circ = [102.6 \pm 25] \text{ kcal/mol}$ $\Delta H_f^{298.15} = [102.8 \pm 25] \text{ kcal/mol}$ $S_{298.15}^\circ = 54.194 \text{ gibbs/mol}$

Ground State Quantum Weight = 3

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	
(808)(1)	
423 (2)	
1475 (1)	

Bond Distance: C-N = 1.232 Å

Bond Angle: N-C-N = 180°

Rotational Constant: $B_0 = 0.3968 \text{ cm}^{-1}$ $\sigma = 2$

Heat of Formation

The heat of formation of NCN radical (ΔH_f°) was calculated from the heat of reaction $\Delta H_r^\circ = 294 \pm 25 \text{ kcal/mol}$ for $\text{N} \rightarrow \text{N}(\text{g}) + \text{C}(\text{g})$ which was estimated as twice the C-N bond dissociation energy (147 kcal/mol). The value of C-N bond dissociation energy was derived from the heat of combustion for n-butyl-isobutylidene amine, determined by G. E. Costes and L. E. Sutton, J. Chem. Soc. 1187 (1948).

Heat Capacity and Entropy

G. Herzberg and D. N. Travis, Can. J. Phys. 42, 1658 (1964), have found NCN radical (g) is a linear symmetric molecule with a $\sum g$ ground state in the rotational spectra by a flash photolysis technique, and determined the bond distance $r_{\text{C-N}} = 1.232 \text{ Å}$ and rotational constant $B_0 = 0.3968 \text{ cm}^{-1}$ which have been adopted in the tabulation. Also the structure "N-C-N" has been suggested by Herzberg and Travis, based on the bond distance of 1.232 Å, which is in good agreement with the C-N bond length observed in the HNCO, HNCS and CH₃NCS. The principal moment of inertia is $7.0601 \times 10^{-39} \text{ g cm}^2$.

D. E. Milligan, M. E. Jacox and A. M. Bana, J. Chem. Phys. 43, 3149 (1965), have found two infrared-active vibrational fundamentals of NCN(g) at 423 and 1475 cm^{-1} in the infrared and ultraviolet spectra by a matrix-isolation method. They also estimated the symmetric stretching frequency ($\nu_1 = 808 \text{ cm}^{-1}$) by valence force calculation.

E. Wesserman, L. Barash and W. A. Yager, J. Am. Chem. Soc. 87, 2075 (1965), have confirmed the NCN radical (g) is a linear molecule with a triplet ground state by electron paramagnetic resonance.

T, K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	Log Kp
0	+0.00	0.00	INFINITE	-2.485	102.639	INFINITE
100	7.284	44.683	102.639	-1.785	102.640	-222.030
200	9.098	50.280	55.114	+0.967	102.677	-110.764
298	10.515	54.194	0.000	0.000	102.800	-73.810
300	10.537	54.259	54.194	0.019	102.802	-73.345
400	11.551	57.437	55.451	1.122	102.865	-63.450
500	12.292	60.099	55.457	2.321	103.139	-43.349
600	12.860	62.391	56.426	3.579	103.307	-35.830
700	13.248	64.402	57.425	4.884	103.459	-30.450
800	13.579	66.183	58.441	6.237	103.598	-26.410
900	13.789	67.653	59.471	7.563	103.728	-23.166
1000	13.970	69.255	60.284	8.981	103.828	-20.763
1100	14.112	70.604	61.163	10.385	103.921	-18.679
1200	14.225	71.837	62.001	11.802	104.001	-16.958
1300	14.318	72.960	62.790	13.230	104.069	-15.501
1400	14.391	74.043	63.536	14.665	104.116	-14.221
1500	14.452	75.038	64.240	16.107	104.176	-13.117
1600	14.504	75.972	65.000	17.555	104.218	-12.218
1700	14.557	76.853	65.672	19.008	104.254	-11.380
1800	14.615	77.685	66.264	20.464	104.282	-10.636
1900	14.635	78.475	66.816	21.924	104.306	-10.000
2000	14.642	79.225	67.332	23.387	104.327	-9.370
2100	14.665	79.940	68.106	24.853	104.344	-8.827
2200	14.686	80.623	68.659	26.320	104.354	-8.333
2300	14.705	81.276	69.190	27.789	104.363	-7.882
2400	14.720	81.902	69.700	29.250	104.370	-7.468
2500	14.734	82.503	70.210	30.733	104.369	-7.089
2600	14.746	83.081	70.694	32.207	104.367	-6.738
2700	14.757	83.638	71.163	33.683	104.364	-6.413
2800	14.766	84.176	71.611	35.159	104.358	-6.111
2900	14.774	84.693	72.040	36.636	104.349	-5.831
3000	14.785	85.194	72.490	38.114	104.337	-5.568
3100	14.782	85.678	72.907	39.593	104.324	-5.323
3200	14.789	86.149	73.314	41.073	104.308	-5.093
3300	14.794	86.600	73.710	42.553	104.288	-4.877
3400	14.801	87.037	74.097	44.034	104.264	-4.674
3500	14.816	87.447	74.472	45.515	104.244	-4.483
3600	14.821	87.893	74.839	46.997	104.218	-4.302
3700	14.825	88.300	75.197	48.479	104.190	-4.131
3800	14.831	88.687	75.547	49.962	104.160	-3.969
3900	14.833	89.055	75.890	51.446	104.128	-3.816
4000	14.836	89.456	76.224	52.928	104.093	-3.670
4100	14.839	89.822	76.551	54.412	104.056	-3.531
4200	14.842	90.180	76.871	55.896	104.016	-3.399
4300	14.845	90.528	77.185	57.380	103.974	-3.273
4400	14.848	90.868	77.494	58.864	103.930	-3.153
4500	14.850	91.204	77.793	60.350	103.883	-3.038
4600	14.853	91.531	78.088	61.835	103.834	-2.929
4700	14.855	91.850	78.378	63.320	103.783	-2.824
4800	14.857	92.163	78.662	64.806	103.728	-2.723
4900	14.859	92.471	78.941	66.292	103.672	-2.627
5000	14.860	92.769	79.214	67.778	103.611	-2.535
5100	14.862	93.064	79.482	69.264	103.550	-2.445
5200	14.864	93.352	79.746	70.750	103.486	-2.360
5300	14.866	93.635	80.006	72.237	103.419	-2.278
5400	14.868	93.915	80.263	73.723	103.350	-2.199
5500	14.868	94.186	80.512	75.210	103.275	-2.125
5600	14.869	94.454	80.758	76.697	103.200	-2.050
5700	14.870	94.717	81.001	78.184	103.121	-1.979
5800	14.871	94.976	81.239	79.671	103.039	-1.911
5900	14.873	95.231	81.476	81.158	102.954	-1.846
6000	14.874	95.480	81.706	82.645	102.866	-1.782

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	INFINITE	4.974	-268.788	-268.788	INFINITE
100	14.477	10.000	35.834	2.867	-268.788	-268.788	13.3127
200	22.500	23.367	35.834	2.424	-270.233	-257.002	280.839
288	26.530	33.173	33.173	0.000	-270.260	-250.496	183.619
300	26.590	33.338	33.174	0.049	-270.258	-250.373	182.387
400	29.600	41.421	34.254	2.867	-271.441	-245.556	153.127
500	31.990	48.540	36.408	6.056	-271.150	-236.735	103.477
600	39.030	55.153	38.083	9.702	-270.456	-229.910	83.745
700	44.830	61.597	41.755	13.890	-269.272	-223.240	69.699
800	50.000	66.889	44.594	17.837	-268.371	-216.743	59.211
900	54.730	71.393	47.322	21.585	-267.641	-210.331	51.075
1000	58.830	75.259	49.947	25.182	-266.640	-204.013	44.587
1100	62.500	78.956	52.484	30.220	-265.376	-197.813	39.302
1200	65.980	81.065	54.966	34.944	-264.340	-190.821	34.753
1300	69.280	82.960	57.337	39.211	-263.302	-183.943	30.419
1400	72.400	84.657	59.657	43.113	-262.306	-177.126	26.750
1500	75.400	86.127	61.907	46.590	-261.393	-170.662	23.534
1600	78.330	87.422	64.087	50.637	-260.766	-164.426	20.766
1700	81.140	88.590	66.199	54.302	-260.495	-158.469	18.380
1800	83.860	89.650	68.246	57.500	-260.320	-152.769	16.269
1900	86.500	90.611	70.231	60.226	-260.240	-147.287	14.387
2000	89.000	91.470	72.156	62.586	-260.260	-142.028	12.668

Dec. 31, 1950; Mar. 31, 1966

$S_{298.15}^{\circ} = 33.17 \pm 0.2$ cal. deg.⁻¹ mole⁻¹
 $T_f = 723.15^{\circ}\text{K.}$
 $T_m = 1123.15^{\circ}\text{K.}$

 $\Delta H_f^{\circ} 0 = -268.79 \pm 0.05$ kcal. mole⁻¹
 $\Delta H_f^{\circ} 298.15 = -270.26 \pm 0.05$ kcal. mole⁻¹
 $\Delta H_f^{\circ} = 0.185$ kcal. mole⁻¹
 $\Delta H_m^{\circ} = 7.090$ kcal. mole⁻¹
Heat of Formation.

The heat of formation was obtained from the heat of solution $\Delta H_{\infty}^{\circ} = -6.35$ kcal. mole⁻¹ and the heats of formation for Na⁺(aq) and CO₃²⁻(aq), -57.59 and -161.84 kcal. mole⁻¹, respectively. The heat of solution was taken from J. P. Rupert, H. P. Hopkins, Jr., and C. A. Wulff, J. Phys. Chem. **69**, 3059-62 (1965). The ionic heats of formation were taken from D. M. Ginzburg, V. B. Parker, S. M. Bailey, and R. H. Schumm "Selected Values of Chemical Thermodynamic Properties" NES Technical Note 270-1, October 1, 1965.

A value of $\Delta H_f^{\circ} 298.15 = -270.9$ kcal. mole⁻¹ has been selected by D. D. Wagman, Natl. Bur. Std. Rept. No. 8628, 87, Jan. 1965.

Heat Capacity and Entropy.

The low temperature heat capacities, 54.6-292.1°K., were measured by C. T. Anderson, J. Am. Chem. Soc. **55**, 3621 (1933). In the temperature range 473.15-873.15°K. Popov and Galchenko (Source 1) measured the heat capacities (by heat conduction calorimetry) and observed two transformations, one at about 623°K. and the other at about 750°K. Popov and Ginzburg (Source 2) measured enthalpies in the temperature range 480-1350°K. and tabulated their data only in the range 476-872°K. Ginzburg (Source 3) has given heat capacity equations based on the data from Source 1 and 2 and has tabulated thermodynamic functions in the range 500-1500°K. There appear to be inconsistencies among the data, equations and functions. Rolin and Recapet (Source 4) also measured the enthalpy in the temperature range 645-1322°K. Janz, Neuenchwander and Kelly (Source 5) have given an enthalpy equation based on their heat content measured data in the range 707-1127°K. May (Source 6) has tabulated smoothed measured enthalpy values in the range 400-1500°K. All the above information was used in a Shomate analysis in order to smooth the enthalpies and calculate heat capacities. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was graphically extrapolated above the melting point.

The entropy was calculated at 54.60° using the Debye and Einstein function $D(\frac{138}{T}) + 2E(\frac{265}{T}) + 2D(\frac{73.7}{T})$ given by Anderson, loc. cit. The value of $S_{54.6}^{\circ} = 3.943$ cal. deg.⁻¹ mole⁻¹.

Source

- 1 M. M. Popov and G. L. Galchenko, Zh. Obshch. Khim. **21**, 2220 (1951).
- 2 M. M. Popov and D. M. Ginzburg, Zh. Obshch. Khim. **26**, 971-80 (1958).
- 3 D. M. Ginzburg, Zh. Obshch. Khim. **25**, 968-70 (1956).
- 4 M. Rolin and J. M. Recapet, Bull. Soc. chim., 2504 (1954).
- 5 G. J. Janz, E. Neuenchwander and F. J. Kelly, Trans. Faraday Soc. **59**, 841 (1963).
- 6 M. N. Mey, Teppl., **35**, 511 (1952).

Transition Data.

T_f was taken from Ginzburg loc. cit. and ΔH_f° was obtained from the above reported enthalpy measurements by means of Shomate function analysis. The heat of transition at 593.15°K. has been incorporated in the heat capacity.

Melting Data.

T_m was taken from Ginzburg loc. cit. and ΔH_m° was obtained from the above reported enthalpy measurements by means of Shomate function analysis.

Sodium Carbonate (Na_2CO_3)

(Liquid) Mol. Wt. = 105.98895



MOL. WT. = 105.98895

(LIQUID)

SODIUM CARBONATE (Na_2CO_3)

$$\begin{aligned} S_{298.15}^{\circ} &= 37.14 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \\ \Delta H_f^{\circ} 298.15 &= -285.21 \pm 0.05 \text{ kcal. mole}^{-1} \\ \Delta H_m^{\circ} &= 7.090 \text{ kcal. mole}^{-1} \\ T_m &= 1123.15^{\circ}\text{K.} \end{aligned}$$

Heat of Formation.

The $\Delta H_f^{\circ} 298.15$ was obtained from $\Delta H_f^{\circ} 298.15(c)$ by adding ΔH_m° and the difference between H_m° and $H_m^{\circ} 298.15$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 723.15°K. The heat capacity below 723.15°K. was obtained from the heat capacity of the crystal. Above 723.15°K. the heat capacity was adopted as $45.30 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, based on the enthalpy measurements in the range $1127\text{--}1210^{\circ}\text{K.}$ reported by G. J. Janz, E. Neuenchwander and F. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $\text{Na}_2\text{CO}_3(c)$ table.

T, °K.	C_p°	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	ΔH_f°	ΔF_f°	Log K _P
0						
100						
200						
298	26.530	37.143	37.143	0.000	-246.625	180.781
300	26.590	37.307	37.144	0.049	-246.509	179.581
400	29.900	45.391	38.224	2.867	-246.386	131.253
500	33.990	52.485	40.378	6.034	-246.097	102.135
600	39.030	59.116	42.952	9.698	-245.405	82.771
700	44.830	65.564	45.723	13.889	-244.218	68.988
800	45.300	71.620	48.590	18.424	-242.729	58.704
900	45.300	76.956	51.451	22.954	-241.287	50.750
1000	45.300	81.729	54.245	27.484	-239.884	44.422
1100	45.300	86.046	56.943	32.014	-238.527	39.272
1200	45.300	89.988	59.535	36.544	-237.213	34.636
1300	45.300	93.614	62.018	41.074	-235.984	30.593
1400	45.300	96.971	64.397	45.604	-234.807	26.976
1500	45.300	100.096	66.674	50.134	-233.654	23.859
1600	45.300	103.020	68.855	54.664	-232.584	21.147
1700	45.300	105.766	70.946	59.194	-231.593	18.767
1800	45.300	108.355	72.953	63.724	-230.674	16.664
1900	45.300	110.805	74.881	68.254	-229.818	14.792
2000	45.300	113.128	76.736	72.784	-229.009	13.117
2100	45.300	115.338	78.522	77.314	-228.242	11.609
2200	45.300	117.446	80.244	81.844	-227.514	10.246
2300	45.300	119.459	81.905	86.374	-226.822	9.008
2400	45.300	121.387	83.511	90.904	-226.166	7.879
2500	45.300	123.236	85.063	95.434	-225.544	6.847



(Ideal Gas) Mol. Wt. = 28.01055

T, °K.	C _p	S°	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	6.000	0.000	0.000	2.072	27.200	27.200	INFINITE
100	6.065	39.613	53.401	1.379	26.806	26.806	6.2809
200	6.095	42.955	48.841	0.900	26.417	26.417	6.2409
298	6.065	47.214	47.113	0.000	26.417	32.783	24.029
300	6.065	47.257	47.113	0.013	26.414	32.783	23.910
400	7.013	49.265	47.488	0.711	26.318	34.975	19.109
500	7.121	50.841	48.006	1.417	26.296	37.144	16.235
600	7.276	52.152	48.591	2.037	26.332	39.311	14.318
700	7.450	53.287	49.182	2.673	26.409	41.468	12.046
800	7.624	54.293	49.759	3.327	26.514	43.612	11.014
900	7.786	55.200	50.314	4.007	26.637	45.744	10.108
1000	7.931	56.028	50.845	5.163	26.771	47.859	10.459
1100	8.057	56.790	51.351	5.793	26.912	49.962	9.926
1200	8.168	57.496	51.834	6.794	27.062	52.049	9.479
1300	8.263	58.134	52.295	7.616	27.218	54.126	9.099
1400	8.346	58.709	52.746	8.446	27.376	56.189	8.771
1500	8.417	59.248	53.196	9.285	27.537	58.241	8.485
1600	8.480	59.753	53.642	10.130	27.700	60.284	8.234
1700	8.535	60.228	54.080	10.980	27.865	62.315	8.011
1800	8.583	60.688	54.522	11.836	28.032	64.337	7.811
1900	8.626	61.133	54.961	12.697	28.201	66.349	7.631
2000	8.664	61.561	55.398	13.561	28.372	68.353	7.469
2100	8.698	62.230	55.835	14.430	28.543	70.346	7.321
2200	8.728	62.635	56.280	15.301	28.719	72.335	7.185
2300	8.756	63.024	56.717	16.175	28.894	74.311	7.061
2400	8.781	63.407	57.147	17.052	29.074	76.282	6.946
2500	8.804	63.776	57.569	17.931	29.254	78.247	6.840
2600	8.825	64.133	57.986	18.813	29.438	80.202	6.741
2700	8.844	64.475	58.397	19.696	29.623	82.153	6.649
2800	8.863	64.797	58.797	20.582	29.810	84.093	6.563
2900	8.880	65.109	59.186	21.471	30.001	86.026	6.483
3000	8.895	65.410	59.566	22.357	30.194	87.952	6.407
3100	8.910	65.662	59.940	23.248	30.388	89.878	6.336
3200	8.924	65.945	60.301	24.139	30.586	91.795	6.269
3300	8.937	66.220	60.634	25.032	30.786	93.707	6.206
3400	8.949	66.487	60.951	25.927	30.988	95.609	6.145
3500	8.961	66.746	61.259	26.822	31.192	97.500	6.086
3600	8.973	66.999	61.559	27.719	31.399	99.400	6.034
3700	8.984	67.245	61.851	28.617	31.608	101.286	5.982
3800	8.994	67.485	62.136	29.516	31.818	103.164	5.933
3900	9.004	67.718	62.411	30.416	32.031	105.039	5.886
4000	9.014	67.946	62.681	31.316	32.247	106.908	5.841
4100	9.024	68.169	62.941	32.218	32.464	108.774	5.798
4200	9.033	68.387	63.191	33.121	32.684	110.630	5.756
4300	9.042	68.599	63.436	34.025	32.906	112.483	5.717
4400	9.050	68.807	63.676	34.930	33.130	114.333	5.680
4500	9.058	69.011	63.911	35.835	33.356	116.177	5.642
4600	9.068	69.210	64.143	36.741	33.584	118.012	5.607
4700	9.076	69.405	64.369	37.649	33.814	119.845	5.573
4800	9.084	69.596	64.589	38.557	34.046	121.672	5.540
4900	9.092	69.783	64.804	39.465	34.280	123.497	5.508
5000	9.100	69.967	65.017	40.373	34.516	125.315	5.477
5100	9.107	70.148	65.225	41.281	34.755	127.132	5.448
5200	9.115	70.325	65.429	42.186	34.995	128.941	5.419
5300	9.123	70.498	65.635	43.088	35.237	130.741	5.391
5400	9.130	70.668	65.837	43.989	35.480	132.542	5.364
5500	9.138	70.836	66.034	44.889	35.727	134.336	5.338
5600	9.145	71.001	66.231	45.784	35.974	136.129	5.312
5700	9.153	71.161	66.425	46.676	36.225	137.919	5.288
5800	9.160	71.322	66.617	47.567	36.476	139.698	5.264
5900	9.167	71.482	66.807	48.457	36.727	141.476	5.240
6000	9.175	71.633	66.991	49.343	36.985	143.249	5.218

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CARBON MONOXIDE (CO)

(IDEAL GAS)

MOL. WT. = 28.01055

Ground State Configuration $1 \Sigma^+$

$$\Delta H_f^0 = -27.20 \pm 0.04 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = -28.42 \pm 0.04 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 13.453 \text{ cm}^{-1}$$

$$\omega_e = 0.01746 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.1281 \text{ Å}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

$$\omega_e = 1.3502 \text{ cm}^{-1}$$

Carbon Oxide Sulfide (COS)
(Ideal Gas) Mol. Wt. = 60.077

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	7.077	46.387	INFINITE	33.111	33.111	INFINITE
100	8.978	51.665	1.676	32.438	32.438	76.911
200	10.599	55.195	5.06	32.269	32.269	49.900
298	9.918	55.323	5.000	32.269	32.269	29.016
300	9.940	55.323	0.18	33.082	39.629	28.669
400	10.959	58.390	5.726	33.735	41.774	22.623
500	11.688	60.920	9.201	34.223	43.726	19.112
600	12.249	63.102	12.436	34.638	45.467	16.404
700	12.700	65.025	15.387	35.003	47.356	14.795
800	13.068	66.746	18.036	35.397	49.307	13.759
900	13.370	68.303	20.239	35.818	51.407	12.290
1000	13.621	69.725	22.117	36.268	53.659	11.115
1100	13.829	71.034	23.781	36.743	56.064	10.153
1200	14.005	72.245	25.267	37.243	58.623	9.351
1300	14.153	73.372	26.612	37.768	61.335	8.672
1400	14.280	74.426	27.842	38.318	64.200	8.090
1500	14.390	75.414	28.990	38.884	67.216	7.566
1600	14.485	76.346	29.971	39.466	70.384	7.144
1700	14.569	77.224	30.812	40.064	73.704	6.784
1800	14.643	78.062	31.532	40.678	77.176	6.468
1900	14.710	78.855	32.161	41.307	80.800	6.171
2000	14.770	79.611	32.712	41.951	84.576	5.899
2100	14.824	80.333	33.187	42.619	88.504	5.646
2200	14.873	81.031	33.590	43.301	92.584	5.409
2300	14.918	81.695	33.922	43.997	96.816	5.186
2400	14.962	82.322	34.190	44.708	101.200	4.976
2500	15.002	82.934	34.390	45.434	105.736	4.776
2600	15.038	83.520	34.530	46.174	110.424	4.584
2700	15.070	84.083	34.615	46.928	115.264	4.400
2800	15.100	84.624	34.648	47.696	120.256	4.224
2900	15.127	85.145	34.631	48.478	125.400	4.056
3000	15.157	85.644	34.566	49.274	130.696	3.896
3100	15.184	86.122	34.454	50.084	136.144	3.744
3200	15.209	86.580	34.298	50.908	141.744	3.596
3300	15.232	87.018	34.098	51.746	147.496	3.456
3400	15.255	87.438	33.854	52.598	153.400	3.324
3500	15.275	87.840	33.568	53.464	159.456	3.196
3600	15.300	88.224	33.240	54.344	165.664	3.076
3700	15.324	88.590	32.872	55.238	172.024	2.964
3800	15.346	88.938	32.468	56.146	178.536	2.856
3900	15.369	89.268	32.030	57.068	185.200	2.756
4000	15.392	89.580	31.558	58.004	192.016	2.664
4100	15.414	90.083	31.044	58.954	199.084	2.576
4200	15.436	90.464	30.488	59.918	206.404	2.496
4300	15.459	91.200	29.890	60.896	213.976	2.424
4400	15.478	91.556	29.250	61.888	221.800	2.356
4500	15.516	91.905	28.568	62.894	229.876	2.296
4600	15.537	92.246	27.828	63.914	238.204	2.244
4700	15.557	92.576	27.048	64.948	246.784	2.196
4800	15.576	92.908	26.224	65.996	255.616	2.156
4900	15.595	93.229	25.356	67.058	264.700	2.124
5000	15.614	93.545	24.444	68.134	274.044	2.096
5100	15.633	93.854	23.488	69.224	283.648	2.076
5200	15.653	94.156	22.488	70.328	293.512	2.056
5300	15.670	94.456	21.444	71.446	303.636	2.044
5400	15.688	94.749	20.356	72.578	314.020	2.036
5500	15.706	95.037	19.224	73.724	324.664	2.036
5600	15.724	95.320	18.048	74.884	335.568	2.044
5700	15.740	95.600	16.828	76.058	346.732	2.056
5800	15.756	95.873	15.564	77.246	358.156	2.076
5900	15.772	96.142	14.256	78.448	369.840	2.096
6000	15.795	96.407	12.904	79.664	381.784	2.124

March 31, 1961

CARBON OXIDE SULFIDE (COS)

(IDEAL GAS)

MOL. WT. = 60.077

COS

ΔH_f⁰ = -33.11 ± 0.25 kcal. mole⁻¹
 ΔH_f⁰ 298.15 = -33.08 ± 0.25 kcal. mole⁻¹
 S_{298.15} = 55.323 cal. deg.⁻¹ mole⁻¹
 Point group C_{∞v}

Vibrational Levels and Multiplicities

(ω, cm. ⁻¹)	(g)
859 (1)	859 (1)
524 (2)	524 (2)
2064 (1)	2064 (1)

Rotational Constant, B₀₀₀ = 0.20287 cm.⁻¹

σ = 1

Ground State Multiplicity = 1

Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm.⁻¹):
 α₁ = 0.0006044 X₁₁ = -4.0 A₀₀₀ = 0
 α₂ = 0.0003559 X₂₂ = -11.5 C₀₀₀ = 0
 α₃ = 0.001838 X₃₃ = -7.0 D₀₀₀ = 4.37 X 10⁻⁸
 ε₂₂ = 3.2 X₁₃ = -4.5

Heat of Formation

E. Ferrer and H. Wesemann, *Angew. Chem.* **45**, 795 (1932), report equilibrium constants from 823° to 873°K for the reaction COS(g) + H₂O(g) = COS(g) + H₂O(g). These yield ΔH_f⁰ 700 = 8.19 ± 0.23 kcal, whence ΔH_f⁰ 298.15 for COS is -33.08 ± 0.25 kcal. mole⁻¹. The same authors report equilibrium constants for the reaction COS(g) + H₂S(g) = CS₂(g) + H₂O(g), but regard these as less reliable than the others. The resulting value of -26.39 kcal. mole⁻¹ for ΔH_f⁰ 298.15 of COS has been disregarded.

Heat Capacity and Entropy

J. S. Gordon (private communication, February 1961) has used the constants listed above to calculate C_p from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, *J. Chem. Phys.* **22**, 1442 (1954), which takes anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The constants have been taken from C. A. Burrus and W. Gordy, *Phys. Rev.* **93**, 897 (1954), H. J. Callomon, D. C. McKean, and H. W. Thompson, *Proc. Roy. Soc. (London)* **A208**, 341 (1951), **A222**, 431 (1954), M. W. P. Strandberg, T. Wentink, and R. L. Kuhl, *Phys. Rev.* **75**, 270 (1949), C. H. Townes, A. N. Holden, and P. R. Merritt, *Phys. Rev.* **74**, 1113 (1948), and T. Wentink, *J. Chem. Phys.* **30**, 105 (1959). The thermodynamic functions below 298.15°K have been calculated for the rigidly rotating harmonic oscillator.

Carbon Dioxide (CO₂)

(Ideal Gas) Mol. Wt. = 44.00995

CARBON DIOXIDE (CO₂)

(IDEAL GAS)

MOL. WT. = 44.00995

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	6.981	42.758	INFINITE	2.238	93.965	93.965	INFINITE
100	7.734	47.769	51.869	816	94.028	94.191	205.645
200	8.474	51.072	51.072	800	94.054	94.265	102.922
298	8.896	53.127	51.072	8016	94.055	94.267	69.095
300	8.877	53.830	51.072	958	94.070	94.335	66.670
400	9.666	56.122	51.072	1.987	94.091	94.399	41.260
500	10.666	58.126	52.081	3.087	94.124	94.458	34.405
600	11.310	59.510	52.081	4.245	94.169	94.510	29.506
700	12.095	60.902	52.081	5.466	94.210	94.566	25.506
800	12.697	62.402	52.081	6.702	94.270	94.596	22.970
900	13.268	64.002	52.081	7.984	94.321	94.628	20.680
1000	13.815	65.594	52.081	9.266	94.371	94.658	18.806
1100	14.243	67.186	52.081	10.548	94.419	94.681	17.243
1200	14.666	68.778	52.081	11.830	94.465	94.706	15.885
1300	15.075	70.370	52.081	13.112	94.515	94.716	14.789
1400	15.475	71.962	52.081	14.394	94.562	94.728	13.801
1500	15.866	73.554	52.081	15.676	94.607	94.739	12.940
1600	16.243	75.146	52.081	16.958	94.650	94.746	12.180
1700	16.615	76.738	52.081	18.240	94.692	94.751	11.520
1800	16.981	78.330	52.081	19.522	94.734	94.755	10.958
1900	17.343	79.922	52.081	20.804	94.776	94.758	10.485
2000	17.700	81.514	52.081	22.086	94.818	94.761	10.098
2100	18.052	83.106	52.081	23.368	94.859	94.764	9.786
2200	18.400	84.698	52.081	24.650	94.900	94.767	9.541
2300	18.743	86.290	52.081	25.932	94.941	94.770	9.354
2400	19.081	87.882	52.081	27.214	94.982	94.773	9.224
2500	19.415	89.474	52.081	28.496	95.023	94.776	9.149
2600	19.743	91.066	52.081	29.778	95.064	94.779	9.124
2700	20.075	92.658	52.081	31.060	95.105	94.782	9.149
2800	20.400	94.250	52.081	32.342	95.146	94.785	9.224
2900	20.728	95.842	52.081	33.624	95.187	94.788	9.354
3000	21.052	97.434	52.081	34.906	95.228	94.791	9.541
3100	21.375	99.026	52.081	36.188	95.269	94.794	9.786
3200	21.698	100.618	52.081	37.470	95.310	94.797	10.098
3300	22.020	102.210	52.081	38.752	95.351	94.800	10.485
3400	22.343	103.802	52.081	40.034	95.392	94.803	10.958
3500	22.666	105.394	52.081	41.316	95.433	94.806	11.520
3600	22.989	106.986	52.081	42.598	95.474	94.809	12.180
3700	23.312	108.578	52.081	43.880	95.515	94.812	12.840
3800	23.635	110.170	52.081	45.162	95.556	94.815	13.520
3900	23.958	111.762	52.081	46.444	95.597	94.818	14.240
4000	24.281	113.354	52.081	47.726	95.638	94.821	15.000
4100	24.604	114.946	52.081	49.008	95.679	94.824	15.840
4200	24.927	116.538	52.081	50.290	95.720	94.827	16.760
4300	25.250	118.130	52.081	51.572	95.761	94.830	17.760
4400	25.573	119.722	52.081	52.854	95.802	94.833	18.840
4500	25.896	121.314	52.081	54.136	95.843	94.836	20.000
4600	26.219	122.906	52.081	55.418	95.884	94.839	21.240
4700	26.542	124.498	52.081	56.700	95.925	94.842	22.560
4800	26.865	126.090	52.081	57.982	95.966	94.845	23.960
4900	27.188	127.682	52.081	59.264	96.007	94.848	25.440
5000	27.511	129.274	52.081	60.546	96.048	94.851	27.000
5100	27.834	130.866	52.081	61.828	96.089	94.854	28.640
5200	28.157	132.458	52.081	63.110	96.130	94.857	30.360
5300	28.480	134.050	52.081	64.392	96.171	94.860	32.160
5400	28.803	135.642	52.081	65.674	96.212	94.863	34.040
5500	29.126	137.234	52.081	66.956	96.253	94.866	36.000
5600	29.449	138.826	52.081	68.238	96.294	94.869	38.040
5700	29.772	140.418	52.081	69.520	96.335	94.872	40.160
5800	30.095	142.010	52.081	70.802	96.376	94.875	42.360
5900	30.418	143.602	52.081	72.084	96.417	94.878	44.640
6000	30.741	145.194	52.081	73.366	96.458	94.881	47.000

Dec. 31, 1960; Mar. 21, 1961; Sept. 30, 1965

Point Group D_{∞h}
S°_{298.15} = 51.07 ± 0.03 cal. deg.⁻¹ mole⁻¹
ΔH°_f 0 = -93.965 ± 0.011 kcal. mole⁻¹
ΔH°_f 298.15 = -94.054 ± 0.011 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies
ω, cm.⁻¹
1342.86 (1)
667.30 (2)
2349.30 (1)

Bond Distance: C-O = 1.16 Å
Bond Angle: O-C-O = 180°
Rotational Constant: B₀ = 0.39038 cm.⁻¹
σ° = 2

Heat of Formation.

The enthalpy change (ΔH°_f 298.15) of the reaction C(c, graphite) + O₂(g) = CO₂(g) has been measured by P. H. Dewey and D. R. Harper, *J. Res. Natl. Bur. Std.* **21**, 457 (1956), R. S. Jessup, *ibid.* **21**, 491 (1956), and E. J. Prosen and F. D. Rosini, *ibid.*, **33**, 439 (1944). Based on these data, the heat of formation (ΔH°_f 298.15) for CO₂(g) was reported to be -94.0518 ± 0.0108 kcal. mole⁻¹, using molecular weight of CO₂ = 44.010, by E. J. Prosen, R. S. Jessup and F. D. Rosini, *J. Research Natl. Bur. Standards* **33**, 447 (1944). This value was recalculated to be -94.054 ± 0.011 kcal. mole⁻¹, based on molecular weight of CO₂ = 44.011, for internal consistency.

Heat Capacity and Entropy.

The functions adopted here were obtained from H. W. Woolley, *J. Research Nat. Bur. Standards* **52**, 289 (1954) who calculated the thermodynamic functions by means of a direct summation for the naturally occurring isotopic composition. The spectroscopic constants used are essentially those selected by T. Wentnik, Jr., *J. Chem. Phys.* **30**, 105 (1959). Slightly different sets of spectroscopic constants were obtained by C. P. Courtney, *Mem. soc. roy. Liège* **18**, 496 (1957) and V. R. Stull, P. J. Wyatt and O. N. Pless, *J. Chem. Phys.* **37**, 1442 (1962). The high-resolution infrared spectrum of O₁₈ - enriched CO₂ was examined in the region 5400-1620 cm.⁻¹, using an Ebert grating Spectrometer with spectral slit widths ranging from 0.4 to 0.2 cm.⁻¹ by G. V. Barney, Ph. D. Thesis, University of Washington, 1962.

The molecular structure was reported by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc. 1945. The rotational constant, B₀, was obtained from H. W. Woolley, loc. cit. The value of bond distance, r_e, was calculated from B₀ which was derived from B₀ using B_e-B₀ = 0.0011 cm.⁻¹ given in G. Herzberg, loc. cit. The principal moment of inertia is I = 7.1495 X 10⁻³⁹ g. cm.²

Heat capacities of CO₂(g) at high pressures were reported by M. P. Vukalovich, V. V. Altunin and A. N. Gureev, *Teploenergetika*, **12** (7), 56 (1965); K. Krueger, *Ver. Daut. Ingr. Z.*, **106** (32) 1620 (1964), and M. P. Vukalovich and A. N. Gureev, *Teploenergetika*, **11** (8), 80 (1964).

Carbon Oxide Sulfide (COS)

(Ideal Gas) Mol. Wt. = 60.077

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H ^o - H ₂₉₈	kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	INFINITE	2.373	33.111	33.111	INFINITE		
100	7.077	46.387	1.676	32.948	32.948	33.111		
200	8.312	51.483	1.000	32.948	32.948	33.111		
300	9.151	55.323	0.000	33.100	33.100	33.111		
400	9.940	55.323	0.018	33.062	33.062	33.111		
500	10.559	56.390	5.726	33.735	33.735	33.111		
600	11.068	60.920	56.519	2.201	33.726	33.111		
700	12.249	63.102	57.438	3.368	34.367	34.367		
800	13.068	66.746	59.326	5.936	34.367	34.367		
900	13.370	68.303	60.239	7.258	34.367	34.367		
1000	13.621	69.725	61.117	8.408	34.367	34.367		
1100	13.829	71.034	61.960	9.981	34.367	34.367		
1200	14.005	72.245	62.767	11.373	34.367	34.367		
1300	14.153	73.372	63.540	12.781	34.367	34.367		
1400	14.280	74.425	64.260	14.203	34.367	34.367		
1500	14.390	75.414	64.990	15.636	34.367	34.367		
1600	14.485	76.346	65.671	17.080	34.367	34.367		
1700	14.569	77.227	66.325	18.533	34.367	34.367		
1800	14.643	78.062	66.954	19.994	34.367	34.367		
1900	14.710	78.855	67.560	21.461	34.367	34.367		
2000	14.770	79.611	68.144	22.935	34.367	34.367		
2100	14.824	80.333	68.707	24.415	34.367	34.367		
2200	14.874	81.024	69.251	25.900	34.367	34.367		
2300	14.920	81.686	69.778	27.390	34.367	34.367		
2400	14.962	82.322	70.287	28.884	34.367	34.367		
2500	15.002	82.934	70.761	30.382	34.367	34.367		
2600	15.038	83.523	71.200	31.884	34.367	34.367		
2700	15.073	84.091	71.724	33.390	34.367	34.367		
2800	15.106	84.640	72.176	34.899	34.367	34.367		
2900	15.137	85.170	72.615	36.411	34.367	34.367		
3000	15.167	85.684	73.042	37.926	34.367	34.367		
3100	15.194	86.182	73.458	39.444	34.367	34.367		
3200	15.223	86.665	73.863	40.965	34.367	34.367		
3300	15.250	87.134	74.258	42.489	34.367	34.367		
3400	15.275	87.589	74.644	44.015	34.367	34.367		
3500	15.300	88.032	75.020	45.544	34.367	34.367		
3600	15.324	88.464	75.387	47.075	34.367	34.367		
3700	15.347	88.884	75.746	48.609	34.367	34.367		
3800	15.370	89.293	76.096	50.144	34.367	34.367		
3900	15.392	89.693	76.441	51.682	34.367	34.367		
4000	15.414	90.083	76.777	53.223	34.367	34.367		
4100	15.436	90.464	77.106	54.765	34.367	34.367		
4200	15.457	90.836	77.429	56.310	34.367	34.367		
4300	15.477	91.200	77.745	57.857	34.367	34.367		
4400	15.496	91.556	78.053	59.405	34.367	34.367		
4500	15.516	91.905	78.359	60.956	34.367	34.367		
4600	15.537	92.246	78.657	62.509	34.367	34.367		
4700	15.557	92.580	78.950	64.068	34.367	34.367		
4800	15.576	92.908	79.237	65.620	34.367	34.367		
4900	15.595	93.229	79.519	67.179	34.367	34.367		
5000	15.614	93.545	79.797	68.739	34.367	34.367		
5100	15.633	93.854	80.069	70.302	34.367	34.367		
5200	15.651	94.158	80.337	71.866	34.367	34.367		
5300	15.670	94.456	80.601	73.432	34.367	34.367		
5400	15.688	94.749	80.860	75.000	34.367	34.367		
5500	15.706	95.037	81.115	76.569	34.367	34.367		
5600	15.724	95.320	81.366	78.141	34.367	34.367		
5700	15.742	95.599	81.614	79.714	34.367	34.367		
5800	15.760	95.873	81.857	81.289	34.367	34.367		
5900	15.777	96.142	82.097	82.866	34.367	34.367		
6000	15.795	96.407	82.333	84.445	34.367	34.367		

March 31, 1961

COS

CARBON OXIDE SULFIDE (COS)

MOL. WT. = 60.077

(IDEAL GAS)

$\Delta H_f^o = -33.11 \pm 0.25 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o = -33.08 \pm 0.25 \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = 55.323 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Vibrational Levels and Multiplicities

ω , cm. ⁻¹	ω , cm. ⁻¹
859 (1)	524 (2)
2064 (1)	2064 (1)

Rotational Constant, B₀₀₀ = 0.20287 cm.⁻¹

Ground State Multiplicity = 1

Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm.⁻¹):
 $\chi_1 = 0.0005044$ $\chi_2 = -6.8$ $\chi_3 = -11.5$
 $\chi_4 = -0.0003539$ $\chi_5 = -7.0$ $\chi_6 = -4.5$
 $\chi_7 = 0.001838$ $\chi_8 = 4.37 \times 10^{-6}$
 $\chi_9 = 3.2$

Heat of Formation

E. Terres and H. Wesemann, Angew. Chem. 45, 795 (1932), report equilibrium constants from 623° to 873°K for the reaction $\text{CO}_2(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{COS}(\text{g}) + \text{H}_2\text{O}(\text{g})$. These yield $\Delta H_f^o = 8.13 \pm 0.23 \text{ kcal.}$ whence $\Delta H_f^o = 298.15$ for COS is $-33.08 \pm 0.25 \text{ kcal. mole}^{-1}$. The same authors report equilibrium constants for the reaction $\text{COS}(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$, but regard these as less reliable than the others. The resulting value of $-26.39 \text{ kcal. mole}^{-1}$ for ΔH_f^o of COS has been disregarded.

Heat Capacity and Entropy

J. S. Gordan (private communication, February 1961) has used the constants listed above to calculate C_p from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The constants have been taken from C. A. Burrus and W. Gordy, Phys. Rev. 93, 897 (1954), H. J. Callomon, D. C. McKean, and H. W. Thompson, Proc. Roy. Soc. (London) A208, 341 (1951), A222, 431 (1954), M. W. P. Strandberg, T. Wentink, and R. L. Kynl, Phys. Rev. 75, 270 (1949), C. H. Townes, A. N. Holden, and P. R. Merritt, Phys. Rev. 74, 1113 (1948), and T. Wentink, J. Chem. Phys. 30, 105 (1959). The thermodynamic functions below 298.15°K have been calculated for the rigidly rotating harmonic oscillator.

(Ideal Gas)

Mol. Wt. = 44.00995

CARBON DIOXIDE (CO₂)

(IDEAL GAS)

MOL. WT. = 44.00995

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH° _f	Log K _p
0	-0.000	INFINITE	-	2.238	- 93.965	INFINITE
100	6.981	42.758	18.188	1.543	- 93.997	205.645
200	7.734	47.769	51.869	.816	- 94.028	102.922
298	8.874	51.072	-	.000	- 94.054	69.095
300	8.896	51.127	-	.016	- 94.055	68.670
400	9.477	53.830	51.072	.958	- 94.367	51.540
500	10.666	56.122	52.148	1.987	- 94.091	41.260
600	11.310	58.126	52.981	3.087	- 94.124	34.458
700	12.293	60.126	54.000	4.256	- 94.218	28.630
800	12.667	61.522	54.706	5.453	- 94.556	25.830
900	12.667	62.992	55.566	6.702	- 94.270	22.970
1000	12.980	64.344	56.359	7.984	- 94.321	20.680
1100	13.243	65.594	57.143	9.296	- 94.371	18.806
1200	13.465	66.781	57.920	10.640	- 94.469	17.201
1300	13.656	67.881	58.620	11.988	- 94.591	15.920
1400	13.815	68.859	59.362	13.362	- 94.515	14.785
1500	13.953	69.817	59.984	14.750	- 94.562	13.801
1600	14.074	70.722	60.627	16.152	- 94.607	12.940
1700	14.178	71.587	61.287	17.569	- 94.650	12.150
1800	14.269	72.391	61.963	18.987	- 94.690	11.506
1900	14.352	73.165	62.648	20.418	- 94.742	10.968
2000	14.424	73.903	62.974	21.857	- 94.788	10.533
2100	14.489	74.608	63.512	23.303	- 94.834	9.860
2200	14.547	75.287	64.055	24.757	- 94.936	9.001
2300	14.600	75.931	64.535	26.212	- 94.735	8.254
2400	14.648	76.554	65.023	27.674	- 94.991	8.625
2500	14.692	77.153	65.466	28.141	- 95.048	8.280
2600	14.734	77.730	65.956	30.613	- 95.107	7.960
2700	14.771	78.284	66.400	33.267	- 95.235	7.580
2800	14.807	78.824	67.259	35.049	- 94.662	7.388
2900	14.841	79.344	67.259	35.049	- 94.639	7.132
3000	14.873	79.848	67.670	36.535	- 95.377	6.892
3100	14.902	80.336	68.071	38.024	- 95.451	6.668
3200	14.928	80.810	68.436	39.516	- 95.521	6.450
3300	14.956	81.270	68.863	41.010	- 95.611	6.250
3400	14.982	81.717	69.215	42.507	- 95.696	6.074
3500	15.006	82.151	69.578	44.006	- 95.784	5.898
3600	15.030	82.574	69.933	45.508	- 95.874	5.732
3700	15.053	82.986	70.280	47.016	- 95.964	5.572
3800	15.075	83.388	70.620	48.518	- 96.064	5.425
3900	15.097	83.780	70.953	50.027	- 96.162	5.283
4000	15.119	84.162	71.278	51.538	- 96.263	5.149
4100	15.139	84.536	71.597	53.051	- 96.367	5.020
4200	15.158	84.901	71.909	54.566	- 96.473	4.898
4300	15.179	85.258	72.216	56.082	- 96.583	4.781
4400	15.197	85.607	72.516	57.601	- 96.694	4.670
4500	15.216	85.949	72.811	59.122	- 96.807	4.563
4600	15.234	86.286	73.100	60.644	- 96.923	4.460
4700	15.254	86.611	73.384	62.169	- 97.040	4.362
4800	15.272	86.933	73.663	63.695	- 97.160	4.268
4900	15.290	87.248	73.937	65.223	- 97.281	4.178
5000	15.306	87.557	74.206	66.753	- 97.404	4.091
5100	15.327	87.860	74.471	68.285	- 97.530	4.008
5200	15.349	88.158	74.731	69.819	- 97.656	3.927
5300	15.371	88.451	74.988	71.355	- 97.783	3.850
5400	15.393	88.738	75.239	72.893	- 97.912	3.775
5500	15.415	89.021	75.488	74.433	- 98.042	3.703
5600	15.437	89.299	75.732	75.976	- 98.173	3.633
5700	15.459	89.572	75.972	77.521	- 98.305	3.566
5800	15.481	89.841	76.209	79.068	- 98.438	3.501
5900	15.503	90.106	76.442	80.617	- 98.572	3.438
6000	15.525	90.367	76.672	82.168	- 98.707	3.377

Dec. 31, 1960; Mar. 21, 1961; Sept. 30, 1965

Point Group D_{∞h} $\Delta H_f^0 = -85.985 \pm 0.011 \text{ kcal. mole}^{-1}$ $\Delta H_f^{298.15} = -94.054 \pm 0.011 \text{ kcal. mole}^{-1}$ $S_{298.15}^0 = 51.07 \pm 0.03 \text{ cal. deg}^{-1} \text{ mole}^{-1}$

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹
1342.86 (1)
667.30 (2)
2349.30 (1)

Bond Distance: C-O = 1.16 Å

Bond Angle: O-C-O = 180°

Rotational Constant: B₀ = 0.39038 cm⁻¹

σ = 2

Heat of Formation.

The enthalpy change ($\Delta H_f^{298.15}$) of the reaction C(c, graphite) + O₂(g) = CO₂(g) has been measured by P. H. Dewey and D. R. Harper, *J. Res. Natl. Bur. Std.* **21**, 457 (1938), R. S. Jessup, *ibid.* **21**, 491 (1938), and E. J. Frosen and F. D. Rossini, *ibid.*, **33**, 439 (1944). Based on these data, the heat of formation ($\Delta H_f^{298.15}$) for CO₂(g) was reported to be -94.0518 ± 0.0108 kcal. mole⁻¹, using molecular weight of CO₂ = 44.010, by E. J. Frosen, R. S. Jessup and F. D. Rossini, *J. Research Natl. Bur. Standards* **33**, 447 (1944). This value was recalculated to be -94.054 ± 0.011 kcal. mole⁻¹, based on molecular weight of CO₂ = 44.011, for internal consistency.

Heat Capacity and Entropy.

The functions adopted here were obtained from H. W. Woolley, *J. Research Nat. Bur. Standards* **52**, 289 (1954) who calculated the thermodynamic functions by means of a direct summation for the naturally occurring isotopic composition.

The spectroscopic constants used are essentially those selected by T. Wentnik, Jr., *J. Chem. Phys.* **30**, 105 (1959). Slightly different sets of spectroscopic constants were obtained by C. P. Courtney, *Mem. acc. roy. Liège* **18**, 496 (1957) and V. R. Stull, P. J. Wyatt and O. N. Pless, *J. Chem. Phys.* **37**, 1442 (1962). The high-resolution infrared spectrum of O₁₈ - enriched CO₂ was examined in the region 5400-1620 cm⁻¹, using an Ebert grating Spectrometer with spectral slit widths ranging from 0.4 to 0.2 cm⁻¹ by C. V. Barney, Ph. D. Thesis, University of Washington, 1962.

The molecular structure was reported by O. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc. 1945. The rotational constant, B₀, was obtained from H. W. Woolley, loc. cit. The value of bond distance, r_e, was calculated from B₀ which was derived from B₀, using B₀-B₀ = 0.0011 cm⁻¹ given in G. Herzberg, loc. cit. The principal moment of inertia is I = 7.1495 × 10⁻³⁹ g. cm².

Heat capacities of CO₂(g) at high pressures were reported by M. P. Vukobratovich, V. V. Altunin and A. N. Gureev, *Teploenergetika*, **12** (7), 56 (1965); K. Krueger, *Ver. Daut. Ingr. Z.*, **106** (32) 1620 (1964), and M. P. Vukobratovich and A. N. Gureev, *Teploenergetika*, **11** (8), 80 (1964).

Carbon Dioxide Unequivocal Ion (CO₂⁻)
(Ideal Gas) GFW = 44.0105

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0						
100						
200						
298	8.746	57.489	•000	- 105.500	- 106.137	77.801
300	8.759	57.543	•016	- 105.510	- 106.141	77.824
400	8.797	57.811	•099	- 105.540	- 106.171	78.041
500	10.226	62.362	1.915	- 106.612	- 106.261	40.447
600	10.864	64.284	2.971	- 107.186	- 106.138	38.661
700	11.369	66.000	4.084	- 107.772	- 105.915	33.068
800	11.811	67.549	5.245	- 108.365	- 105.611	28.951
900	12.149	68.860	6.461	- 108.964	- 105.231	25.554
1000	12.417	70.255	8.292	- 109.566	- 104.784	22.950
1100	12.632	71.449	8.925	- 110.172	- 104.278	20.718
1200	12.807	72.555	64.058	- 110.781	- 103.714	18.869
1300	12.950	73.586	64.751	- 111.395	- 103.099	17.333
1400	13.068	74.551	65.417	- 112.016	- 102.439	15.991
1500	13.166	75.456	66.057	- 112.631	- 101.733	14.822
1600	13.249	76.308	66.671	- 113.254	- 100.987	13.794
1700	13.318	77.113	67.262	- 113.878	- 100.200	12.882
1800	13.378	77.876	67.830	- 114.507	- 99.377	12.066
1900	13.431	78.601	68.378	- 115.141	- 98.520	11.332
2000	13.479	79.291	68.907	- 115.778	- 97.630	10.688
2100	13.512	79.949	69.417	- 116.417	- 96.703	10.064
2200	13.546	80.579	69.910	- 117.065	- 95.753	9.512
2300	13.575	81.182	70.487	- 117.712	- 94.768	9.005
2400	13.602	81.766	71.035	- 118.360	- 93.750	8.516
2500	13.625	82.330	71.567	- 119.027	- 92.720	8.100
2600	13.646	82.880	72.091	- 119.692	- 91.651	7.704
2700	13.664	83.366	72.513	- 120.361	- 90.564	7.331
2800	13.681	83.863	72.962	- 121.035	- 89.445	6.982
2900	13.696	84.366	73.427	- 121.714	- 88.300	6.658
3000	13.710	84.898	73.907	- 122.399	- 87.140	6.348
3100	13.722	85.258	73.724	- 123.087	- 85.952	6.060
3200	13.734	85.694	74.091	- 123.781	- 84.748	5.788
3300	13.744	86.116	74.469	- 124.480	- 83.517	5.531
3400	13.754	86.526	74.866	- 125.183	- 82.262	5.288
3500	13.762	86.926	75.139	- 125.892	- 80.997	5.058
3600	13.770	87.313	75.472	- 126.604	- 79.700	4.838
3700	13.777	87.691	75.797	- 127.322	- 78.385	4.630
3800	13.784	88.058	76.115	- 128.043	- 77.050	4.431
3900	13.790	88.416	76.426	- 128.768	- 75.693	4.242
4000	13.796	88.766	76.730	- 129.497	- 74.333	4.061
4100	13.802	89.106	77.028	- 130.231	- 72.941	3.888
4200	13.807	89.439	77.320	- 130.968	- 71.538	3.723
4300	13.811	89.764	77.605	- 131.710	- 70.133	3.564
4400	13.815	90.082	77.884	- 132.456	- 68.718	3.411
4500	13.819	90.392	78.160	- 133.204	- 67.290	3.264
4600	13.824	90.696	78.429	- 133.957	- 65.849	3.123
4700	13.827	90.993	78.693	- 134.713	- 64.246	2.987
4800	13.831	91.284	78.952	- 135.473	- 62.734	2.856
4900	13.835	91.570	79.207	- 136.236	- 61.222	2.731
5000	13.837	91.844	79.457	- 137.002	- 59.682	2.609
5100	13.840	92.123	79.703	- 137.773	- 58.126	2.491
5200	13.842	92.392	79.944	- 138.546	- 56.563	2.377
5300	13.845	92.656	80.181	- 139.321	- 54.972	2.267
5400	13.848	92.914	80.415	- 140.101	- 53.371	2.160
5500	13.850	93.168	80.644	- 140.883	- 51.755	2.057
5600	13.852	93.418	80.870	- 141.668	- 50.130	1.956
5700	13.854	93.663	81.093	- 142.457	- 48.498	1.860
5800	13.856	93.904	81.311	- 143.248	- 46.835	1.765
5900	13.857	94.141	81.527	- 144.043	- 45.164	1.673
6000	13.859	94.374	81.739	- 144.840	- 43.488	1.584

June 30, 1966; Dec. 31, 1966

CARBON DIOXIDE UNEQUIVOCAL ION (CO₂⁻) (IDEAL GAS) GFW = 44.0105

Point group [C_{2v}]

S°_{298.15} = [57.5] gibbs/mol

Ground State Quantum Weight = [2]

ΔHf°₀ = [-104.1 ± 27] kcal/mol

ΔHf°_{298.15} = [-105.5 ± 27] kcal/mol

Vibrational Frequencies and Degeneracies

ω cm ⁻¹
[1400] (1)
[800] (1)
1671 (1)

Bond Distance: C-O = [1.25] Å

Bond Angle: O-C-O = 127° ± 8°

Product of the Moments of Inertia: I_AI_BI_C = [2.1296] × 10⁻¹¹⁶ g³ cm⁶

σ = [2]

Heat of Formation

The heat of formation, ΔHf°₂₉₈ (CO₂⁻, g) = -105.5 ± 27 kcal/mol, is estimated from ΔHf°₂₉₈ = 88.6 ± 10 kcal/mol for HCO₂⁻(g) → H(g) + CO₂⁻(g), using the ΔHf°₂₉₈ (HCO₂⁻, g) = -142 ± 17 kcal/mol and ΔHf°₂₉₈ (H, g) = 52.1 kcal/mol. The value of ΔHf°₂₉₈ is assumed to be the same as that for HCOOH(g) → H(g) + COOH(g). The values of ΔHf°₂₉₈ (HCOOH, g) and ΔHf°₂₉₈ (H, g), -90.5 and 52.1 kcal/mol, respectively, are from "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Std. Tech. Note 270-1, Washington, D. C., Oct. 1965, and the value of ΔHf°₂₉₈ (COOH, g), -54 ± 3 kcal/mol, is from S. W. Benson, J. Chem. Ed. 42, 502 (1965). The value of ΔHf°₂₉₈ (HCO₂⁻, g) is estimated from an approximate lattice energy calculation for sodium formate. The derived electron affinity of CO₂(g) is 11.5 kcal/mol (0.5 eV) with an estimated uncertainty range of 0-40 kcal/mol.

Heat Capacity and Entropy

The correlations of A. D. Walsh, J. Chem. Soc. 1953, 2266, predict a bent molecular structure for CO₂⁻ based on its 17 valence electrons. K. O. Hartman and I. C. Hisataune, J. Chem. Phys. 44, 1913 (1966), measured the asymmetric C-O stretching frequency and derived the bond angle of 127° ± 8° from the infrared spectrum of matrix-isolated CO₂⁻. They also estimated the bond distance C-O and the symmetric stretching and the bending vibrational frequencies by the valence force method. These molecular constants are adopted in the tabulation. The three principal moments of inertia are I_A = 0.4511 × 10⁻³⁵, I_B = 6.6491 × 10⁻³⁵ and I_C = 7.1002 × 10⁻³⁵ g cm².

D. W. Overall and D. H. Whiffen, Mol. Phys. 4, 135 (1961), have derived a bond angle of 134° which is in good agreement with the value selected. This result was obtained from electron spin resonance for the CO₂⁻ radical trapped in sodium formate.

Carbon Phosphide (CP)

(Ideal Gas) Mol. Wt. = 42.986

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	Log K _p
0	0.000	0.000	INFINITE	- 2.083	110.731	INFINITE
100	6.957	44.923	57.505	- 1.388	111.321	- 234.031
200	6.981	48.848	57.308	- .692	112.719	- 112.241
298	7.149	51.661	51.661	0.000	111.700	98.337 = 72.072
300	7.154	51.705	51.661	.013	98.244	
400	7.450	55.245	51.661	1.502	88.764	- 71.568
500	7.741	58.598	51.661	1.502	111.520	- 39.034
600	7.989	56.930	53.115	2.289	111.328	84.879 = 30.916
700	8.184	58.177	53.751	3.098	111.079	80.490 = 25.129
800	8.335	59.280	54.274	3.925	90.364	70.830 = 19.349
900	8.454	60.269	54.693	4.764	84.879	64.879 = 16.610
1000	8.545	61.164	55.050	5.614	90.185	65.965 = 14.410
1100	8.619	61.982	56.098	6.473	90.080	63.547 = 12.625
1200	8.679	62.735	56.920	7.338	89.066	61.141 = 11.135
1300	8.728	63.432	57.118	8.208	89.843	58.744 = 9.875
1400	8.768	64.086	57.683	9.082	89.586	56.451 = 8.784
1500	8.805	64.686	58.045	9.962	89.580	53.980 = 7.864
1600	8.835	65.256	58.478	10.844	89.451	51.608 = 7.049
1700	8.861	65.792	58.893	11.729	89.314	49.248 = 6.331
1800	8.884	66.299	59.290	12.616	89.174	46.895 = 5.694
1900	8.905	66.778	59.668	13.505	88.985	44.581 = 5.138
2000	8.923	67.237	60.033	14.397	88.889	42.212 = 4.613
2100	8.940	67.673	60.392	15.290	88.745	39.884 = 4.151
2200	8.955	68.089	60.733	16.185	88.598	37.559 = 3.731
2300	8.969	68.486	61.061	17.081	88.451	35.244 = 3.349
2400	8.982	68.865	61.378	17.977	88.304	32.944 = 2.984
2500	8.994	69.237	61.688	18.877	88.153	30.630 = 2.678
2600	9.005	69.590	61.983	19.777	88.001	28.330 = 2.381
2700	9.016	69.930	62.271	20.678	87.849	26.037 = 2.107
2800	9.026	70.258	62.552	21.581	87.698	23.771 = 1.854
2900	9.036	70.578	62.827	22.487	87.546	21.541 = 1.618
3000	9.045	70.881	63.085	23.388	87.389	19.366 = 1.398
3100	9.054	71.178	63.341	24.293	87.234	16.926 = 1.193
3200	9.063	71.465	63.591	25.199	87.077	14.659 = 1.001
3300	9.071	71.744	63.834	26.105	86.919	12.397 = .821
3400	9.078	72.017	64.071	27.011	86.762	10.140 = .659
3500	9.087	72.279	64.301	27.921	86.600	7.890 = .493
3600	9.095	72.535	64.526	28.830	86.439	5.642 = .342
3700	9.102	72.784	64.746	29.740	86.277	3.401 = .201
3800	9.109	73.027	64.961	30.651	86.115	1.166 = .060
3900	9.117	73.265	65.171	31.562	85.955	- 1.069 = -.080
4000	9.124	73.495	65.376	32.474	85.785	- 3.297 = -.480
4100	9.131	73.720	65.577	33.387	85.619	- 5.524 = -.894
4200	9.137	73.940	65.773	34.300	85.450	- 7.739 = -1.303
4300	9.144	74.155	65.966	35.214	85.280	- 9.961 = -1.706
4400	9.151	74.365	66.155	36.128	85.111	- 12.181 = -2.103
4500	9.157	74.571	66.339	37.044	84.937	- 14.383 = -2.498
4600	9.164	74.772	66.520	37.960	84.764	- 16.569 = -2.888
4700	9.170	74.970	66.698	38.877	84.590	- 18.789 = -3.274
4800	9.176	75.165	66.873	39.794	84.415	- 20.984 = -3.655
4900	9.182	75.352	67.042	40.712	84.235	- 23.177 = -4.030
5000	9.189	75.538	67.211	41.631	84.056	- 25.367 = -4.399
5100	9.195	75.720	67.376	42.550	83.873	- 27.560 = -4.764
5200	9.201	75.898	67.539	43.470	83.691	- 29.743 = -5.125
5300	9.207	76.073	67.700	44.390	83.508	- 31.906 = -5.481
5400	9.213	76.245	67.858	45.311	83.320	- 34.056 = -5.834
5500	9.219	76.415	68.009	46.233	83.132	- 36.266 = -6.181
5600	9.225	76.581	68.160	47.155	82.942	- 38.437 = -6.521
5700	9.231	76.744	68.310	48.078	82.750	- 40.605 = -6.857
5800	9.237	76.904	68.458	49.000	82.558	- 42.764 = -7.188
5900	9.243	77.063	68.603	49.925	82.361	- 44.924 = -7.514
6000	9.248	77.218	68.743	50.850	82.164	- 47.083 = -7.835

June 30, 1962

CARBON PHOSPHIDE (CP)

(IDEAL GAS)

MOL. WT. = 42.986

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$S_0^{298.15} = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$

Carbon Monosulphide (CS)

(Ideal Gas) Mol. Wt. = 44.077

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100	6.900	∞	∞	54.224	54.224	INFINITE
100	6.957	42.653	2.081	54.740	50.791	-110.999
200	6.972	47.426	1.387	54.740	48.736	-31.069
298	7.122	50.299	0.000	55.000	42.684	-31.287
300	7.126	50.343	0.013	54.999	42.607	-31.038
400	7.401	52.429	0.739	54.380	38.508	-21.039
500	7.690	54.112	1.494	53.878	34.598	-15.122
600	7.939	55.537	2.276	53.425	30.785	-11.213
700	8.137	56.776	3.080	53.004	27.069	-8.451
800	8.293	57.873	3.902	52.642	22.125	-6.044
900	8.415	58.858	4.737	52.352	19.952	-4.845
1000	8.512	59.749	5.584	52.116	17.791	-3.888
1100	8.589	60.564	6.439	51.921	15.638	-3.107
1200	8.651	61.314	7.301	51.763	13.499	-2.458
1300	8.703	62.009	8.169	51.639	11.369	-1.911
1400	8.746	62.656	9.041	51.535	9.250	-1.444
1500	8.783	63.260	9.918	51.451	7.137	-1.040
1600	8.814	63.828	10.798	51.383	5.030	-0.688
1700	8.841	64.363	11.681	51.330	2.942	-0.378
1800	8.865	64.869	12.566	51.290	0.857	-0.104
1900	8.886	65.349	13.453	51.264	-1.217	-0.140
2000	8.904	65.805	14.343	51.251	-3.287	-0.359
2100	8.921	66.240	15.234	51.247	-5.348	-0.557
2200	8.937	66.656	16.127	51.250	-7.403	-0.735
2300	8.951	67.053	17.022	51.260	-9.450	-0.898
2400	8.964	67.435	17.917	51.277	-11.491	-1.046
2500	8.976	67.801	18.814	51.300	-13.526	-1.182
2600	8.987	68.151	19.713	51.328	-15.555	-1.307
2700	8.998	68.492	20.612	51.360	-17.580	-1.423
2800	9.008	68.820	21.512	51.396	-19.597	-1.530
2900	9.018	69.136	22.413	51.436	-21.607	-1.628
3000	9.027	69.442	23.316	51.480	-23.612	-1.720
3100	9.036	69.738	24.219	51.526	-25.612	-1.806
3200	9.044	70.025	25.123	51.574	-27.608	-1.885
3300	9.052	70.303	26.028	51.624	-29.602	-1.960
3400	9.060	70.574	26.933	51.674	-31.594	-2.030
3500	9.067	70.837	27.839	51.726	-33.586	-2.096
3600	9.075	71.092	28.747	51.780	-35.576	-2.158
3700	9.082	71.341	29.654	51.834	-37.564	-2.216
3800	9.089	71.583	30.563	51.888	-39.550	-2.271
3900	9.095	71.819	31.472	51.942	-41.534	-2.322
4000	9.102	72.050	32.382	52.000	-43.517	-2.371
4100	9.109	72.274	33.292	52.058	-45.500	-2.418
4200	9.115	72.494	34.202	52.116	-47.482	-2.461
4300	9.121	72.709	35.115	52.174	-49.464	-2.503
4400	9.128	72.918	36.028	52.232	-51.446	-2.543
4500	9.134	73.124	36.941	52.290	-53.428	-2.580
4600	9.140	73.324	37.855	52.348	-55.410	-2.616
4700	9.146	73.521	38.769	52.406	-57.392	-2.650
4800	9.152	73.714	39.684	52.464	-59.374	-2.682
4900	9.157	73.902	40.599	52.522	-61.356	-2.713
5000	9.163	74.087	41.515	52.580	-63.338	-2.743
5100	9.169	74.269	42.432	52.638	-65.320	-2.771
5200	9.175	74.447	43.350	52.696	-67.302	-2.798
5300	9.180	74.622	44.267	52.754	-69.284	-2.824
5400	9.186	74.793	45.185	52.812	-71.266	-2.849
5500	9.191	74.962	46.104	52.870	-73.248	-2.873
5600	9.197	75.128	47.023	52.928	-75.230	-2.895
5700	9.202	75.291	47.943	52.986	-77.212	-2.917
5800	9.208	75.451	48.864	53.044	-79.194	-2.938
5900	9.213	75.608	49.785	53.102	-81.176	-2.958
6000	9.219	75.763	50.706	53.160	-83.158	-2.977

Dec. 31, 1980; Dec. 31, 1982

CS

CARBON MONOSULPHIDE (CS) (IDEAL GAS)

MOL. WT. = 44.077

$$\Delta H_f^0 = 54.2 \pm 5 \text{ kcal. mole}^{-1}$$

$$\Delta H_{298.15}^0 = 55.0 \pm 5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 50.3 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Configuration $\sum^+$

Electronic Level and Multiplicity

$$\epsilon, \text{ cm.}^{-1} \quad \frac{g_1}{g_0}$$

$$\omega_e x_e = 6.46 \text{ cm.}^{-1}$$

$$\alpha_e = 0.82005 \text{ cm.}^{-1}$$

$$r_e = 1.535 \text{ \AA}$$

Heat of Formation.

A. Lagerqvist, H. Westerlund, C. V. Wright and R. P. Barrow, Arkiv for Fysik **14**, 387 (1958) examined the UV band system of CS and made a new extrapolation of the ground state vibrational levels to find $D_0^0 = 7.85 \text{ e.v.}$, which leads to $\Delta H_f^0 \text{ CS} = 55 \pm 5.0 \text{ kcal. mole}^{-1}$. H. Scharfer and H. Wiedemeier, Paper presented at the XVIIIth IUPAC Congress Montreal (1961). have measured $\Delta H_f^0 \text{ CS} = 55 \pm 3 \text{ kcal. mole}^{-1}$ by an equilibrium method and found $58 \pm 3 \text{ kcal. mole}^{-1}$. E. Gallegos and R. W. Kiser, J. Phys. Chem. **65**, 1177 (1961) obtained a value of $\Delta H_f^0 \text{ CS(g)} = 55.0 \text{ kcal. mole}^{-1}$ from the heat of formation of CS^+ and the ionization potential of CS. C. J. Fincham and R. A. Bergman, J. Metals, **9**, 680 (1957) measured the equilibrium between CS_2 and sulphur containing ore. Combining these with similar experiments for H_2S the heat of formation of CS at 298 K is calculated to be $69.0 \text{ kcal. mole}^{-1}$. The gases assumed are CS_2 , CS, S, S_2 , H_2 , H_2S , and HS — because of the complex equilibria and the use of outside data for the H_2S equilibrium, the assumption of $P_{\text{H}_2} = 1 \text{ atm.}$ and the uncertainty in HS values, this value was given no weight.

Heat Capacity and Entropy.

A. Lagerqvist, et al., loc. cit., give the vibrational constants. The rotational constants are from the microwave measurements of R. C. Mockler and R. Bird, Phys. Rev. **98**, 1837 (1955).

Carbon Disulfide (CS₂)

(Ideal Gas) Mol. Wt. = 76.143

CS₂CARBON DISULFIDE (CS₂) (IDEAL GAS)

MOL. WT. = 76.143

T, °K.	C _p	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	7.000	0.000	INF	0.000	27.787	27.787	INF
100	7.009	47.009	2.451	27.787	27.787	27.787	27.787
200	7.461	52.776	1.004	28.128	28.128	28.128	28.128
298	10.675	56.632	0.000	29.860	29.860	29.860	29.860
300	10.685	56.699	0.000	29.860	29.860	29.860	29.860
400	11.650	60.136	0.020	27.976	27.976	27.976	27.976
500	12.480	62.680	2.375	25.492	25.492	25.492	25.492
600	12.974	65.200	3.649	24.874	24.874	24.874	24.874
700	13.346	67.230	4.866	24.166	24.166	24.166	24.166
800	13.638	68.931	6.016	23.383	23.383	23.383	23.383
900	13.858	70.121	7.091	22.556	22.556	22.556	22.556
1000	14.033	72.121	8.1035	21.686	21.686	21.686	21.686
1100	14.172	73.465	9.097	20.782	20.782	20.782	20.782
1200	14.283	74.703	10.071	19.843	19.843	19.843	19.843
1300	14.375	75.850	11.019	18.870	18.870	18.870	18.870
1400	14.450	76.916	11.942	17.873	17.873	17.873	17.873
1500	14.513	77.917	12.845	16.856	16.856	16.856	16.856
1600	14.567	78.856	13.726	15.820	15.820	15.820	15.820
1700	14.612	79.740	14.586	14.767	14.767	14.767	14.767
1800	14.650	80.579	15.428	13.698	13.698	13.698	13.698
1900	14.682	81.370	16.253	12.615	12.615	12.615	12.615
2000	14.716	82.124	17.066	11.518	11.518	11.518	11.518
2100	14.742	82.843	17.866	10.408	10.408	10.408	10.408
2200	14.769	83.529	18.644	9.285	9.285	9.285	9.285
2300	14.796	84.182	19.401	8.149	8.149	8.149	8.149
2400	14.806	84.816	20.138	7.000	7.000	7.000	7.000
2500	14.824	85.420	20.856	5.838	5.838	5.838	5.838
2600	14.839	86.002	21.556	4.663	4.663	4.663	4.663
2700	14.854	86.562	22.238	3.476	3.476	3.476	3.476
2800	14.867	87.102	22.902	2.276	2.276	2.276	2.276
2900	14.880	87.625	23.548	1.063	1.063	1.063	1.063
3000	14.892	88.139	24.176	0.000	0.000	0.000	0.000
3100	14.902	88.648	24.789	0.000	0.000	0.000	0.000
3200	14.913	89.143	25.386	0.000	0.000	0.000	0.000
3300	14.923	89.624	25.968	0.000	0.000	0.000	0.000
3400	14.931	89.996	26.535	0.000	0.000	0.000	0.000
3500	14.940	90.459	27.088	0.000	0.000	0.000	0.000
3600	14.948	90.890	27.628	0.000	0.000	0.000	0.000
3700	14.956	91.299	28.154	0.000	0.000	0.000	0.000
3800	14.963	91.687	28.667	0.000	0.000	0.000	0.000
3900	14.971	92.057	29.167	0.000	0.000	0.000	0.000
4000	14.977	92.426	29.654	0.000	0.000	0.000	0.000
4100	14.984	92.796	30.128	0.000	0.000	0.000	0.000
4200	14.991	93.157	30.588	0.000	0.000	0.000	0.000
4300	14.997	93.509	31.035	0.000	0.000	0.000	0.000
4400	15.003	93.855	31.469	0.000	0.000	0.000	0.000
4500	15.009	94.192	31.891	0.000	0.000	0.000	0.000
4600	15.015	94.522	32.300	0.000	0.000	0.000	0.000
4700	15.021	94.846	32.696	0.000	0.000	0.000	0.000
4800	15.026	95.164	33.079	0.000	0.000	0.000	0.000
4900	15.031	95.477	33.450	0.000	0.000	0.000	0.000
5000	15.037	95.775	33.811	0.000	0.000	0.000	0.000
5100	15.042	96.073	34.162	0.000	0.000	0.000	0.000
5200	15.047	96.365	34.501	0.000	0.000	0.000	0.000
5300	15.052	96.653	34.829	0.000	0.000	0.000	0.000
5400	15.057	96.933	35.146	0.000	0.000	0.000	0.000
5500	15.062	97.209	35.454	0.000	0.000	0.000	0.000
5600	15.066	97.481	35.754	0.000	0.000	0.000	0.000
5700	15.071	97.749	36.046	0.000	0.000	0.000	0.000
5800	15.076	98.013	36.331	0.000	0.000	0.000	0.000
5900	15.080	98.287	36.611	0.000	0.000	0.000	0.000
6000	15.085	98.521	36.886	0.000	0.000	0.000	0.000

June 30, 1961

ΔH_f° = 27.79 ± 0.19 kcal. mole⁻¹
ΔH_f° 298.15 = 27.98 ± 0.19 kcal. mole⁻¹
Point Group D_{∞h}
S_{298.15} = 56.633 cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

(0), cm. ⁻¹	(1)	(2)
658	(1)	396.8 (2)
1532.5	(1)	

Bond Length and Angle C-S dist. = 1.553 Å S-C-S angle = 180°

Moment of Inertia I = 25.6805 X 10⁻³⁹ g. cm.²

Heat of Formation

W. Good and J. P. McCullough, private communication, September 21, 1960, report ΔH_f° 298.15 from analysis of combustion calorimetry data of CS₂.

Heat Capacity and Entropy

Functions at 100° and 200°K were calculated by the RRHO approximation using the fundamental vibrational levels of T. Wentink, Jr., J. Chem. Phys. 29, 188 (1958) calculated from zero order levels reported by B. P. Stoicheff, Can. J. Phys. 36, 218 (1958). S_{298.15} and C_p from 298.15° to 6000°K taken from J. S. Gordon, private communication, February 7, 1961. In addition to the fundamental levels listed above, Gordon, in his calculation of this function, used the anharmonic constants derived from high resolution Raman spectra by Stoicheff, and the vibration-rotation interaction constants reported by A. H. Guenther, T. A. Wiggins and D. H. Rank, J. Chem. Phys. 28, 682 (1958).

J. P. McCullough, private communication, February 17, 1961, has correlated and summarized the experimental thermodynamic data for CS₂ by a set of empirical equations. The result for C_p is

$$C_p (\pm 0.5\%) = 6.478 + 1.8931 \times 10^{-2} T - 1.3873 \times 10^{-5} T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \text{ (325-502°K.)}$$

The experimental values of C_p were then fit within 0.08% by a given set of molecular parameters different from that used by Gordon. However, in the temperature range given above, Gordon's calculation is within the uncertainty indicated by McCullough.

Since no method of calculating anharmonic corrections for polyatomic molecules has been programmed, Gordon's values were employed.

CS₂

SILICON CARBIDE, ALPHA (SiC)

(CRYSTAL)

OPW = 40.09715

T, °K	Cp ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0	-0.000	INFINITE	-	.777	-16.956	-	INFINITE
100	1.003	1.201	4.492	-	-16.762	-	9.905
200	2.001	2.402	-	-510	-17.026	-	10.213
298	6.396	3.940	-	-	-17.100	-	12.039
300	6.437	3.980	-	-	-17.101	-	12.039
400	8.150	6.086	4.216	.748	-17.118	-	12.039
500	9.228	8.079	4.787	1.621	-17.100	-	12.039
600	9.972	9.781	5.476	2.583	-17.077	-	12.039
700	10.518	11.361	6.206	3.604	-17.072	-	12.039
800	10.939	12.794	6.941	4.682	-17.062	-	12.039
900	11.274	14.102	7.665	5.793	-17.050	-	12.039
1000	11.549	15.305	8.370	6.935	-17.038	-	12.039
1100	11.779	16.417	9.051	8.102	-17.029	-	12.039
1200	11.976	17.450	9.709	9.290	-17.022	-	12.039
1300	12.147	18.416	10.342	10.496	-17.020	-	12.039
1400	12.297	19.321	10.951	11.718	-17.019	-	12.039
1500	12.431	20.174	11.538	12.951	-17.021	-	12.039
1600	12.552	20.981	12.103	14.204	-17.027	-	12.039
1700	12.661	21.745	12.648	15.465	-17.028	-	12.039
1800	12.762	22.472	13.174	16.736	-17.036	-	12.039
1900	12.854	23.168	13.681	18.017	-17.046	-	12.039
2000	12.940	23.836	14.172	19.307	-17.058	-	12.039
2100	13.020	24.479	14.637	20.605	-17.071	-	12.039
2200	13.094	25.096	15.107	21.910	-17.084	-	12.039
2300	13.165	25.650	15.553	23.223	-17.096	-	12.039
2400	13.232	26.212	15.985	24.543	-17.107	-	12.039
2500	13.296	26.753	16.405	25.870	-17.116	-	12.039
2600	13.356	27.276	16.813	27.202	-17.124	-	12.039
2700	13.414	27.781	17.210	28.541	-17.130	-	12.039
2800	13.470	28.270	17.597	29.885	-17.135	-	12.039
2900	13.523	28.743	17.973	31.247	-17.139	-	12.039
3000	13.575	29.203	18.340	32.599	-17.142	-	12.039
3100	13.625	29.649	18.697	33.950	-17.145	-	12.039
3200	13.673	30.082	19.046	35.314	-17.147	-	12.039
3300	13.720	30.503	19.379	36.684	-17.149	-	12.039
3400	13.765	30.914	19.700	38.054	-17.150	-	12.039
3500	13.810	31.313	20.006	39.437	-17.151	-	12.039
3600	13.853	31.703	20.344	40.820	-17.152	-	12.039
3700	13.895	32.083	20.676	42.206	-17.153	-	12.039
3800	13.937	32.454	20.981	43.599	-17.154	-	12.039
3900	13.977	32.817	21.280	44.995	-17.155	-	12.039
4000	14.017	33.171	21.572	46.395	-17.156	-	12.039

Dec. 31, 1960; Dec. 31, 1962; Mar. 31, 1967

$S^\circ_{298.15} = 3.94 \pm 0.03 \text{ gibbs/mol}$
 $T_d = [3245]^\circ \text{K}$
 $\Delta H^\circ_0 = -16.9 \pm 1.5 \text{ kcal/mol}$
 $\Delta H^\circ_{298.15} = -17.1 \pm 1.5 \text{ kcal/mol}$

Heat of Formation.

The heat of formation is calculated from $\Delta H^\circ_{298} = -591.9 \text{ kcal/mol}$ for $\text{SiC}(\alpha) + 4\text{F}_2(\text{g}) \rightarrow \text{SiF}_4(\text{g}) + \text{CF}_4(\text{g})$ based on the tentative value of $\Delta H^\circ_{298} = -223.1 \text{ kcal/mol}$ for $\text{CF}_4(\text{g})$. Greenberg¹ determined the enthalpy of reaction by fluorine bomb calorimetry. Data of Humphrey² obtained by oxygen bomb calorimetry yield a ΔH° which is over 2 kcal more negative; however, this difference is probably within the uncertainty due to use of large amounts of Ti as a kindling agent and to corrections for incomplete combustion. Decomposition pressure data obtained mass spectrometrically by Drowart³ are in close agreement with the selected ΔH° , but Knudsen weight loss data of Orievason⁴ and solubility-activity data of Kirkwood⁵ yield values less negative by 2 and 3 kcal, respectively. The results are summarized below.

The data of Drowart show a significant drift while those of Orievason do not, but the latter should be corrected for $\text{C}_2\text{Si}(\text{g})$ and $\text{CSi}_2(\text{g})$ which are present in amounts of about 4 and 3%, respectively, at 2000°K. Silicon carbide may have a small vaporization coefficient, since rates of free evaporation reported by Voronin⁶ and Ghoastagore⁷ yield apparent pressures which are smaller by factors of 1/50 to 1/1000.

Source	Method	Reaction	Range, °K	No. of Points	ΔH°_{298} (kcal/mol)	Drift ΔH°_{298} (eu)
Greenberg (1966)	F_2 Calorimetry	A	298	1	-591.9	-17.1
Humphrey (1952)	O_2 Calorimetry	B	303	1	-232.0	-19.6
Drowart (1958)	Mass Spec.	C	2149-2316	7	136.9±0.7	124.61 -5.6±0.3
Orievason (1960)	Knudsen Wt. Loss	C	1785-2004	10	122.9±0.7	122.66 -0.2±0.4
Kirkwood (1961)	Sol. in Pb	D	1693	1	25.66	-14.1
A) $\text{SiC}(\alpha) + 4\text{F}_2(\text{g}) \rightarrow \text{SiF}_4(\text{g}) + \text{CF}_4(\text{g})$						
B) $\text{SiC}(\alpha) + 2\text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{low-qtz}) + \text{CO}_2(\text{g})$						
*Value in parentheses is based on authors' data for $\text{Si}(\text{l}) \rightarrow \text{Si}(\text{g})$ rather than JANAF value.						

Heat Capacity and Entropy.

Low temperature heat capacities are from data (54-296°K) of Humphrey² and are in good agreement with earlier data (54-295°K) of Kelley⁸. The entropy is obtained from Op° using $S^\circ_{50} = 0.038 \text{ eu}$. Op° above room temperature is based on enthalpy data of Humphrey² [389-1789°K], Walker⁹ [373-1073°K] and Magna¹⁰ [372-1172°K]. Maximum deviations of the data from the selected values are 1.4, 2 and -1.7%, respectively; these occur in the range 370-621°K. Kirklin¹¹ obtained enthalpy data (1114-2843°K) for SiC mixed with 12% free carbon. When corrected for free carbon but not for 0.7% iron impurity, these data deviate by -1.1-5% from the selected values. Enthalpies (793-1790°K) of Fieldhouse¹² are high by 1-8% while those of Makaimenko¹³ were not available for analysis.

Transition Data.

$\text{SiC}(\alpha)$, also called hexagonal II or 6H, is one of the more common of many hexagonal forms which arise from various possible stacking sequences of the hexagonal SiC layers¹⁴. The properties of these phases are so similar that they have not been adequately differentiated thermodynamically. It has frequently been assumed that cubic $\text{SiC}(\beta)$ transforms to α at about 2300°K, but this seems unlikely since both phases have been prepared over temperature ranges of 1700-3000°K.¹⁴ Heat of formation and equilibrium data indicate that α is less stable up to 2000°K. The adopted functions suggest that this is the case at all temperatures; however, the stability difference is small.

Decomposition Data.

The decomposition temperature is calculated as the value at which the total pressure reaches one atm for vapor containing of $\text{C}_2\text{Si}(44.3 \text{ mol } \%)$, $\text{Si}(32.0\%)$, $\text{CSi}_2(21.2\%)$, $\text{Si}_2(1.9\%)$, $\text{CSi}(0.7\%)$, and $\text{Si}_3(0.25\%)$. The tables predict decomposition to graphite and pure liquid silicon at about 3280°K; however, Sease¹⁵ observed peritectic decomposition to graphite and solution containing 19 atom percent of carbon at 3103±40°K. In contrast, Dolloff¹⁶ reported the peritectic at 2813±40°K and 27 percent carbon. Badami¹⁷ has shown that decomposition in vacuum at lower temperatures (2400°K) leads to graphite.

References.

1. B. Greenberg et al., Argonne National Laboratory, ANL-7175, 138 (1966); ANL-7020, 169 (1965).
2. J. Drowart, S. S. G. K. King, P. Coughlin and K. O. King, U. S. Bur. Min. 11 488 (1952).
3. J. Drowart, G. DeMaria and M. O. Inghram, J. Chem. Phys. 29, 1015 (1958); J. Drowart and G. DeMaria, pp 16-23 in reference (14).
4. P. Orievason and C. B. Alcock, "Special Ceramics," Proc. Symposium Brit. Ceram. Research Assoc., Stoke-on-Trent 1959, 183-208, Haywood & Co., London, 1960.
5. D. H. Kirkwood and J. Chipman, J. Phys. Chem. 65, 1082 (1961).
6. N. Voronin, N. L. Makarov and B. P. Rudin, Izvestia v Obi. Khim. Silikatov 1 Okialov, Akad. Nauk SSSR, Sb. State 1965, 203-208.
7. R. N. Ghoastagore, Solid-State Electronics 9, 178 (1966).
8. K. K. Kelley, J. Am. Chem. Soc. 83, 1137 (1961).
9. B. E. Walker, C. T. Ewing and R. R. Miller, J. Chem. Eng. Data 7, 595 (1962).
10. V. Magna, Ann. Physik 303, 303 (1923); Ya. Chetkovskoi, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR 2, 9 (1964).
11. J. B. Kirklin, J. Appl. Phys. 33, 30 (1962).
12. J. B. Fieldhouse and A. S. Polubelova, Trudy Leningrad. Tekhn. Inst. im. Lensovet 33, 30 (1955).
13. M. S. Makaimenko and J. S. Smilana, editors, "Silicon Carbide," Pergamon Press, London, 1960.
14. J. R. O'Connor and J. Smilana, editors, "Silicon Carbide," Pergamon Press, London, 1960.
15. R. Sease and G. A. Slack, J. Chem. Phys. 30, 1551 (1959); pp 24-30 in ref. (14).
16. R. T. Dolloff, U. S. Dept. Comm. Clearinghouse, PB Rept. 171,585, 28 pp (1960).
17. D. V. Badami, Nature 125, 369 (1962).

T, °K	C_p°	S°	$-(C_p^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	-	7.782	-	17.261	INFINITE
100	1.019	7.002	-	7.795	-	17.235	37.666
200	3.896	4.879	-	5.512	-	17.110	16.697
298	6.415	3.970	-	-	-	16.937	12.415
300	6.455	3.970	-0.02	-	-	16.934	12.336
400	8.150	4.118	4.246	7.749	-	16.741	9.147
500	9.235	4.818	1.622	1.622	-	16.547	7.233
600	9.988	5.615	5.597	2.585	-	16.358	5.958
700	10.665	6.574	5.674	3.460	-	16.172	5.049
800	10.965	7.335	6.974	4.680	-	15.986	4.046
900	11.301	8.146	7.699	5.603	-	15.800	3.037
1000	11.573	8.405	8.405	6.947	-	15.621	3.414
1100	11.798	9.088	9.088	8.116	-	15.442	3.768
1200	12.024	9.666	9.666	9.116	-	15.263	3.760
1300	12.191	10.160	10.160	10.512	-	15.085	2.536
1400	12.292	10.990	10.990	11.372	-	14.905	2.327
1500	12.415	20.224	11.578	11.975	-	14.726	2.146
1600	12.524	21.029	12.144	12.217	-	14.548	1.987
1700	12.768	21.515	12.715	12.741	-	14.371	1.834
1800	12.768	23.205	13.723	18.016	-	14.194	1.681
1900	12.858	23.862	14.213	19.298	-	14.017	1.527
2000	12.923	24.691	14.689	20.587	-	13.840	1.373
2100	13.039	25.672	15.192	21.881	-	13.663	1.219
2200	13.137	26.228	15.624	23.181	-	13.486	1.065
2300	13.200	26.726	16.024	24.490	-	13.309	0.911
2400	13.137	26.764	16.443	25.801	-	13.132	0.757
2500	13.182	27.280	16.850	27.117	-	12.955	0.603
2600	13.263	27.620	17.430	28.762	-	12.778	0.449
2700	13.299	28.726	18.005	31.090	-	12.601	0.295
2800	13.334	29.177	18.370	32.422	-	12.424	0.141
2900	13.367	29.615	18.726	33.757	-	12.247	0.086
3000	13.400	30.052	19.172	35.092	-	12.070	0.031
3100	13.433	30.489	19.742	37.781	-	11.893	-0.024
3200	13.456	30.854	19.742	37.781	-	11.716	-0.079
3300	13.483	31.244	20.065	38.128	-	11.539	-0.134
3400	13.509	31.624	20.381	40.477	-	11.362	-0.189
3500	13.557	32.592	20.992	43.184	-	11.185	-0.244
3600	13.580	32.709	21.268	44.591	-	11.008	-0.299
3700	13.602	33.053	21.578	45.900	-	10.831	-0.354

Mar. 31, 1967

$\Delta H^\circ_{298} = -17.3 \pm 1.5$ kcal/mol
 $\Delta H^\circ_{298,15} = -17.5 \pm 1.5$ kcal/mol

$S^\circ_{298,15} = 3.97 \pm 0.03$ gibbs/mol
 $T_d = [3259]^\circ K$

Heat of Formation.

The heat of formation is calculated from $\Delta H^\circ_{298} = -591.5$ kcal/mol for $SiC(\beta) + 4P_2(g) \rightarrow SiP_4(g) + 4C(s)$, based on the tentative value of $\Delta H^\circ_{298} = -223 \pm 1$ kcal/mol for $CP_4(g)$. Greenberg¹ determined the enthalpy of reaction by fluorine bomb calorimetry. Data of Humphrey² obtained by oxygen bomb calorimetry yield a ΔH° which is over 3 kcal more negative; however, this difference is probably within the uncertainties due to use of large amounts of Ti as a kindling agent and to corrections for incomplete combustion. Decomposition pressure data obtained with the Knudsen weight loss method by Davis³ are in good agreement with the selected ΔH° , but similar data of Oriveason⁴ and solubility-activity data of Rein⁵ and d'Entremont⁶ yield values less negative by 1.6 to 2.5 kcal. The results are summarized below. Other equilibrium data⁵ relating SiC and SiO₂ are not included, pending the revision of tables for SiO₂.

The data of Davis show a serious drift, while those of Oriveason do not; but the latter should be corrected for $C_2Si(g)$ and $CSi_2(g)$ which are present in amounts of about 4 and 3%, respectively, at 2000°K. Silicon carbide may have a small vaporization coefficient, since rates of free evaporation reported by Voronin⁷ and Ohoatagore⁸ yield apparent pressures which are smaller by factors of 1/30 to 1/10000.

Source	Method	Reaction	Range, T°K	No. of Points	ΔH°_{298} (kcal/mol)	Drift (eu)	ΔH°_{298} (kcal/mol)
Greenberg (1966)	P ₂ Calorimetry	A	298	-	-591.5	-	-17.5
Humphrey (1962)	O ₂ Calorimetry	B	303	-	-290.9	-	-20.6
Davis (1961)	Knudsen Mt. Loss	C	2117-2171	8	167.428	126.10	-19.13
Oriveason (1960)	" "	D	1808-1973	6	123.340.3	122.65	-0.440.2
Rein (1963)	Soln. in C-Fe	D	1823-1873	2	32.0	27.43	-15.9
d'Entremont (1963)	Soln. in Ag	D	1693	1	-	27.31	-15.7
A) $SiC(\beta) + 4P_2(g) \rightarrow SiP_4(g) + 4C(s)$							
B) $SiC(\beta) + 2O_2(g) \rightarrow SiO_2(\text{low quartz}) + CO_2(g)$							
C) $SiC(\beta) \rightarrow C(\text{graph}) + Si(g)$							
D) $SiC(\beta) \rightarrow C(\text{graph}) + Si(l)$							

*Value in parentheses is based on author's data for Si(l) $\rightarrow$ Si(g) rather than JANAF value.

Heat Capacity and Entropy.

Low temperature heat capacities are from data (54-296°K) of Humphrey². The entropy is obtained from Op° using $S^\circ_{298} = 0.041$ eu. Op° above room temperature is based on Humphrey's enthalpy data (389-1693°K), which show a maximum deviation of $\pm 1.5\%$ from the selected functions. Humphrey's sample contained about 1% of α -SiC and about 0.6% of other impurities. Kirillin⁹ obtained enthalpy data (1114-2843°K) for SiC mixed with 12% free carbon. When corrected for free carbon but not for 0.73% iron impurity, these data deviate by $\pm 1.2\%$ from the selected values.

Transition Data.

$SiC(\beta)$, also called cubic or 3C, has a structure of the diamond or zinc blende type¹⁰. The cubic phase differs from the many hexagonal forms only in the order of the stacking sequence of the hexagonal SiC layers. It has frequently been assumed that β transforms into α at about 2300°K, but this seems unlikely, since both phases have been prepared over temperature ranges of 1700-3000°K¹¹. Heat of formation and equilibrium data indicate that β is more stable up to 2000°K. The adopted functions suggest that this is the case at all temperatures; however, the stability difference is small.

Decomposition Data.

The decomposition temperature is calculated as the value at which the total pressure reaches one atm for vapor con-
sisting of $C_2Si(45.4 \text{ mol } \%)$, $Si(32.1\%)$, $CSi_2(20.1\%)$, $Si_2(1.8\%)$, $CSi(0.28\%)$ and $Si_3(0.23\%)$. The tables predict decomposition to graphite and pure liquid silicon at about 3337°K; however, Seacell¹¹ observed peritectic decomposition to graphite and solution containing 19 atom percent of carbon at 3103-40°K. In contrast, Dolloff¹² reported the peritectic at 2813-40°K and 27 percent carbon.

References.

1. E. Greenberg et al., Argonne National Laboratory, ANL-7175, 138 (1966); ANL-7020, 169 (1965).
2. G. L. Humphrey, S. S. Todd, J. P. Coughlin and E. G. King, U.S. Bur. Mines RI 4888 (1952).
3. S. O. Davis, D. P. Anthop and A. W. Seary, J. Chem. Phys. 34, 659 (1961).
4. P. Oriveason and C. B. Alcock, "Special Ceramics," Proc. Symposium Brit. Ceram. Research Assoc., Stoke-on-Trent 1959, 183-208, Haywood & Co., London, 1960.
5. R. H. Rein and J. Chipman, J. Phys. Chem. 67, 839 (1963).
6. J. C. d'Entremont and J. Chipman, J. Phys. Chem. 67, 499 (1963).
7. N. I. Voronin, N. L. Makarova and B. P. Yudin, Izvest. v Otd. Khim. Silykatov 1 Okladov, Akad. Nauk SSSR, Sb. Statei 1965, 203-8.
8. R. N. Ohoatagore, Solid-State Electronics 9, 178 (1966).
9. V. A. Kirillin, A. E. Sheindlin and V. Ya. Chekhovskoi, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR 2, 9 (1964).
10. J. R. O'Connor and J. Smiltens, editors, "Silicon Carbide," Pergamon Press, London, 1960.
11. R. I. Seacell and O. A. Slack, J. Chem. Phys. 30, 1551 (1959); pp 24-30 in ref. 10.
12. R. T. Dolloff, U. S. Dept. Comm., Clearinghouse, PB Rept. 171,365, 28 pp (1960).

Silicon Carbide (SiC)

(Ideal Gas) $\Delta H_f^\circ = 40.09715$

T, K	C_p°	gibbs/mol $S^\circ - (G^\circ - H^\circ_{298})/T$	enthalpy/mol $H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	INFINITE	-2.215	170.806	170.806	INFINITE
100	6.958	42.719	57.917	171.423	167.264	-3.365,555
200	7.441	47.617	51.671	171.773	162.951	-1.785,065
298	7.182	50.892	50.892	172.000	158.573	-1.162,237
300	9.216	50.949	50.892	172.004	158.489	-1.155,459
400	10.574	51.913	51.273	172.250	153.948	-0.84,113
500	10.857	52.619	52.030	172.466	149.347	-0.65,279
600	10.510	52.180	52.597	172.595	144.709	-0.52,710
700	10.294	51.740	53.060	172.640	140.056	-0.43,966
800	10.110	51.300	53.460	172.656	135.356	-0.37,998
900	9.961	50.860	53.801	172.646	130.765	-0.31,754
1000	9.820	50.433	54.143	172.606	126.139	-0.27,568
1100	9.692	50.038	54.488	172.532	121.532	-0.24,166
1200	9.583	49.662	54.839	172.423	116.945	-0.21,299
1300	9.495	49.300	55.194	172.281	112.371	-0.18,333
1400	9.426	48.950	55.562	172.106	107.812	-0.16,033
1500	9.374	48.613	55.923	171.904	103.266	-0.15,052
1600	9.337	48.284	56.279	171.679	98.739	-0.13,495
1700	9.314	47.962	56.630	171.428	94.216	-0.12,138
1800	9.300	47.648	56.879	171.152	89.700	-0.10,998
1900	9.294	47.340	57.125	170.852	85.191	-0.09,998
2000	9.297	47.038	57.368	170.529	80.695	-0.09,091
2100	9.301	46.740	57.607	170.184	76.216	-0.07,272
2200	9.304	46.446	57.842	169.818	71.751	-0.05,630
2300	9.307	46.155	58.073	169.432	67.298	-0.04,061
2400	9.309	45.868	58.300	169.026	62.858	-0.02,561
2500	9.310	45.584	58.523	168.600	58.432	-0.01,113
2600	9.311	45.302	58.742	168.154	53.921	0.00,336
2700	9.311	45.021	58.957	167.688	49.324	0.01,662
2800	9.311	44.740	59.168	167.201	44.642	0.02,982
2900	9.310	44.460	59.374	166.694	39.874	0.04,302
3000	9.309	44.181	59.576	166.166	35.021	0.05,619
3100	9.307	43.902	59.773	165.616	30.082	0.06,933
3200	9.304	43.623	59.965	165.044	25.058	0.08,244
3300	9.300	43.344	60.152	164.450	19.948	0.09,552
3400	9.295	43.065	60.335	163.833	14.751	0.10,857
3500	9.289	42.786	60.513	163.194	9.468	0.12,159
3600	9.282	42.507	60.686	162.533	4.097	0.13,458
3700	9.274	42.228	60.854	161.850	-1.364	0.14,754
3800	9.265	41.948	61.017	161.144	-5.744	0.16,047
3900	9.255	41.668	61.174	160.415	-10.104	0.17,337
4000	9.244	41.388	61.326	159.663	-14.440	0.18,624
4100	9.232	41.107	61.473	158.888	-18.753	0.19,908
4200	9.219	40.826	61.615	158.090	-23.044	0.21,190
4300	9.205	40.545	61.752	157.269	-27.312	0.22,469
4400	9.190	40.264	61.884	156.426	-31.559	0.23,746
4500	9.174	39.983	62.011	155.561	-35.776	0.25,021
4600	9.157	39.699	62.134	154.674	-39.973	0.26,294
4700	9.139	39.414	62.252	153.763	-44.159	0.27,565
4800	9.120	39.128	62.365	152.828	-48.334	0.28,834
4900	9.099	38.842	62.473	151.870	-52.498	0.30,101
5000	9.077	38.556	62.576	150.889	-56.651	0.31,365
5100	9.054	38.269	62.674	149.885	-60.794	0.32,627
5200	9.030	37.981	62.767	148.858	-64.927	0.33,887
5300	9.005	37.692	62.855	147.808	-69.050	0.35,144
5400	8.979	37.402	62.938	146.734	-73.163	0.36,398
5500	8.952	37.111	63.016	145.636	-77.258	0.37,649
5600	8.924	36.819	63.089	144.514	-81.340	0.38,897
5700	8.895	36.526	63.157	143.368	-85.409	0.40,142
5800	8.865	36.232	63.220	142.198	-89.465	0.41,384
5900	8.834	35.937	63.278	141.004	-93.508	0.42,623
6000	8.802	35.642	63.331	139.786	-97.538	0.43,858

Mar. 31, 1967

SILICON CARBIDE (SiC)

(IDEAL GAS)

 $\Delta H_f^\circ = 40.09715$ Ground State Configuration $[1^1\Sigma]$ $\Delta H_f^\circ = 170.8 \pm 8 \text{ kcal/mol}$ $S_{298,15}^\circ = [50.9] \text{ gibbs/mol}$ $\Delta H_f^\circ = 172 \pm 8 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i	$\epsilon_i, \text{cm}^{-1}$	g_i
0	(1)	[8000]	(2)
[1000]	(6)	[14000]	(2)
[5000]	(3)	[18000]	(1)

$w_e = [1226] \text{ cm}^{-1}$
 $B_e = [0.6933] \text{ cm}^{-1}$
 $w_e x_e = [5] \text{ cm}^{-1}$
 $\alpha_e = [0.006] \text{ cm}^{-1}$
 $r_e = [1.7] \text{ \AA}$

Heat of Formation.

Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor equilibrium over the systems SiC-graphite¹ and boron-silicon-graphite². Third law analysis of the partial pressures of Si and C yields the results summarized below. The adopted value, $\Delta H_f^\circ = 172 \pm 8$, is the mean of the two results and the uncertainty reflects the possible effect of an error of up to 4 eu in the functions. The corresponding dissociation energy is $D_0^\circ = 106.5 \pm 8 \text{ kcal/mol}$.

Source	Method	Range, T°K	No. of Points	ΔH_f° (kcal/mol)* 2nd Law	3rd Law	Drift (eu)
Drowart (1959)	Mass Spec.	2181-2316	3	27.144	65.94	174.2
Verhaegen (1964)	"	2249-2344	3	48.744	62.67	170.4

*For the reaction C(graphite) + Si(g) = SiC(g)

Heat Capacity and Entropy.

The ground state is assumed to be $1^1\Sigma$, as suggested by Weltner and McLeod³. By analogy with C_2 , there should be a low-lying 3Π excited state; this would dominate the thermodynamic functions at temperatures above 2000°K if the level lies below 5000 cm^{-1} . The 3Π level is assumed to lie at 1000 cm^{-1} , intermediate between the value⁴ observed for C_2 and that estimated for Si_2 (see JANAF table). Additional excited states, 3Σ , 1Π , 1Δ and $1^3\Sigma$, are estimated by comparison with those observed or predicted⁵ for C_2 . The estimates for the electronic levels are relatively uncertain and probably yield an upper limit for the entropy at temperatures where SiC(g) is significant. A probable lower limit for the electronic contribution may be obtained by increasing the 3Π level to 7000 cm^{-1} and omitting the other excited states. This would reduce the entropy by 3.5 and 2.0 eu at 2000 and 4000°K.

The vibrational frequency is that estimated by Weltner³ from a valence bond calculation using $k = 7.44 \times 10^5 \text{ dyn/cm}$ obtained from C_2Si . The constants $w_e x_e$, α_e and r_e are estimated by interpolation between those ^{6,4} for the $1^1\Pi_u$ states of Si_2 and C_2 . Use of constants based on the 3Π state is consistent with the assumption that this state dominates the electronic partition function at high temperatures. B_e is calculated from r_e .

References.

1. J. Drowart, G. DeMaria and M. G. Inghram, J. Chem. Phys. **29**, 1015 (1958).
2. G. Verhaegen, P. E. Stafford and J. Drowart, J. Chem. Phys. **40**, 1622 (1964).
3. W. Weltner, Jr., and D. McLeod, Jr., J. Chem. Phys. **31**, 235 (1964).
4. E. A. Ballik and D. A. Ramsay, Astrophys. J. **137**, 64 (1963).
5. P. F. Fougere and R. K. Nease, J. Chem. Phys. **44**, 285 (1966).
6. A. E. Douglas, Can. J. Phys. **33**, 801 (1955).

CSI

Disilicon Carbide (SiC₂)

(Ideal Gas) GFW = 68.18315

DISILICON CARBIDE (CSi₂)

(IDEAL GAS)

OPW = 68.1815

Point Group [D_{∞h}]
 $S_{298.15}^\circ = [57.9] \text{ gtbbs/mol}$
 $\Delta H_f^\circ = 127.1 \pm 6 \text{ kcal/mol}$
 $\Delta H_f^\circ = 128 \pm 6 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

ϵ , cm ⁻¹	ϵ_1
0	(1)
[12000]	(6)
[19000]	(2)

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	
[670] (1)	
[275] (2)	
[1600] (1)	

Bond Distance: C-Si = [1.75] Å
 Bond Angle: C-Si-Si = [180°]
 Rotational Constant: B₀ = [0.0980] cm⁻¹

Heat of Formation

The selected value is an average based on the equilibrium data summarized below. Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor species over the SiC-graphite¹, SiC-silicon² and boron-carbon-silicon³ systems. Third law analysis of the partial pressures of CSi₂ and Si yields the concordant values 127.4, 127.9 and 128.6 kcal/mol. Two of the drifts are rather large, but they are opposite in sign so that no consistent entropy difference is apparent between the data and the tabulated functions. The drifts may be related to the low condensation coefficient for CSi₂ suggested by Drowart¹. Rates of free evaporation reported by Voronin⁴ yield apparent pressures which are lower by a factor of 1/30, thus confirming the existence of a low evaporation coefficient. The adopted value of $\Delta H_f^\circ = 128 \pm 6 \text{ kcal/mol}$ includes allowance for an error in the entropy of up to 3 eu.

Source	Method	Reaction	Range, °K	No. of Points	ΔH_f° (kcal/mol)	Drift (eu)	ΔH_f° (kcal/mol)
Drowart (1958)	Mass Spec.	A	2149-2316	7	-1047.7	-88.0	7.443.0
Drowart (1960)	"	B	1825-2160	7	141.3	134.4	-3.441.7
Verhaegen (1964)	"	A	2083-2344	6	-68.25	-86.8	-9.412
A) C(graph) + 2 Si(g) = CSi ₂ (g)							
B) SiC(α) + Si(l) = CSi ₂ (g)							

Heat Capacity and Entropy

Weltner and McLeod⁵ observed a band system in absorption at 5300 Å in matrix isolation and assigned this tentatively to the transition ${}^1\Pi_u - X\Sigma_g^+$ of CSi₂. This assignment is adopted, although the evidence is not at all conclusive. A ${}^3\Pi_u$ excited state is assumed to lie at 12000 cm⁻¹, presumably arising from the same molecular orbital configuration as the ${}^1\Pi_u$ state. A linear, symmetric structure is assumed, as suggested by Weltner. The bond distance is estimated by comparison with Si₂, C₂ and C₃. Vibrational frequencies are estimated from a valence bond calculation using $k_1 = 7.46 \times 10^5$ and $k_2/k_1 = 0.11 \times 10^5 \text{ dyn/cm}$. The stretching force constant is taken from C₂Si₂, while the bending force constant is from C₂Si and the ${}^1\Pi_u$ excited state of C₃. The moment of inertia is $28.56 \times 10^{-39} \text{ g cm}^2$.

References

1. J. Drowart, O. Demaria and M. O. Ingraham, J. Chem. Phys. **29**, 1015 (1958).
2. J. Drowart and G. DeMaria, pp. 16-23 in "Silicon Carbide," Edited by J. R. O'Connor and J. Skliten, Pergamon Press, New York, 1960.
3. O. Vorhagen, P. E. Stafford and J. Drowart, J. Chem. Phys. **40**, 1622 (1964).
4. N. I. Voronin, N. L. Mokarova and B. F. Yudin, Izvest. v Otd. Khim. Silikatov i Okislov, Akad. Nauk SSSR, Sb. Statei 1965, 203-8.
5. W. Weltner, Jr., and D. McLeod, Jr., J. Chem. Phys. **41**, 235 (1964); **40**, 1305 (1964); **45**, 3096 (1966).

Mar. 31, 1967

Titanium Carbide (TiC)

CTI

(Crystal)

GFW = 59.91115

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^b	ΔG ^c	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	3.577	3.054	1.456	1.101	43.697	43.697	INCALCULATED
200	3.577	3.054	1.456	1.101	43.697	43.697	INCALCULATED
298	8.680	5.791	5.791	0.000	43.697	43.697	31.421
300	8.111	5.641	5.791	0.15	44.000	43.132	31.422
400	9.724	8.468	6.130	0.911	43.668	42.475	23.410
500	10.795	10.702	8.680	1.941	43.603	42.379	16.605
600	11.388	12.727	7.639	3.053	43.435	42.314	15.413
700	11.719	14.569	8.496	4.209	43.790	42.064	13.133
800	11.927	16.087	9.348	5.392	43.776	41.818	11.424
900	12.087	17.502	10.177	6.592	43.769	41.573	10.005
1000	12.232	18.783	10.974	7.808	43.853	41.373	9.031
1100	12.379	19.955	11.738	9.039	43.934	41.067	8.159
1200	12.535	21.039	12.469	10.284	44.977	40.763	7.424
1300	12.702	22.049	13.167	11.546	44.978	40.413	6.794
1400	12.881	22.997	13.836	12.825	44.984	40.061	6.254
1500	13.071	23.892	14.477	14.123	44.995	39.709	5.766
1600	13.272	24.742	15.092	15.440	45.011	39.356	5.376
1700	13.481	25.553	15.683	16.777	45.031	39.003	5.014
1800	13.699	26.329	16.253	18.136	45.056	38.648	4.693
1900	13.923	27.076	16.804	19.517	45.084	38.291	4.404
2000	14.154	27.796	17.335	20.921	45.116	37.937	4.128
2100	14.390	28.492	17.850	22.348	45.153	37.583	3.870
2200	14.631	29.167	18.349	23.799	45.195	37.230	3.636
2300	14.876	29.823	18.834	25.275	45.242	36.878	3.422
2400	15.125	30.461	19.305	26.775	45.294	36.525	3.226
2500	15.377	31.084	19.764	28.300	45.350	36.168	3.046
2600	15.631	31.692	20.211	29.850	45.409	35.806	2.880
2700	15.889	32.287	20.647	31.426	45.472	35.436	2.727
2800	16.148	32.869	21.073	33.028	45.540	35.059	2.585
2900	16.410	33.440	21.490	34.656	45.613	34.676	2.453
3000	16.673	34.001	21.898	36.310	45.694	34.286	2.330
3100	16.938	34.552	22.297	37.991	45.781	33.889	2.216
3200	17.204	35.094	22.689	39.698	45.874	33.484	2.110
3300	17.472	35.628	23.073	41.431	45.972	33.070	2.011
3400	17.740	36.153	23.450	43.192	46.075	32.646	1.917
3500	18.010	36.671	23.820	44.979	46.183	32.213	1.830
3600	18.280	37.182	24.184	46.794	46.296	31.773	1.749
3700	18.552	37.687	24.542	48.636	46.414	31.326	1.673
3800	18.824	38.185	24.895	50.504	46.537	30.872	1.599
3900	19.097	38.678	25.242	52.400	46.665	30.410	1.526
4000	19.371	39.165	25.584	54.324	46.798	29.939	1.456

TITANIUM CARBIDE (TiC)

(CRYSTAL)

GFW = 59.91115

 $\Delta H_f^\circ = -43.7 \pm 1$ kcal/mol $\Delta H_f^\circ_{298.15} = -44.0 \pm 1$ kcal/mol $\Delta H_m^\circ = [17]$ kcal/mol $S^\circ_{298.15} = 5.79 \pm 0.05$ gibbs/mol $T_m = 3290 \pm 15^\circ K$

Heat of Formation

The adopted $\Delta H_f^\circ_{298}$ is derived from $\Delta H_f^\circ_{298} = -275.72$ kcal/mol for reaction (a) determined by Humphrey (1) who burned TiC(c) in an oxygen bomb calorimeter. The author reported that the combustion product TiO_2 was >95 per cent rutile and <5 per cent anatase, the heat of formation is calculated assuming the above distribution. The uncertainty adopted is due mainly to the uncertainty in TiO_2 (rutile).

Using atomic absorption spectroscopy Vidale (2) determined that the pressure (log $P_{Ti} = -7.269$) of Ti(g) at 1666°K was equal to the pressure of TiC(c) at 2220°K. Using this data for reaction (b) we obtain a $\Delta H_f^\circ_{298} = -43.02$ kcal/mol. Lowell and Williams (3) measured the ΔH_f° of TiC(c) directly using a high temperature calorimeter, which reduces to $\Delta H_f^\circ_{298} = -37.7 \pm 4$ kcal/mol.

Fujishiro and Gokcen (4) determined the equilibrium pressure of Ti(g) in reaction (d) in the temperature range 2383-2593°K. Third law analysis of the data yields a $\Delta H_f^\circ_{298} = -31.6$ kcal/mol. Brantley and Beckman (5) measured equilibrium pressures of CO for reaction (e) in the temperature range 1276 - 1428°K. Third law analysis of the data yields a $\Delta H_f^\circ_{298} = -61.9$ kcal/mol.

Heat Capacity and Entropy

Low temperature heat capacities (55 - 295°K) have been taken from Kelley (6). Naylor (7) measured heat contents from 360 to 1738°K and Levinson (8) from 1274 to 2799°K. High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. Above 2799°K the heat capacity is graphically extrapolated. The entropy is based on $S^\circ_0 - S^\circ_0 = 0.065$ eu.

Melting Data

See liquid table.

Reference	Method	Reaction	T°K	2nd Law	3rd Law	Drift eu	$\Delta H_f^\circ_{298}$ kcal/mol
1	Calorimetry	(a) TiC(c) + $2O_2(g) + CO_2(g) + TiO_2(rutile)$	298	-275.72			-44.00
2	Equilibrium	(b) TiC(c) + Ti(c) + C(c)			156.02		-43.02
3	Calorimetry	(c) Ti(c) + C(c) + TiC(c)			-37.74		-37.7
4	Equilibrium	(d) TiC(c) + C(graph) + Ti(g)	2383-2593		169.5±10.3	144.6	-10.0±4.1
5	Equilibrium	(e) $TiO_2(rutile) + 3C(graph) + TiC(c) + 2CO(g) + TiO_2(l)$	1276-1428		48.07±1.83	111.07	-61.90

References

- G. L. Humphrey, J. Am. Chem. Soc. **73**, 2261 (1951).
- G. L. Vidale, General Electric Co., R61SD147, Contract AF 33(616)-5841, August, 1961.
- C. E. Lowell and W. S. Williams, Rev. Sci. Instr. **32**, 1120-1123 (1961).
- S. Fujishiro and N. A. Gokcen, J. Phys. Chem. **65**, 161 (1961).
- L. R. Brantley and A. O. Beckman, J. Am. Chem. Soc. **52**, 3956 (1930).
- K. K. Kelley, Ind. Eng. Chem. **36**, 865 (1944).
- B. F. Naylor, J. Am. Chem. Soc. **68**, 370 (1946).
- L. S. Levinson, J. Chem. Phys. **42**, 2891 (1965).

CTI

(Liquid) $\Delta H_f^\circ = 59.91115$

T, °K	Cp°	$\frac{g\text{Btu/mol}}{S^\circ - (T^\circ - T^\circ_{\text{fus}})/T}$	$H^\circ - H^\circ_{\text{fus}}$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
100						
200						
298	8.060	11.329	.000	- 25.802	- 26.681	19.587
300	8.111	11.379	.015	- 25.802	- 26.686	19.640
350	8.744	11.448	.091	- 25.802	- 26.953	19.726
500	10.745	12.260	1.941	- 25.795	- 27.234	11.164
600	11.388	12.265	3.053	- 25.727	- 27.529	10.027
700	11.719	12.034	4.209	- 25.682	- 27.833	8.690
800	11.927	11.600	5.465	- 25.650	- 28.146	7.402
900	12.057	10.971	6.792	- 25.631	- 28.469	6.284
1000	12.232	10.281	8.188	- 25.624	- 28.794	5.312
1100	12.379	9.543	9.639	- 25.626	- 29.051	4.572
1200	12.535	8.767	11.144	- 25.636	- 29.301	4.036
1300	12.702	7.956	12.705	- 25.650	- 29.535	3.657
1400	12.879	7.114	14.324	- 25.667	- 29.755	3.392
1500	13.071	6.250	16.001	- 25.687	- 29.960	3.219
1600	13.272	5.368	17.726	- 25.712	- 30.150	3.106
1700	13.481	4.474	19.501	- 25.740	- 30.325	3.047
1800	13.699	3.578	21.324	- 25.770	- 30.486	3.032
1900	13.934	2.681	23.194	- 25.802	- 30.632	3.059
2000	14.184	1.784	25.109	- 25.835	- 30.764	3.126
2100	14.350	0.887	27.069	- 25.869	- 30.882	3.196
2200	14.500	0.000	29.074	- 25.904	- 30.986	3.267
2300	14.600	- 0.887	31.124	- 25.939	- 31.076	3.338
2400	14.650	- 1.784	33.219	- 25.974	- 31.152	3.409
2500	14.650	- 2.681	35.358	- 26.009	- 31.214	3.480
2600	14.600	- 3.578	37.541	- 26.044	- 31.262	3.551
2700	14.500	- 4.474	39.769	- 26.079	- 31.297	3.622
2800	14.350	- 5.368	42.041	- 26.114	- 31.322	3.693
2900	14.184	- 6.250	44.356	- 26.149	- 31.338	3.764
3000	14.000	- 7.114	46.714	- 26.184	- 31.344	3.835
3100	13.800	- 7.956	49.114	- 26.219	- 31.340	3.906
3200	13.600	- 8.767	51.554	- 26.254	- 31.326	3.977
3300	13.400	- 9.543	54.034	- 26.289	- 31.302	4.048
3400	13.200	- 10.281	56.554	- 26.324	- 31.268	4.119
3500	13.000	- 11.000	59.114	- 26.359	- 31.224	4.190
3600	12.800	- 11.699	61.714	- 26.394	- 31.170	4.261
3700	12.600	- 12.379	64.354	- 26.429	- 31.106	4.332
3800	12.400	- 13.034	67.034	- 26.464	- 31.032	4.403
3900	12.200	- 13.664	69.754	- 26.499	- 30.948	4.474
4000	12.000	- 14.269	72.514	- 26.534	- 30.854	4.545
4100	11.800	- 14.849	75.314	- 26.569	- 30.750	4.616
4200	11.600	- 15.404	78.154	- 26.604	- 30.636	4.687
4300	11.400	- 15.934	81.034	- 26.639	- 30.512	4.758
4400	11.200	- 16.439	83.954	- 26.674	- 30.378	4.829
4500	11.000	- 16.919	86.914	- 26.709	- 30.234	4.900

Dec. 31, 1960; Dec. 31, 1964; June 30, 1968

TITANIUM CARBIDE (TiC)

(LIQUID)

GFW = 59.9115

$$S_{298.15}^\circ = [11.329] \text{ gibbs/mol}$$

$$\Delta H_{298.15}^\circ = [-25.892 \pm 1] \text{ kcal/mol}$$

$$\Delta H_m^\circ = [17] \text{ kcal/mol}$$

$$T_m = 3290 \pm 15^\circ \text{K}$$

Heat of Formation

The heat of formation is obtained from $\Delta H_{298}^\circ(\text{c})$ by adding ΔH_m° and the differences between H_{298}° and H_{298}° for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2200°K the heat capacity is obtained from that of the crystal, above 2200°K it is assumed constant and estimated as 15 gibbs/mol or 7.5 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The adopted T_m is taken from the phase diagram of the system Ti-C, at the composition 50% Ti and 50% C, reported by E. Rudy and D. P. Harmon, Aerojet-General Corporation, BSP No. 64-6699-735001, Contract AF-33(611), April 1, 1965. Earlier reports by E. Friederich and L. Sittig, Z. Anorg. Chem. 144, 171(1925) and C. Agte and K. Moers, Z. Anorg. Chem. 193, 233 (1931), gave a T_m of 3430 $\pm$ 100°K and 3410 $\pm$ 90°K, respectively. ΔH_m° is derived from an estimated $\Delta S_m = 2.5$ gibbs/g-atom, as suggested by O. Kubaschewski, E. L. Evans and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon Press, New York, 1957.

CTi

Zirconium Carbide (ZrC)

(Crystal) Mol. Wt. = 103.231

T, °K	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	3.055	1.394	1.400	-46.832	-46.832	INFINITE
200	6.661	4.773	7.91	-46.738	-46.738	102.142
298	9.058	7.964	∞	-47.049	-46.410	50.777
300	9.089	8.020	∞	-47.000	-46.104	33.859
400	10.565	11.257	2.086	-46.998	-46.188	33.446
500	11.265	13.257	9.086	-46.898	-45.976	15.976
600	11.802	15.362	9.960	-46.727	-45.492	16.570
700	12.181	17.215	10.867	-46.675	-45.280	16.140
800	12.445	18.599	11.765	-46.640	-45.094	12.319
900	12.628	19.875	12.653	-46.600	-44.873	10.319
1000	12.760	21.073	13.475	-46.609	-44.713	9.772
1100	12.861	22.199	14.277	-46.615	-44.524	8.846
1200	12.945	23.031	15.043	-46.615	-44.285	8.065
1300	13.029	23.775	15.775	-46.615	-44.010	7.398
1400	13.103	24.445	16.475	-46.615	-43.712	6.827
1500	13.169	25.060	17.144	-46.615	-43.443	6.351
1600	13.221	25.629	17.785	-46.615	-43.171	5.897
1700	13.265	26.143	18.400	-46.615	-42.890	5.514
1800	13.304	26.615	18.981	-46.615	-42.604	5.173
1900	13.337	27.050	19.529	-46.615	-42.317	4.867
2000	13.365	27.450	20.046	-46.615	-42.028	4.592
2100	13.381	27.829	20.534	-46.615	-41.737	4.343
2200	13.385	28.167	21.000	-46.615	-41.440	4.101
2300	13.386	28.460	21.444	-46.615	-41.137	3.872
2400	13.385	28.714	21.867	-46.615	-40.824	3.653
2500	13.377	28.937	22.270	-46.615	-40.504	3.470
2600	13.354	29.124	22.646	-46.615	-40.179	3.292
2700	13.305	29.274	22.992	-46.615	-39.844	3.127
2800	13.239	29.394	23.309	-46.615	-39.500	2.974
2900	13.157	29.480	23.590	-46.615	-39.147	2.831
3000	13.057	29.532	23.832	-46.615	-38.785	2.698
3100	12.941	29.551	24.034	-46.615	-38.414	2.573
3200	12.805	29.537	24.198	-46.615	-38.034	2.456
3300	12.650	29.480	24.324	-46.615	-37.644	2.347
3400	12.477	29.380	24.411	-46.615	-37.244	2.243
3500	12.287	29.237	24.459	-46.615	-36.834	2.146
3600	12.081	29.054	24.466	-46.615	-36.414	2.055
3700	11.850	28.834	24.434	-46.615	-35.984	1.967
3800	11.597	28.574	24.362	-46.615	-35.544	1.885
3900	11.327	28.274	24.250	-46.615	-35.094	1.807
4000	11.037	27.934	24.098	-46.615	-34.634	1.734
4100	10.727	27.554	23.804	-46.615	-34.164	1.663
4200	10.397	27.134	23.374	-46.615	-33.684	1.597
4300	10.047	26.674	22.804	-46.615	-33.194	1.533
4400	9.677	26.174	22.094	-46.615	-32.694	1.473
4500	9.287	25.634	21.244	-46.615	-32.184	1.415
4600	8.877	25.054	20.254	-46.615	-31.664	1.360
4700	8.447	24.434	19.124	-46.615	-31.134	1.307
4800	7.997	23.774	17.854	-46.615	-30.594	1.257
4900	7.527	23.074	16.444	-46.615	-30.044	1.212
5000	7.037	22.334	14.894	-46.615	-29.484	1.171

MOL. WT. = 103.231

(CRYSTAL)

ZIRCONIUM CARBIDE (ZrC)

$$\Delta H_f^0 = -46.8 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = -47.0 \pm 3 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [19] \text{ kcal. mole}^{-1}$$

$$T_m = 3805 \pm 125^\circ \text{K}$$

$$S_{298.15}^0 = 7.964 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Heat of Formation.

ΔH_f^0 298.15 = -47.16 ± 1.5 kcal. mole⁻¹ was calculated from the standard free energy of formation of -38.9 ± 1.5 kcal. mole⁻¹ at 2875°K. reported by B. D. Pollock, J. Phys. Chem. **65**, 733 (1961). Using spectrophotometric data reported by G. L. Vidale, Missile and Space Vehicle Department, General Electric R61SD147, August, 1961, we calculated ΔH_f^0 298.15 = -46.9 ± 1 kcal. mole⁻¹. These values were averaged with ΔH_f^0 298.15 = 47.0 ± 0.6 kcal. mole⁻¹ reported by A. D. Mah, U. S. Bureau of Mines RI6518 (1964). The equilibria data reported by C. H. Prescott Jr., J. Am. Chem. Soc. **49**, 2534 (1926) and V. A. Epel'baum, Doklady Akad. Nauk SSSR **104**, 567 (1955) were considered but not used.

Heat Capacity and Entropy.

Heat content data over the range 470.8° to 1,174.4°K. were taken from a preliminary report by R. Mezaki, T. P. Jambois, A. K. Gungoradhyay, and J. L. Margrave, Univ. of Wisconsin, Madison, Wisconsin, "Thermodynamic Properties of Inorganic Substances VIII. The High Temperature Heat Contents of Zirconium Carbide and Tantalum Carbide". These data were smoothed by means of the Shomate plot into low temperature data reported by E. F. Westrum Jr. and G. Peick, J. Chem. Eng. Data, **8**, 176 (1963). High temperature data reported by D. S. Neel, C. D. Peers, S. Ogleby Jr., Southern Research Institute, Birmingham, Alabama, Technical Documentary Report No. WADD 60-924, p. 134, February 1962, and R. A. McDonald, P. L. Oettinger, and H. Prophet, CPFA Publication No. 44(u), p. 213, February 1964 were then used to obtain the heat capacity above 1174°K.

Melting Data.

Melting points were measured by C. Agte and H. Alvertum, Z. tech. Physik **11**, 182 (1930) and E. Friederich and L. Sittig, Z. Anorg. Chem., **144**, 169 (1925). The value of 3805 ± 125°K. by Agte and Alvertum was chosen. Friederich and Sittig obtained a measurement of 3300°K. but estimated 3500°K. because of the clouding formation of ZrO₂. Wayne L. Worrell, J. Phys. Chem., **68**, 954 (1964) quoted a value of 3480°K. taken from E. K. Storms, Los Alamos Scientific Lab Report LAMS-2674, (1962). The heat of melting is derived from an estimated $\Delta S_m = 2.5 \text{ cal. deg.}^{-1} \text{ gm. atom}^{-1}$.

Zirconium Carbide (ZrC)

CZr

(Liquid) Mol. Wt. = 103.231

MOL. WT. = 103.231

(LIQUID)

ZIRCONIUM CARBIDE (ZrC)

$$S_{298.15}^{\circ} = [12.815] \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad \Delta H_f^{\circ} 298.15 = [-29.39] \text{ kcal. mole}^{-1}$$

$$T_m = 3805 \pm 125^{\circ}\text{K.} \quad \Delta H_m^{\circ} = [19] \text{ kcal. mole}^{-1}$$

Heat of Formation.

$\Delta H_f^{\circ} 298.15$ (1) was obtained from $\Delta H_f^{\circ} 298.15(c)$ by adding ΔH_m° and the difference between $\Delta H_{Tm}^{\circ} - H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

$C_p(1)$ at and below 2500°K. were assumed to be equal to those of $\text{ZrC}(c)$. Above 2500°K. the heat capacity was estimated to be constant. $S_{298.15}(1)$ is calculated based on $S_{298.15}(c)$ and an estimated $\Delta S_m^{\circ} = 2.5 \text{ cal. deg.}^{-1} \text{ g. atom}^{-1}$.

Melting Data.

See ZrC(c) table for details.

CZr

T, °K.	C _p	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH ^o	ΔF _T ^o	Log K _P
0								
100								
200								
298	9.058	12.815	12.815		0.000	-28.366	-29.026	21.275
300	9.089	12.871	12.815		0.017	-28.384	-29.030	21.147
400	10.419	15.684	13.190		0.968	-28.284	-29.260	15.966
500	11.245	18.104	13.937		2.086	-28.186	-29.515	12.900
600	11.802	20.213	14.811		3.241	-28.113	-29.788	10.850
700	12.154	22.066	15.718		4.444	-28.061	-30.072	9.388
800	12.415	23.696	16.646		5.690	-28.024	-30.365	8.144
900	12.628	25.187	17.488		6.929	-28.004	-30.655	7.144
1000	12.760	26.524	18.326		8.108	-27.995	-30.950	6.364
1100	12.901	27.750	19.128		9.485	-28.001	-31.246	5.708
1200	13.045	28.884	19.894		10.855	-28.025	-31.542	5.175
1300	13.179	29.939	20.634		12.195	-28.080	-31.840	4.691
1400	13.213	30.905	21.326		13.411	-28.010	-31.909	4.252
1500	13.297	31.820	21.995		14.737	-29.036	-32.116	4.679
1600	13.381	32.680	22.636		16.071	-29.067	-32.319	4.414
1700	13.465	33.494	23.251		17.413	-29.102	-32.523	4.181
1800	13.549	34.264	23.878		18.760	-29.149	-32.731	3.976
1900	13.633	35.001	24.510		20.123	-29.178	-32.916	3.784
2000	13.717	35.702	24.957		21.490	-29.220	-33.116	3.619
2100	13.801	36.374	25.485		22.866	-29.261	-33.310	3.466
2200	13.885	37.018	25.995		24.250	-29.208	-33.339	3.312
2300	13.969	37.634	26.487		25.643	-29.170	-33.364	3.160
2400	14.053	38.223	26.965		27.044	-29.107	-33.352	3.028
2500	15.000	38.808	27.427		28.454	-29.036	-33.207	2.903
2600	15.000	39.397	27.876		29.854	-29.261	-33.166	2.788
2700	15.000	39.963	28.313		31.254	-29.236	-33.124	2.681
2800	15.000	40.508	28.738		32.654	-29.187	-33.082	2.580
2900	15.000	41.038	29.154		34.054	-29.117	-33.032	2.484
3000	15.000	41.543	29.559		35.454	-29.096	-33.004	2.400
3100	15.000	42.035	29.953		37.854	-29.052	-32.970	2.324
3200	15.000	42.511	30.338		39.254	-29.010	-32.935	2.249
3300	15.000	42.978	30.714		40.654	-28.940	-32.898	2.179
3400	15.000	43.421	31.081		42.054	-28.830	-32.870	2.119
3500	15.000	43.856	31.440		43.454	-28.894	-32.844	2.051
3600	15.000	44.278	31.791		44.854	-28.858	-32.814	1.992
3700	15.000	44.689	32.134		46.254	-28.824	-32.785	1.936
3800	15.000	45.090	32.460		47.654	-28.771	-32.752	1.884
3900	15.000	45.483	32.778		49.054	-28.702	-32.702	1.787
4000	15.000	45.859	33.120		50.454	-28.702	-32.702	1.787
4100	15.000	46.229	33.435		52.854	-28.702	-32.677	1.742
4200	15.000	46.590	33.764		55.254	-28.702	-32.647	1.699
4300	15.000	46.941	34.087		57.654	-28.702	-32.625	1.658
4400	15.000	47.288	34.408		59.054	-28.702	-32.608	1.618
4500	15.000	47.625	34.636		60.454	-28.702	-32.582	1.582
4600	15.000	47.955	34.922		62.854	-28.702	-32.559	1.547
4700	15.000	48.278	35.202		65.254	-28.702	-32.537	1.513
4800	15.000	48.593	35.478		67.654	-28.702	-32.515	1.481
4900	15.000	48.901	35.748		69.054	-28.702	-32.493	1.450
5000	15.000	49.206	36.015		70.454	-28.702	-32.471	1.421
5100	15.000	49.503	36.276		71.854	-28.702	-32.449	1.391
5200	15.000	49.794	36.534		73.254	-28.702	-32.427	1.362
5300	15.000	50.080	36.787		74.654	-28.702	-32.405	1.333
5400	15.000	50.360	37.037		76.054	-28.702	-32.383	1.304
5500	15.000	50.635	37.290		77.454	-28.702	-32.361	1.275
5600	15.000	50.906	37.521		78.854	-28.702	-32.339	1.246
5700	15.000	51.171	37.758		80.254	-28.702	-32.317	1.217
5800	15.000	51.432	37.992		81.654	-28.702	-32.295	1.188
5900	15.000	51.691	38.226		83.054	-28.702	-32.273	1.159
6000	15.000	51.941	38.458		84.454	-28.702	-32.251	1.130

Mar. 31, 1982; June 30, 1984; Dec. 31, 1984

Carbon, Diatomic (C₂)

(Ideal Gas)

GFW = 24.0223

Symmetry number = 2

S_{298.15} = 47.627 ± 0.01 gibbs/mol

ΔHf° = 198.2 ± 0.9 kcal/mol

ΔHf°_{298.15} = 200.2 ± 0.9 kcal/molC₂

T, °K	Cp°	gibbs/mol S°	-(Cp° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔHf°	Log Kp
0	0.000	0.000	INFINITE	2.528	198.200	INFINITE
100	7.114	37.918	1.632	196.664	195.118	426.429
200	9.669	43.548	1.005	199.539	191.118	208.844
298	10.312	47.627	0.000	200.224	196.835	136.953
300	10.301	47.690	0.019	200.235	196.751	136.048
400	9.476	50.544	48.022	200.733	192.175	99.536
500	8.877	52.587	48.740	201.010	177.500	77.565
600	8.604	54.178	49.519	201.125	172.784	62.936
700	8.509	55.232	50.113	201.153	168.300	52.422
800	8.598	55.826	50.601	201.103	164.029	44.222
900	8.743	57.036	51.667	200.941	158.629	38.520
1000	8.955	58.538	52.328	200.786	153.936	33.643
1100	8.655	59.360	52.931	200.603	149.259	29.655
1200	8.719	60.118	53.498	200.397	144.606	26.326
1300	8.852	61.070	54.543	200.174	139.984	23.127
1400	8.952	61.670	55.005	199.946	135.339	20.127
1500	8.920	62.083	55.025	199.707	130.732	17.048
1600	8.889	62.661	55.485	199.462	126.139	14.230
1700	9.057	63.208	55.923	199.217	121.564	11.526
1800	9.165	63.723	56.342	198.972	117.014	8.924
1900	9.165	64.223	56.742	198.720	112.458	6.426
2000	9.256	64.696	57.130	198.472	107.924	4.179
2100	9.320	65.149	57.501	198.227	103.405	2.162
2200	9.381	65.584	57.859	197.980	98.902	0.428
2300	9.438	66.005	58.207	197.734	94.408	-1.187
2400	9.494	66.416	58.547	197.488	89.908	-2.786
2500	9.554	66.794	58.860	197.255	85.429	-4.368
2600	9.607	67.170	59.172	197.015	80.961	-5.905
2700	9.659	67.534	59.475	196.778	76.500	-7.402
2800	9.710	67.887	59.770	196.542	72.048	-8.861
2900	9.758	68.229	60.055	196.310	67.610	-10.295
3000	9.805	68.559	60.333	196.078	63.175	-11.702
3100	9.852	68.881	60.604	195.849	58.751	-13.082
3200	9.897	69.195	60.867	195.620	54.332	-14.442
3300	9.941	69.500	61.124	195.392	49.914	-15.786
3400	9.981	69.799	61.374	195.164	45.502	-17.116
3500	10.029	70.087	61.620	194.941	41.111	-18.432
3600	10.071	70.371	61.859	194.718	36.719	-19.736
3700	10.114	70.647	62.093	194.495	32.335	-21.028
3800	10.156	70.917	62.321	194.275	27.957	-22.310
3900	10.197	71.186	62.544	194.052	23.582	-23.582
4000	10.242	71.441	62.763	193.837	19.219	-24.847
4100	10.284	71.694	62.979	193.619	14.851	-26.102
4200	10.327	71.942	63.189	193.402	10.499	-27.346
4300	10.370	72.186	63.396	193.185	6.154	-28.582
4400	10.412	72.426	63.596	192.965	1.816	-29.812
4500	10.456	72.659	63.797	192.755	-2.550	-31.036
4600	10.500	72.889	63.992	192.541	-6.885	-32.256
4700	10.544	73.116	64.184	192.329	-11.217	-33.472
4800	10.587	73.340	64.372	192.117	-15.548	-34.684
4900	10.632	73.559	64.552	191.905	-19.868	-35.892
5000	10.676	73.772	64.740	191.694	-24.187	-37.096
5100	10.721	73.984	64.919	191.482	-28.512	-38.296
5200	10.766	74.193	65.095	191.272	-32.850	-39.492
5300	10.811	74.398	65.268	191.063	-37.184	-40.684
5400	10.855	74.600	65.438	190.854	-41.512	-41.872
5500	10.903	74.800	65.608	190.645	-45.725	-43.056
5600	10.949	74.997	65.774	190.437	-50.021	-44.236
5700	10.995	75.191	65.938	190.228	-54.321	-45.412
5800	11.041	75.379	66.099	190.020	-58.608	-46.584
5900	11.084	75.562	66.259	189.812	-62.892	-47.752
6000	11.134	75.759	66.415	189.604	-67.175	-48.916

Sept. 30, 1961; Dec. 31, 1969

Electronic Levels and Molecular Constants

State	ϵ_i , cm ⁻¹	g_i	r_e , Å	B_e , cm ⁻¹	a_e , cm ⁻¹	ω_e , cm ⁻¹	$\omega_e x_e$, cm ⁻¹
X ¹ Σ ⁺	0	1	1.2425	1.81984	0.01765	1854.71	13.34
X ³ Π _u	610	6	1.3119	1.63246	0.01661	1841.35	11.67
A ³ Σ ⁺	6243.5	3	1.3693	1.49852	0.01634	1470.45	11.19
b ¹ Π _g	8268.33	2	1.3184	1.61634	0.01686	1608.35	12.078
A ¹ Σ ⁺	13365	3	1.23	1.87	[0.018]	1961.6	13.65
1 _g	[15000]	2	[1.39]	[1.454]	[0.015]	[1510]	[11.1]
1 _u	[18570]	1	[1.38]	[1.475]	[0.013]	[1510]	[10.0]
1 _g	19916	6	1.266	1.7527	0.01608	1788.2	16.44
S _{II}	[22260]	10	[1.46]	[1.324]	[0.012]	[1400]	[9.9]
S _{II}	[30320]	5	[1.35]	[1.557]	[0.015]	[1550]	[11.7]
c ¹ Π _g	34262	2	1.2552	1.7334	0.018	1809.1	15.81
3 _u	[34530]	6	[1.51]	[1.23]	[0.013]	[1160]	[9.2]
1 _u	[34760]	1	[1.90]	[0.778]	[0.005]	[1025]	[5.8]
3 _g	[36020]	6	[1.53]	[1.20]	[0.011]	[1290]	[9.0]
B ³ Π _g	40590	6	1.535	1.1922	0.0242	1106.56	39.26
3 _u	[40780]	6	[1.51]	[1.23]	[0.011]	[1380]	[9.2]
3 _g	[42370]	6	[1.49]	[1.265]	[0.012]	[1340]	[9.5]
1 _g	[42860]	2	[1.51]	[1.232]	[0.011]	[1360]	[9.2]
d ¹ Σ ⁺	43240	1	1.2378	1.8334	0.0204	1829.57	13.97
3 _u	[43360]	3	[1.44]	[1.355]	[0.011]	[1660]	[10.2]

Heat of Formation

Messierle and Kraus (1) have reported the dissociation energy as 49300 ± 300 cm⁻¹ from the variation of the rotational structure cut-off with vibrational level in the c¹Π_g state. This state dissociates into C³P + C³P, due to an avoided crossing (2), these dissociation products are those of the ground state. The uncertainty in the determination is generous and thus we adopt D₀ = 140.95 ± 0.9 kcal/mol, using ΔHf₀(C, g) = 169.576 kcal/mol (3).

Brewer et al. (4) have reviewed several other earlier determinations which confirm ΔHf₀ = 185 ± 5 kcal/mol. The extensive mass spectrometric data of Drowart et al. (5) yield a 3rd law ΔHf₀ = 199.2 ± 1.4 kcal/mol in excellent agreement with the adopted value.

Heat Capacity and Entropy

The observed molecular constants and electronic levels were taken from Ballik and Ramsay (2). The estimated parameters are from the correlation calculations of Fougere and Nesbet (6) and Clementi (7), the electronic levels are T₀ values. Not all predicted states were included since the contribution of levels above 40000 cm⁻¹ is negligible. The functions were calculated from the partition function $Q = Q_e \sum_i g_i \exp(-C_2 \epsilon_i / T)$, the values for Q_e and C₂ were calculated with first order anharmonic corrections. The functions are similar to those reported by Altman (8) and Clementi (7) but include several additional states.

References

1. G. Messierle and L. Kraus, Z. Naturforsch. **22a**, 2023 (1967); **22a** 1744 (1967) and **22a**, 2015 (1967).
2. E. A. Ballik and D. A. Ramsay, Astrophys. Journ. **137**, 84 (1963).
3. JANAF Table dated Mar. 31, 1961.
4. L. Brewer, W. T. Hicks, and O. H. Krikorian, J. Chem. Phys. **35**, 182 (1962).
5. J. Drowart, R. P. Burns, G. DeMaría and M. G. Inghram, J. Chem. Phys. **31**, 1131 (1959).
6. P. F. Fougere and R. K. Nesbet, J. Chem. Phys. **44**, 285 (1966).
7. E. Clementi, Astrophys. Journ. **133**, 303 (1961).
8. R. Altman, J. Chem. Phys. **23**, 615 (1960).

C₂

Dimeric Carbon Uninegative Ion (C₂⁻)
(Ideal Gas) GFW = 24.02285

$$\Delta H_F^0 = 106 \pm 20 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 46.96 \pm 0.05 \text{ gibbs/mol}$$

Ground State Configuration [2]



Electronic Levels and Quantum Weights

$$\frac{g_i}{Z} = \frac{g_i}{2} \quad \begin{matrix} [4] \\ [2] \end{matrix}$$

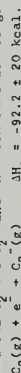
$$\omega_e = 1781.04 \text{ cm}^{-1} \quad \sigma = 2$$

$$B_e = 1.74685 \text{ cm}^{-1}$$

$$r_e = 1.2682 \text{ \AA}$$

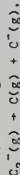
Heat of Formation

The electron affinity of C₂ has been obtained by Honig (1) as 4 ± 0.8 ev from the difference in heats of sublimation of neutral C₂ and C₂⁻ and the work function of graphite. Thus, we have the reaction



Using $\Delta H_F^0(C_2, g) = 198.2 \text{ kcal/mol}$ (2), we obtain $\Delta H_F^0(C_2^-, g) = 106 \pm 20 \text{ kcal/mol}$, which is adopted.

A value for the heat of formation may be obtained from a linear Birge-Sponer extrapolation of the ground state vibrational levels, which gives 195.8 kcal for the reaction



With auxiliary data (2) this yields $\Delta H_F^0(C_2^-, g) = 114.5 \text{ kcal/mol}$, in good agreement with the adopted value.

Heat Capacity and Entropy

The molecular constants and electronic levels are from Herzberg and Lagerqvist (3). The values are not definitely ascribed to C₂⁻ by Herzberg and Lagerqvist, but there is a good deal of evidence to support this assignment. Recently Milligan and Jacox (4) have shown that matrix isolated bands previously attributed to C₂(g) are enhanced in the presence of a photoelectron source. The matrix spectra correspond to the gas system reported by Herzberg and Lagerqvist (3) and leave little doubt that the species is C₂⁻.

The estimated electronic level is assumed to be a ²Π state and is obtained from the isoelectronic CN(g) (2).

References

1. R. E. Honig, J. Chem. Phys. **22**, 126 (1954).
2. JANAF Thermochemical Tables, Dec. 31, 1969.
3. G. Herzberg and A. Lagerqvist, Can. J. Phys. **42**, 2363 (1958).
4. D. E. Milligan and M. E. Jacox, J. Chem. Phys. **51**, 1952 (1969).

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0							
100							
200							
298	6.989	46.961	46.961	.000	106.000	94.296	-49.121
300	6.990	47.004	46.941	.013	105.996	94.224	-68.442
400	7.105	49.029	47.236	.717	105.711	90.339	-49.359
500	7.292	50.633	47.761	1.436	105.295	86.541	-37.027
600	7.506	51.982	48.355	2.176	104.782	82.834	-30.173
700	7.737	53.119	48.989	2.937	104.192	79.226	-24.731
800	7.987	54.097	49.589	3.718	103.563	75.702	-20.981
900	8.055	55.136	50.119	4.516	102.890	72.256	-17.566
1000	8.189	55.992	50.664	5.328	102.193	68.890	-15.056
1100	8.303	56.776	51.184	6.153	101.475	65.593	-13.032
1200	8.390	57.501	51.682	6.993	100.744	62.364	-11.395
1300	8.459	58.181	52.153	7.843	99.992	59.197	-9.952
1400	8.571	58.813	52.609	8.686	99.236	56.090	-8.756
1500	8.648	59.407	53.042	9.547	98.472	53.034	-7.727
1600	8.724	59.968	53.458	10.416	97.704	50.028	-6.833
1700	8.797	60.508	53.850	11.276	96.915	47.141	-6.032
1800	8.873	61.028	54.260	12.117	96.115	44.361	-5.362
1900	8.960	61.548	54.608	13.068	95.196	41.623	-4.820
2000	9.044	61.984	54.964	13.968	94.629	38.465	-4.203
2100	9.130	62.391	55.307	14.877	93.667	35.480	-3.713
2200	9.216	62.780	55.630	15.790	92.653	32.692	-3.270
2300	9.303	63.150	55.933	16.720	91.593	30.208	-2.870
2400	9.398	63.528	56.271	17.656	90.490	27.520	-2.504
2500	9.489	64.013	56.573	18.600	90.455	24.864	-2.174
2600	9.580	64.387	56.867	19.553	90.113	22.240	-1.869
2700	9.670	64.700	57.132	20.512	89.581	19.650	-1.586
2800	9.759	65.008	57.373	21.487	88.951	17.073	-1.333
2900	9.844	65.488	57.700	22.468	87.924	14.510	-1.095
3000	9.928	65.783	57.964	23.456	87.209	12.012	-0.875
3100	10.009	66.110	58.222	24.453	86.497	9.519	-0.671
3200	10.086	66.470	58.471	25.450	85.684	7.050	-0.504
3300	10.160	66.760	58.713	26.470	84.768	4.590	-0.364
3400	10.230	67.045	58.959	27.490	83.766	2.165	-0.139
3500	10.294	67.342	59.195	28.516	82.689	.248	.015
3600	10.359	67.633	59.425	29.539	81.537	-2.636	.160
3700	10.417	67.910	59.651	30.569	80.309	-5.550	.295
3800	10.470	68.183	59.873	31.600	78.998	-8.490	.423
3900	10.523	68.469	60.088	32.682	77.605	-11.454	.542
4000	10.569	68.736	60.302	33.737	76.147	-14.444	.655
4100	10.612	68.997	60.511	34.796	74.628	-17.462	.762
4200	10.652	69.254	60.716	35.854	73.046	-20.509	.862
4300	10.689	69.507	60.916	36.910	71.406	-23.584	.952
4400	10.720	69.753	61.115	37.956	69.712	-26.688	1.034
4500	10.749	69.992	61.310	39.070	67.967	-29.827	1.133
4600	10.775	70.228	61.501	40.166	66.168	-32.999	1.216
4700	10.799	70.450	61.680	41.265	64.318	-36.204	1.290
4800	10.821	70.661	61.856	42.366	62.422	-39.444	1.354
4900	10.837	70.811	62.056	43.388	60.486	-42.719	1.412
5000	10.852	71.130	62.236	44.473	58.510	-46.034	1.468
5100	10.865	71.345	62.412	45.559	56.500	-49.387	1.561
5200	10.876	71.557	62.586	46.656	54.456	-52.776	1.620
5300	10.886	71.767	62.762	47.766	52.380	-56.200	1.674
5400	10.892	71.967	62.926	48.823	50.280	-59.659	1.731
5500	10.898	72.167	63.092	49.912	48.156	-63.154	1.783
5600	10.901	72.364	63.256	51.002	46.000	-66.689	1.832
5700	10.903	72.557	63.418	52.093	43.818	-70.260	1.890
5800	10.904	72.743	63.576	53.186	41.610	-73.868	1.948
5900	10.904	72.935	63.716	54.273	39.386	-77.514	2.009
6000	10.902	73.116	63.849	55.364	37.146	-81.199	



Beryllium Carbide (BeC₂)

(Ideal Gas) Mol. Wt. = 33.035

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	-0.00	INFINITE	-2.436	133.535	133.535	INFINITE
100	7.292	42.924	1.336	133.535	133.535	-1.336
200	8.694	46.481	0.925	134.715	125.509	-1.371
298	9.867	52.232	0.000	135.000	120.917	-86.630
300	9.881	52.293	0.018	135.003	120.830	-86.020
400	10.755	57.631	1.051	135.095	116.087	-63.424
500	11.156	57.691	2.127	135.039	111.359	-48.664
600	11.696	59.733	3.269	134.883	106.611	-38.831
700	12.174	61.573	4.463	134.655	101.917	-31.819
800	12.580	63.226	5.702	134.381	97.260	-26.569
900	12.916	64.727	6.977	134.065	92.636	-22.494
1000	13.197	66.113	8.283	133.719	88.051	-19.243
1100	13.427	67.372	9.615	133.341	83.502	-16.589
1200	13.618	68.549	10.968	132.933	78.990	-14.385
1300	13.776	69.646	12.338	132.493	74.512	-12.526
1400	13.909	70.672	13.722	132.029	70.071	-10.938
1500	14.021	71.635	15.119	131.538	65.662	-9.567
1600	14.115	72.543	16.526	128.266	61.363	-8.381
1700	14.196	73.401	17.941	127.840	57.195	-7.353
1800	14.266	74.215	19.364	127.407	53.052	-6.441
1900	14.326	74.988	20.794	126.970	48.934	-5.628
2000	14.378	75.724	22.229	126.527	44.838	-4.899
2100	14.423	76.426	23.669	126.080	40.767	-4.242
2200	14.463	77.098	25.114	125.625	36.711	-3.647
2300	14.499	77.742	26.563	125.166	32.685	-3.106
2400	14.530	78.360	28.013	124.699	28.673	-2.611
2500	14.558	78.951	29.468	124.228	24.679	-2.157
2600	14.583	79.525	30.925	123.749	20.708	-1.741
2700	14.605	80.076	32.384	123.266	16.752	-1.356
2800	14.625	80.607	33.846	122.772	12.806	-1.007
2900	14.644	81.121	35.309	122.272	8.871	-0.688
3000	14.660	81.618	36.774	121.768	4.946	-0.409
3100	14.675	82.099	38.241	121.259	1.021	-0.169
3200	14.689	82.565	39.709	120.745	-2.904	0.087
3300	14.701	83.017	41.179	120.226	-6.787	0.344
3400	14.713	83.456	42.650	119.702	-10.669	0.601
3500	14.723	83.883	44.121	119.174	-14.551	0.858
3600	14.733	84.297	45.594	118.641	-18.433	1.115
3700	14.742	84.701	47.068	118.102	-22.315	1.372
3800	14.750	85.094	48.543	117.558	-26.197	1.629
3900	14.758	85.478	49.999	117.009	-30.079	1.886
4000	14.765	85.851	51.454	116.455	-33.961	2.143
4100	14.771	86.216	52.907	115.896	-37.843	2.400
4200	14.778	86.572	54.364	115.332	-41.725	2.657
4300	14.783	86.920	55.821	114.763	-45.607	2.914
4400	14.789	87.260	57.278	114.189	-49.489	3.171
4500	14.794	87.592	58.735	113.610	-53.371	3.428
4600	14.798	87.917	60.192	113.026	-57.253	3.685
4700	14.803	88.236	61.648	112.437	-61.135	3.942
4800	14.807	88.547	63.105	111.843	-65.017	4.199
4900	14.811	88.853	64.562	111.244	-68.899	4.456
5000	14.814	89.152	66.019	110.640	-72.781	4.713
5100	14.818	89.445	67.476	110.031	-76.663	4.970
5200	14.821	89.733	68.933	109.417	-80.545	5.227
5300	14.824	90.016	70.390	108.798	-84.427	5.484
5400	14.827	90.293	71.847	108.174	-88.309	5.741
5500	14.830	90.565	73.304	107.545	-92.191	6.000
5600	14.833	90.832	74.761	106.911	-96.073	6.257
5700	14.835	91.095	76.218	106.272	-100.000	6.514
5800	14.837	91.353	77.675	105.628	-103.927	6.771
5900	14.840	91.606	79.132	104.979	-107.854	7.028
6000	14.842	91.856	80.589	104.325	-111.781	7.285

Dec. 31, 1960; Sept. 30, 1962; June 30, 1963; Dec. 31, 1963

C₂Be

BERYLLIUM CARBIDE (BeC₂)

(IDEAL GAS)

MOL. WT. = 33.035

Point Group [C_{∞v}]
 $\Delta H_f^0 = [134]$ kcal. mole⁻¹
 $\Delta F_f^0 = [135]$ kcal. mole⁻¹
 $S_{298.15}^0 = [52.2]$ cal. deg.⁻¹ mole⁻¹
 Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	σ
[1580] (1)	[423] (1)
[1947] (1)	[1947] (1)

Bond Distances: Be-C = [1.407] Å C-C = [1.2] Å
 Bond Angle: Be-C-C = [180°]
 Rotational Constant: B₀ = [0.4809] cm.⁻¹

Heat of Formation

ΔH_f^0 298.15 was estimated as a lower positive limit by National Bureau of Standards Report No. 6645, "Preliminary Report on the Thermodynamic Properties of Light-Element Compounds," January, 1960.

Heat Capacity and Entropy

The vibrational frequencies, bond angle, configuration and moment of inertia, 5.82×10^{-39} g. cm.², were estimated by Chupka, Berkowitz, Gleason, and Inghram, J. Phys. Chem. 62, 611 (1958). Bond distances were calculated assuming the C-C bond distance was the same as in acetylene.



$\Delta H_f^\circ = [49.3 \pm 10] \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = [50.1 \pm 10] \text{ kcal/mol}$

Point Group D_{∞h}
S_{298.15} = [65 ± 3] gibbs/mol
Ground State Quantum Weight = 1

Dichloroacetylene (C₂Cl₂)
(Ideal Gas) GFW = 94.9283

T, °K	C _p ^a	gibbs/mol S° ^b - (G° - H° ₂₉₈)/T	kcal/mol ΔH° ^c	Log Kp
0	10.000	0.000	49.317	INFINITE
100	10.720	1.513	49.398	- 106.620
200	13.823	59.086	49.735	- 52.711
258	15.672	64.989	50.100	- 34.761
300	15.698	65.086	50.406	- 34.535
400	16.782	67.782	50.412	- 35.383
500	17.507	68.682	49.441	- 19.692
600	18.048	76.831	50.792	- 16.167
700	18.478	79.687	50.691	- 13.522
800	18.827	82.138	50.953	- 11.535
900	19.115	84.373	50.846	- 9.987
1000	19.352	86.339	51.004	- 8.748
1100	19.549	88.253	51.066	- 7.735
1200	19.713	89.962	50.998	- 6.891
1300	19.850	91.585	50.976	- 6.176
1400	19.966	93.020	50.951	- 5.565
1500	20.064	94.401	50.918	- 5.035
1600	20.148	95.699	50.881	- 4.571
1700	20.220	96.923	50.843	- 4.162
1800	20.282	98.080	50.799	- 3.799
1900	20.335	99.176	50.754	- 3.474
2000	20.382	100.223	50.705	- 3.183
2100	20.423	101.218	50.656	- 2.920
2200	20.460	102.169	50.600	- 2.680
2300	20.492	103.079	50.545	- 2.462
2400	20.520	103.952	50.484	- 2.262
2500	20.546	104.770	50.422	- 2.078
2600	20.568	105.536	50.354	- 1.908
2700	20.589	106.253	50.284	- 1.751
2800	20.607	106.912	50.211	- 1.606
2900	20.624	107.519	50.132	- 1.471
3000	20.639	108.075	50.049	- 1.345
3100	20.653	109.222	49.962	- 1.228
3200	20.665	109.678	49.870	- 1.118
3300	20.677	110.514	49.772	- 1.015
3400	20.687	111.131	49.672	- .918
3500	20.697	111.731	49.564	- .827
3600	20.706	112.314	49.453	- .741
3700	20.714	112.682	49.336	- .660
3800	20.722	113.434	49.216	- .583
3900	20.729	113.990	49.099	- .511
4000	20.736	114.497	48.979	- .442
4100	20.742	115.010	48.850	- .377
4200	20.747	115.509	48.698	- .315
4300	20.753	115.998	48.536	- .256
4400	20.758	116.485	48.366	- .200
4500	20.762	116.941	48.231	- .147
4600	20.767	117.398	48.073	- .096
4700	20.771	117.844	47.911	- .048
4800	20.774	118.282	47.742	- .001
4900	20.778	118.710	47.571	- .053
5000	20.781	119.110	47.396	- .105
5100	20.785	119.582	47.215	- .156
5200	20.788	119.985	47.032	- .207
5300	20.791	120.341	46.843	- .258
5400	20.793	120.710	46.652	- .309
5500	20.796	121.111	46.454	- .360
5600	20.798	121.486	46.255	- .411
5700	20.801	121.854	46.049	- .462
5800	20.803	122.216	45.840	- .513
5900	20.805	122.567	45.626	- .564
6000	20.807	122.921	45.409	- .615

Dec. 31, 1968



Tetrachloroethylene (C₂Cl₄)
(Ideal Gas) GFW = 165.8343

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	+∞	+∞	+∞	-	-	-	INFINITE
100	13.589	62.201	99.856	-4.759	-2.637	2.637	INFINITE
200	19.812	78.412	116.412	-3.766	-2.412	2.412	5.900
298	22.836	82.052	122.836	-3.000	-2.153	2.153	5.777
300	22.867	82.194	123.000	-2.966	-2.153	2.153	5.777
400	25.194	89.115	128.981	-2.454	-2.706	2.706	4.309
500	26.764	94.916	134.803	-2.057	-2.447	2.447	4.592
600	27.905	99.506	140.515	-1.795	-2.203	2.203	4.762
700	28.712	104.272	146.166	-1.601	-1.976	1.976	4.871
800	29.304	108.146	151.230	-1.454	-1.764	1.764	4.944
900	29.749	111.425	155.309	-1.339	-1.564	1.564	5.000
1000	30.089	114.777	158.301	-1.246	-1.372	1.372	5.030
1100	30.353	117.658	160.204	-1.169	-1.189	1.189	5.055
1200	30.562	120.108	161.921	-1.105	-1.015	1.015	5.073
1300	30.730	122.761	163.454	-1.052	-0.852	0.852	5.086
1400	30.866	125.054	164.808	-1.009	-0.692	0.692	5.096
1500	30.979	127.177	166.000	-0.974	-0.539	0.539	5.103
1600	31.072	129.180	167.052	-0.945	-0.393	0.393	5.106
1700	31.151	131.066	168.000	-0.920	-0.248	0.248	5.109
1800	31.217	132.848	168.840	-0.898	-0.109	0.109	5.110
1900	31.274	134.538	169.575	-0.878	0.028	0.028	5.111
2000	31.323	136.143	170.215	-0.859	0.157	0.157	5.111
2100	31.365	137.673	170.765	-0.841	0.286	0.286	5.109
2200	31.402	139.133	171.230	-0.824	0.408	0.408	5.107
2300	31.435	140.529	171.615	-0.808	0.528	0.528	5.106
2400	31.463	141.868	171.925	-0.792	0.641	0.641	5.103
2500	31.489	143.153	172.162	-0.776	0.749	0.749	5.101
2600	31.511	144.388	172.422	-0.761	0.851	0.851	5.098
2700	31.532	145.578	172.699	-0.746	0.947	0.947	5.095
2800	31.550	146.725	172.989	-0.731	1.037	1.037	5.093
2900	31.566	147.832	173.289	-0.716	1.119	1.119	5.090
3000	31.581	148.903	173.599	-0.701	1.194	1.194	5.086
3100	31.594	149.938	173.917	-0.686	1.263	1.263	5.084
3200	31.606	150.942	174.243	-0.671	1.323	1.323	5.081
3300	31.617	151.914	174.577	-0.656	1.378	1.378	5.078
3400	31.628	152.858	174.917	-0.641	1.428	1.428	5.076
3500	31.637	153.775	175.262	-0.626	1.474	1.474	5.072
3600	31.645	154.667	175.612	-0.611	1.516	1.516	5.068
3700	31.653	155.534	175.967	-0.596	1.555	1.555	5.065
3800	31.661	156.378	176.327	-0.581	1.592	1.592	5.062
3900	31.668	157.201	176.691	-0.566	1.626	1.626	5.060
4000	31.674	158.002	177.059	-0.551	1.658	1.658	5.057
4100	31.680	158.785	177.432	-0.536	1.688	1.688	5.054
4200	31.685	159.548	177.809	-0.521	1.716	1.716	5.051
4300	31.691	160.294	178.190	-0.506	1.743	1.743	5.048
4400	31.696	161.022	178.575	-0.491	1.768	1.768	5.045
4500	31.700	161.735	178.964	-0.476	1.792	1.792	5.042
4600	31.705	162.431	179.357	-0.461	1.816	1.816	5.039
4700	31.709	163.113	179.754	-0.446	1.840	1.840	5.036
4800	31.714	163.781	180.154	-0.431	1.863	1.863	5.033
4900	31.718	164.435	180.557	-0.416	1.886	1.886	5.030
5000	31.722	165.076	180.964	-0.401	1.909	1.909	5.027
5100	31.726	165.704	181.374	-0.386	1.932	1.932	5.024
5200	31.729	166.320	181.787	-0.371	1.955	1.955	5.021
5300	31.733	166.924	182.203	-0.356	1.978	1.978	5.018
5400	31.737	167.518	182.621	-0.341	1.999	1.999	5.015
5500	31.741	168.100	183.041	-0.326	2.021	2.021	5.012
5600	31.745	168.672	183.464	-0.311	2.043	2.043	5.009
5700	31.749	169.234	183.890	-0.296	2.065	2.065	5.006
5800	31.753	169.786	184.317	-0.281	2.086	2.086	5.003
5900	31.757	170.329	184.745	-0.266	2.107	2.107	5.000
6000	31.762	170.863	185.174	-0.251	2.128	2.128	4.997

Sept. 30, 1967

TETRACHLOROETHYLENE (C₂Cl₄)
(IDEAL GAS) GFW = 165.8343

Point Group D_{2h}
S°_{298.15} = 82.052 gibbs/mol
ΔHf° = -2.64 ± 0.7 kcal/mol
ΔHf°_{298.15} = -2.97 ± 0.7 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	1	63557	1
[37700] [1]		70097	1
[50350] [1]		72410	1
[59000] [1]			

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	ω_i , cm ⁻¹	ω_i , cm ⁻¹
1571 (1)	1000 (1)	918 (1)
447 (1)	347 (1)	176 (1)
235 (1)	324 (1)	777 (1)
110 (1)	512 (1)	288 (1)

Bond Distances: C1 - C = 1.724 Å C - C = 1.327 Å
Bond Angle: C1 - C - C1 = 113.3° σ = 4
Product of the Moments of Inertia: I_AI_BI_C = 3.43114 × 10⁻¹¹² g cm⁶

Heat of Formation

The heat of combustion (ΔE₂₉₃) of C₂Cl₄(g) has been determined by the "Quartz Wool" method by L. Smith, L. Bjellerup, S. Krook and H. Westermarck, Acta Chem. Scand. Z, 65 (1953). The free chlorine produced from combustion was reduced to hydrogen chloride by a quartz spiral moistened with a solution of arsenious acid in the combustion bomb. Based on the reported results, the enthalpy change at 298°K for the reaction C₂Cl₄(g) + 2H₂O(l) = 2CO₂(g) + 4HCl(600H₂O) is evaluated as -198.40 kcal/mol, using recent auxiliary data from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965 and V. B. Parker, U. S. Natl. Bur. Std. NBS-2, 1965, and Cp for C₂Cl₄(l) from V. Y. Kurbatov, J. Gen. Chem. USSR(Eng. Transl.) 16, 372 (1948). Employing ΔH_{f298} = -94.054, -39.823 and -68.315 kcal/mol for CO₂(g), HCl(600H₂O) and H₂O(l), respectively, we calculate the heat of formation for C₂Cl₄(g) as -12.367 kcal/mol. Incorporating this value with the value ΔH_{f298} = 9.4 kcal/mol obtained from E. Efring, Ph.D. Thesis, University of Lund, 1938, we derive ΔH_{f298} = -2.97 ± 0.7 kcal/mol for C₂Cl₄(g).

Heat Capacity and Entropy

The molecular structure of C₂Cl₄(g) was investigated by the sector-visual method of electron diffraction by C. H. Ramachandra and R. L. Livingston, Current Sci. 27, 330 (1958). The reported bond distances and angle are in agreement with those measured by I. L. Karle and J. Karle, J. Chem. Phys. 20, 63 (1952), using the sector-microphotometer method, and W. N. Lipscomb, Ph.D. Thesis, California Institute of Technology, 1946. The molecular structure has also been determined by L. O. Brockway, J. Y. Beach and L. Pauling, J. Am. Chem. Soc. 57, 2693 (1935), H. de Laszlo, Nature 135, 474 (1935), and R. W. Dornte, J. Chem. Phys. 1, 566 (1933), by use of electron diffraction. The values reported by Ramachandra and Livingston, loc. cit., are adopted. The vibrational spectra of tetrachloroethylene have been studied by numerous investigators. The vibrational frequencies assigned by D. E. Mann, N. Acquista and E. K. Plyler, J. Res. Natl. Bur. Std. 52, 67 (1954), are adopted here. These authors also reviewed the results of earlier investigations in detail. The electronic levels and quantum weights are obtained from G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966. The three principal moments of inertia are: I_A = 4.88344 × 10⁻³⁶, I_B = 6.28884 × 10⁻³⁶ and I_C = 1.11723 × 10⁻³⁷ g cm².

T, °K	Cp°	μHbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	Log Kp
0	18.253	67.631	120.572	-5.354	-32.468	55.905
100	21.266	68.414	120.572	-3.141	-32.468	55.905
200	23.206	69.069	120.572	-1.000	-32.000	55.905
300	24.286	69.575	120.572	-0.082	-32.071	6.615
400	24.677	69.955	120.572	3.573	-31.542	6.817
500	24.781	70.182	120.572	7.354	-30.956	6.602
600	24.681	70.261	120.572	11.305	-30.370	6.237
700	24.401	70.209	120.572	15.367	-29.792	5.803
800	24.014	70.035	120.572	19.507	-29.228	5.554
900	23.574	69.781	120.572	23.703	-28.674	5.434
1000	23.111	69.476	120.572	27.941	-28.132	5.423
1100	22.631	69.124	120.572	32.210	-27.600	5.423
1200	22.141	68.739	120.572	36.502	-27.080	5.423
1300	21.641	68.324	120.572	40.813	-26.573	5.423
1400	21.131	67.889	120.572	45.136	-26.074	5.423
1500	20.611	67.434	120.572	49.470	-25.586	5.423
1600	20.081	66.959	120.572	53.811	-25.109	5.423
1700	19.541	66.464	120.572	58.155	-24.640	5.423
1800	18.991	65.949	120.572	62.502	-24.184	5.423
1900	18.431	65.414	120.572	66.851	-23.735	5.423
2000	17.861	64.869	120.572	71.200	-23.301	5.423
2100	17.281	64.314	120.572	75.549	-22.871	5.423
2200	16.691	63.749	120.572	79.906	-22.441	5.423
2300	16.091	63.174	120.572	84.242	-22.015	5.423
2400	15.481	62.589	120.572	88.585	-21.595	5.423
2500	14.861	61.994	120.572	92.926	-21.188	5.423
2600	14.231	61.389	120.572	97.266	-20.791	5.423
2700	13.591	60.774	120.572	101.603	-20.408	5.423
2800	12.941	60.149	120.572	105.939	-20.027	5.423
2900	12.281	59.514	120.572	110.273	-19.650	5.423
3000	11.611	58.869	120.572	114.605	-19.286	5.423
3100	10.941	58.214	120.572	118.935	-18.935	5.423
3200	10.261	57.549	120.572	123.263	-18.599	5.423
3300	9.571	56.874	120.572	127.589	-18.278	5.423
3400	8.871	56.189	120.572	131.913	-17.971	5.423
3500	8.161	55.494	120.572	136.236	-17.678	5.423
3600	7.441	54.789	120.572	140.556	-17.390	5.423
3700	6.711	54.074	120.572	144.875	-17.117	5.423
3800	5.971	53.349	120.572	149.193	-16.851	5.423
3900	5.221	52.614	120.572	153.508	-16.595	5.423
4000	4.461	51.869	120.572	157.823	-16.348	5.423
4100	3.691	51.114	120.572	162.135	-16.101	5.423
4200	2.911	50.349	120.572	166.447	-15.861	5.423
4300	2.121	49.574	120.572	170.757	-15.621	5.423
4400	1.321	48.789	120.572	175.067	-15.381	5.423
4500	0.511	47.994	120.572	179.377	-15.141	5.423
4600	-0.291	47.189	120.572	183.681	-14.901	5.423
4700	-1.081	46.374	120.572	187.985	-14.661	5.423
4800	-1.871	45.549	120.572	192.292	-14.421	5.423
4900	-2.661	44.714	120.572	196.595	-14.181	5.423
5000	-3.451	43.879	120.572	200.898	-13.941	5.423
5100	-4.241	43.034	120.572	205.199	-13.701	5.423
5200	-5.031	42.189	120.572	209.500	-13.461	5.423
5300	-5.821	41.334	120.572	213.800	-13.221	5.423
5400	-6.611	40.479	120.572	218.099	-12.981	5.423
5500	-7.401	39.614	120.572	222.397	-12.741	5.423
5600	-8.191	38.749	120.572	226.694	-12.501	5.423
5700	-8.981	37.884	120.572	230.991	-12.261	5.423
5800	-9.771	37.019	120.572	235.286	-12.021	5.423
5900	-10.561	36.154	120.572	239.582	-11.781	5.423
6000	-11.351	35.289	120.572	243.876	-11.541	5.423

Sept. 30, 1967

ν, cm ⁻¹	ν, cm ⁻¹	ν, cm ⁻¹
976 (1)	778 (1)	778 (2)
431 (1)	377 (1)	778 (2)
164 (1)	858 (2)	267 (2)
340 (2)	340 (2)	139 (2)

C-C = 1.55 Å

C-Cl = 1.74 Å

Cl-C-Cl = 110°

Product of the Moments of Inertia: I_AI_BI_C = 1.2358 × 10⁻¹¹¹ g³ cm⁶C₂Cl₆ = 109°

Heat of Formation

Smith et al. (1) determined the heat of combustion of C₂Cl₆(g) to be ΔH₂₉₃ = -718.7 ± 2 cal/g (uncorrected) by use of the "Quartz Wool" method. The free chlorine produced was reduced to HCl by employing the quartz spiral moistened with a solution of arsenious acid in the combustion bomb. Adopting the reported results and recent auxiliary data (2, 3, 4), we evaluate the values ΔH₂₉₈ = -717.525 and ΔH₂₉₈ = -48.58 kcal/mol for C₂Cl₆(g). Kirkbride (5) measured the enthalpy changes as -32.0 and 4.7 kcal/mol for the following two reactions by solution calorimetry: C₂Cl₆(l) + Cl₂(g) = C₂Cl₄(aq) and C₂Cl₆(g) = C₂Cl₄(aq). Hence we obtain ΔH₂₉₈ = -49.07 kcal/mol for C₂Cl₆(g), using ΔH₂₉₈ (C₂Cl₄, l) = -12.37 kcal/mol. This value is in reasonable agreement with the adopted value -48.58 kcal/mol.

Hexachloroethane (c) has three modifications, namely triclinic, monoclinic and cubic, with transition temperatures of 318 and 345°K (4). The sublimation pressures over the different phases have been measured by Ivin (8), Lee (2), and Nitta (25). Based on these data, values for ΔH₂₉₈ (triclinic) are derived by a modified second law method to be 16.5, 17.1 and 14.8 kcal/mol, respectively. The analysis depends on the Cp and ΔH₂₉₈ data determined by (4). The order of chemical Company, Midland, Michigan. Pressures reported by Nelson (6) are systematically lower than the above data by about 10 per cent; therefore, his data are not used. Third law analysis is not applicable to the pressure data due to lack of S₂₉₈ (triclinic). Adopting ΔH₂₉₈ = 16.5 and ΔH₂₉₈ = -48.58 kcal/mol for C₂Cl₆ (triclinic), we obtain ΔH₂₉₈ = -32.08 kcal/mol for C₂Cl₆(g).

The equilibrium constant at 776°K for the reaction C₂Cl₆(g) = C₂Cl₄(g) + Cl₂(g) was reported as 0.8 ± 0.1 (atm) by Puyo et al. (3). The corresponding enthalpy change at 298°K is evaluated to be 30.8 kcal/mol by the third law method, yielding ΔH₂₉₈(C₂Cl₆, g) = -33.77 kcal/mol which is in fair agreement with the adopted one.

Heat Capacity and Entropy

The molecular structure of C₂Cl₆ has been studied previously by means of infrared and Raman spectroscopy (10), X-ray (11), and electron diffraction (12-18). The molecule was found to be in the staggered position in the vapor and solid states. The bond distances and angles adopted here are those reported by Swick et al. (16).

Incomplete assignments of vibrational frequencies for C₂Cl₆(g) were reported by many investigators (21-24). The adopted frequencies, except the torsional mode ν₁, are obtained from Carney et al. (19). The torsional mode ν₁ is treated as a hindered internal rotation, and thermodynamic properties are calculated (25) from the barrier height of V₀ = 12.6 kcal/mol which was evaluated by Karle (20) from electron diffraction data. The value of S₂₉₈ is calculated based on S₂₉₈ = 105.355 eu which is derived from the free rotor value S₂₉₈ = 104.121 eu by subtraction of the entropy difference between a free rotor and hindered rotor at 400°K. Internal rotation contributions to Cp at temperatures below 350°K could not be calculated since they are beyond the range of the values tabulated by Pitzer (25). These Cp contributions are estimated by graphical interpolation between internal rotation values above 350°K and the corresponding harmonic oscillator values (ν₁ = 67 cm⁻¹, below 150°K. This calculation presumes that the internal rotation approaches harmonic oscillation as V₀/RT > 1.

The three principal moments of inertia are: I_A = I_C = 1.1367 × 10⁻³⁷ and I_B = 9.564 × 10⁻³⁶ g cm².

References

1. L. Smith, L. Bjellerup, S. Krook and H. Westmark, *Acta Chem. Scand.* **7**, 65 (1953).
2. L. Smith, L. Bjellerup, S. Krook and H. Westmark, *Acta Chem. Scand.* **7**, 65 (1953).
3. V. B. Parker, U. S. Natl. Bur. Stand., *Monograph* **2**, 1965.
4. S. Seki and M. Honotani, *Bull. Chem. Soc. Japan* **23**, 30 (1950).
5. F. O. Nelson, *J. Appl. Chem.* **6**, 11 (1956).
6. O. A. Nelson, *Ind. Eng. Chem.* **24**, 971 (1930); 304 - 328°K, seven data points.
7. P. J. V. d. Lee, *Z. Anorg. Allgem. Chem.* **223**, 213 (1935); 346 - 458°K, 32 data points.
8. J. V. d. Lee, *Z. Anorg. Allgem. Chem.* **223**, 213 (1935); 346 - 458°K, 32 data points.
9. J. Puyo, *Unpublished data*.
10. Landolt-Bornstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik*, Springer-Verlag, Berlin, 1951.
11. Y. Sasada and M. Atoji, *J. Chem. Phys.* **21**, 145 (1953).
12. S. Mizushima, Y. Morino and S. Yamaguchi, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)* **42**, 5 (1944).
13. M. Kikawa and Y. Morino, *Acta Chem. Scand.* **1**, 149 (1947).
14. Y. Morino and M. Iwasaki, *J. Chem. Phys.* **17**, 216 (1949).
15. D. A. Swick, I. L. Karle and J. Karle, *J. Chem. Phys.* **22**, 1242 (1954).
16. Y. Morino and E. Hirota, *J. Chem. Phys.* **28**, 185 (1958).
17. A. Allen, *Chem. Phys.* **23**, 419 (1966).
18. R. A. Carney, E. A. Piotrowski, A. G. Meister, J. H. Braun and F. H. Cleveland, *J. Mol. Spectry*, **2**, 203 (1961).
19. R. A. Carney, *J. Chem. Phys.* **23**, 419 (1966).
20. D. T. Hamilton, *J. Chem. Phys.* **32**, 208 (1944).
21. H. Gerdling and H. G. Harig, *Rec. Trav. Chim.* **65**, 70 (1946).
22. S. Mizushima, Y. Morino, T. Simanont and K. Kuratani, *J. Chem. Phys.* **17**, 638 (1949).
23. S. Mizushima, *Bull. Chem. Soc. Japan* **31**, 296 (1958).
24. G. N. Lewis and M. Randall, *Thermodynamics*, revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Company, Inc., New York, 1931.
25. I. Nitta and S. Seki, *J. Chem. Soc. Japan* **62**, 501 (1941). 290 - 343°K, 24 data points.

(Ideal Gas) GFW = 62.0191

T, °K	C _p	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	-0.00	-0.00	INFINITE	-2.964	4.650	4.650	INFINITE
100	4.228	46.483	66.902	-2.242	4.649	4.112	-8.988
200	11.556	53.280	59.499	-1.242	4.793	3.534	-3.462
298	13.508	58.305	58.305	.000	5.000	2.871	-2.105
300	13.430	58.380	58.305	.025	5.003	2.958	-2.082
400	15.117	62.525	58.855	1.467	5.183	1.585	-1.582
500	16.242	66.025	59.951	3.037	5.308	1.132	-1.582
600	17.111	69.066	61.222	4.706	5.389	.528	-1.92
700	17.785	71.757	62.539	6.453	5.435	.089	-1.082
800	18.210	74.167	63.844	8.259	5.455	-1.104	.302
900	18.528	76.339	65.141	10.121	5.458	-2.104	1.119
1000	18.782	78.339	66.339	12.000	5.451	-2.787	1.600
1100	19.311	80.167	67.514	13.919	5.432	-3.566	1.709
1200	19.523	81.857	68.639	15.861	5.405	-4.391	1.798
1300	19.696	83.426	69.717	17.922	5.365	-5.196	1.863
1400	19.838	84.879	70.759	20.000	5.318	-5.982	1.902
1500	19.958	86.266	71.735	21.789	5.274	-6.741	1.922
1600	20.058	87.556	72.687	23.790	5.220	-7.468	1.941
1700	20.143	88.774	73.598	25.800	5.164	-8.149	1.957
1800	20.215	89.928	74.473	27.818	5.102	-8.779	1.971
1900	20.276	91.015	75.315	29.855	5.035	-9.356	1.982
2000	20.335	92.063	76.127	31.873	4.972	-9.878	1.990
2100	20.379	93.057	76.910	33.909	4.904	-10.346	1.996
2200	20.420	94.006	77.666	35.969	4.829	-10.766	1.999
2300	20.456	94.915	78.396	37.993	4.754	-11.147	1.999
2400	20.488	95.786	79.103	39.990	4.679	-11.492	1.998
2500	20.516	96.623	79.787	42.000	4.599	-11.796	1.995
2600	20.542	97.428	80.450	44.143	4.502	-12.069	1.990
2700	20.568	98.204	81.093	46.199	4.412	-12.317	1.984
2800	20.585	98.952	81.718	48.256	4.321	-12.548	1.977
2900	20.603	99.575	82.325	50.315	4.228	-12.756	1.968
3000	20.620	100.373	82.915	52.374	4.120	-12.936	1.958
3100	20.635	101.050	83.489	54.439	4.017	-13.096	1.948
3200	20.649	101.705	84.048	56.503	3.909	-13.245	1.938
3300	20.662	102.341	84.593	58.569	3.795	-13.385	1.927
3400	20.673	102.963	85.124	60.635	3.678	-13.518	1.915
3500	20.684	103.557	85.642	62.704	3.557	-13.645	1.902
3600	20.694	104.140	86.148	64.772	3.432	-13.768	1.889
3700	20.703	104.707	86.642	66.866	3.302	-13.887	1.875
3800	20.711	105.259	87.124	68.913	3.169	-13.999	1.861
3900	20.718	105.798	87.591	70.957	3.034	-14.106	1.846
4000	20.726	106.322	88.058	73.057	2.898	-14.210	1.831
4100	20.733	106.838	88.510	75.129	2.739	-14.312	1.816
4200	20.738	107.338	88.952	77.203	2.586	-14.411	1.801
4300	20.744	107.822	89.385	79.277	2.428	-14.508	1.785
4400	20.749	108.293	89.810	81.332	2.265	-14.603	1.769
4500	20.755	108.765	90.220	83.427	2.097	-14.695	1.753
4600	20.759	109.221	90.638	85.503	1.924	-14.784	1.737
4700	20.764	109.668	91.034	87.579	1.746	-14.871	1.721
4800	20.768	110.105	91.427	89.655	1.561	-14.956	1.705
4900	20.772	110.532	91.802	91.732	1.372	-15.039	1.689
5000	20.775	110.953	92.161	93.810	1.178	-15.120	1.673
5100	20.779	111.364	92.563	95.887	.975	-15.200	1.657
5200	20.782	111.768	92.928	97.966	.770	-15.278	1.641
5300	20.785	112.164	93.287	100.044	.555	-15.355	1.625
5400	20.788	112.553	93.638	102.122	.338	-15.431	1.609
5500	20.791	112.938	93.988	104.200	.115	-15.506	1.593
5600	20.793	113.308	94.330	106.281	.115	-15.580	1.577
5700	20.796	113.676	94.666	108.360	.153	-15.654	1.561
5800	20.798	114.038	94.997	110.440	.595	-15.728	1.545
5900	20.801	114.398	95.324	112.520	.843	-15.802	1.529
6000	20.803	114.743	95.645	114.600	1.099	-15.876	1.513

Dec. 31, 1960; Dec. 31, 1966; Dec. 31, 1967

DIFLUOROACETYLENE (C₂F₂)

(IDEAL GAS)

GFW = 62.0191

Point Group [D_{∞h}]ΔH_{f,0}^o = {4.65 ± 5} kcal/molS_{298.15} = {58.3 ± 1.5} gibbs/molΔH_{f,298.15} = {5 ± 5} kcal/mol

Vibrational Frequencies and Degeneracies

$\frac{\sigma}{\text{cm}^{-1}}$	$\frac{\sigma}{\text{cm}^{-1}}$	$\frac{\sigma}{\text{cm}^{-1}}$
[1050] (1)	[450] (2)	
[1900] (1)	[300] (2)	
1149 (1)		

Bond Distance: C-F = {1.28} Å

C-C = {1.20} Å

Bond Angle: F-C-C = {180°}

Rotational Constant: B₀ = {0.1179} cm⁻¹

σ = 2

Heat of Formation

M. Farber, M. A. Greenbaum, M. A. Frisch, H. C. Ko, G. Grenier and E. Graper, Rocket Power Inc., 3rd Quarterly Report, AFPL-TR-67-147, Contract F04611-67-C-0010, May 1967, have obtained equilibrium-weight-change data over the C-CF₄ system. Our reanalysis of these data assumes that the equilibrium constants for CF₄, CF₃ and CF₂ are those in the JANAF Tables, and that C₂F₂ was the only other C-F species present at equilibrium. This gives maximum possible concentrations of C₂F₂ and places a lower limit on the heat of formation. The ΔH_{f,298}(C₂F₂, g) values so obtained range from +10 kcal/mol from data at 2200°K to -10 kcal/mol from data at 2373°K; we adopt a weighted mean of +5.5 kcal/mol. This value still predicts complete dimerization of CF at 1 atmosphere pressure below about 2200°K, but only CF would exist under experimental conditions such as the study by Farber.

Farber et al. also investigated the mass spectrum of the vapor over the C-CF₄ system and did not detect any ion ascribable to C₂F₂. This is additional support for the value adopted.

The C-C bond dissociation energy in C₂F₂ is 113 kcal/mol, using the JANAF CF(g) table (Dec. 31st, 1967). This value is 115 kcal weaker than the bond dissociation energy of acetylene. In order to explain such a large decrease, a crossing of the repulsive approach of two ²H CF molecules with an attractive approach of two ¹F CF molecules may be postulated. This follows the reasoning used by J. P. Simons, Nature 203, 1308 (1965), to explain the bond dissociation energy of C₂F₄.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that for C₂H₂(g). The C-F and C-C bond distances are estimated from those in HC = CF reported by J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 59, 2661, 1956. The asymmetric stretching frequency, ν₃ = 1149 cm⁻¹, was observed by J. Heicklen and V. Knight, J. Phys. Chem. 69, 2484 (1965). The other vibrational frequencies were estimated by comparison with those for C₂H₂(g) and C₂H₂F₂(g) reported by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., New York, 1945, G. R. Hunt and M. K. Wilson, J. Chem. Phys. 34, 1301 (1961), and J. K. Brown and J. K. Tyler, Proc. Chem. Soc. 1961, 13 (1961). The moment of inertia is 2.3735 x 10⁻³⁸ g cm².

Trifluoroacetoneitrile (CF₃CN)

GFW = 95.0242

(Ideal Gas)

Point Group C_{3v} $\Delta H_f^\circ = -117.5 \pm 0.7$ kcal/mol $S_{298.15}^\circ = 71.32 \pm 0.1$ gibbs/mol $\Delta H_f^\circ = -117.5 \pm 0.7$ kcal/mol

Ground State Quantum Weight = 1

C₂F₃N

T, °K	C _p ^o	S ^o	-(C _p ^o -H _{298.15})/T	H ^o -H _{298.15}	ΔH ^o	ΔG ^o	Log Kp
0	+0.00	INFINITE	-	3.799	-	-117.494	INFINITE
100	10.450	56.071	85.281	-2.026	-	-115.585	249.611
200	14.924	64.627	72.920	-1.659	-	-113.000	123.480
298	18.703	71.324	-	-0.000	-	-110.365	80.365
300	18.765	71.440	-	-0.035	-	-110.316	80.365
400	21.692	77.250	72.007	-2.061	-	-107.622	58.402
500	23.724	82.313	73.445	-4.334	-	-104.944	45.871
600	25.285	86.783	75.469	-6.748	-	-102.282	37.256
700	26.465	90.774	77.376	-9.163	-	-97.085	31.508
800	27.372	94.306	79.072	-11.608	-	-91.790	27.501
900	28.074	97.436	81.140	-14.866	-	-84.384	22.921
1000	28.618	100.624	82.941	-17.781	-	-74.781	20.059
1100	29.087	103.375	84.675	-20.570	-	-64.191	17.721
1200	29.480	105.592	86.341	-23.424	-	-52.624	15.723
1300	29.800	107.306	87.941	-26.341	-	-40.094	13.928
1400	29.995	108.506	89.473	-29.358	-	-26.598	12.716
1500	30.201	112.582	90.945	-32.455	-	-11.255	11.495
1600	30.375	114.537	92.359	-35.484	-	-76.347	10.428
1700	30.522	116.383	93.727	-38.458	-	-61.139	9.452
1800	30.646	118.126	95.027	-41.379	-	-45.852	8.452
1900	30.757	119.781	96.287	-44.258	-	-30.478	7.404
2000	30.851	121.371	97.502	-47.139	-	-15.185	6.323
2100	30.934	122.879	98.675	-50.020	-	-0.658	5.205
2200	31.006	124.319	99.808	-52.925	-	-16.604	4.074
2300	31.066	125.697	100.897	-55.845	-	-31.952	2.923
2400	31.126	127.023	101.965	-58.780	-	-47.100	1.767
2500	31.176	128.294	102.993	-61.734	-	-62.100	0.605
2600	31.221	129.518	103.989	-64.704	-	-76.949	4.293
2700	31.261	130.697	104.957	-67.694	-	-91.571	3.492
2800	31.296	131.833	105.897	-70.707	-	-105.978	2.719
2900	31.329	132.933	106.810	-73.757	-	-120.167	2.043
3000	31.359	133.996	107.699	-76.842	-	-134.142	1.467
3100	31.386	135.025	108.564	-82.029	-	-147.902	0.927
3200	31.410	136.022	109.406	-85.169	-	-161.455	0.423
3300	31.431	137.000	110.220	-88.262	-	-174.802	0.000
3400	31.453	137.927	111.028	-91.315	-	-187.955	1.785
3500	31.472	138.839	111.810	-94.402	-	-200.922	1.584
3600	31.489	139.726	112.573	-97.750	-	-212.707	1.394
3700	31.505	140.599	113.318	-101.064	-	-224.324	1.219
3800	31.523	142.229	114.046	-104.346	-	-235.778	1.063
3900	31.533	142.268	114.760	-107.203	-	-247.066	0.923
4000	31.546	143.047	115.457	-110.357	-	-258.192	0.800
4100	31.558	143.826	116.140	-113.513	-	-269.158	0.726
4200	31.568	144.586	116.808	-116.669	-	-279.965	0.652
4300	31.576	145.333	117.461	-119.819	-	-290.613	0.579
4400	31.589	146.056	118.104	-122.995	-	-301.112	0.505
4500	31.598	146.766	118.733	-126.144	-	-311.564	0.431
4600	31.606	147.460	119.350	-129.304	-	-321.967	0.357
4700	31.614	148.140	119.956	-132.465	-	-332.324	0.282
4800	31.622	148.806	120.553	-135.626	-	-342.537	0.207
4900	31.628	149.458	121.133	-138.789	-	-352.606	0.132
5000	31.635	150.097	121.706	-141.952	-	-362.533	0.057
5100	31.641	150.723	122.269	-145.116	-	-372.324	0.000
5200	31.646	151.338	122.822	-148.281	-	-381.978	0.000
5300	31.651	151.942	123.369	-151.446	-	-391.495	0.000
5400	31.657	152.532	123.900	-154.611	-	-400.872	0.000
5500	31.662	153.113	124.426	-157.777	-	-410.112	0.000
5600	31.667	153.684	124.944	-160.943	-	-419.224	0.000
5700	31.671	154.248	125.453	-164.110	-	-428.207	0.000
5800	31.676	154.806	125.953	-167.278	-	-437.062	0.000
5900	31.679	155.357	126.447	-170.445	-	-445.787	0.000
6000	31.683	155.869	126.933	-173.613	-	-454.381	0.000

Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	$\frac{\omega_e}{\omega_e - 1}, \text{cm}^{-1}$
2271 (1)	1215 (2)
1228 (1)	625 (2)
801 (1)	464 (2)
521 (1)	192 (2)

Bond Distances: C-F = 1.335 Å C-C = 1.461 Å CN = 1.153 Å
 Bond Angle: F-C-F = 107.5° F-C-C = 111.38°
 Product of the Moments of Inertia: $I_A I_B I_C = 1.18645 \times 10^{-113} \text{ g}^3 \text{ cm}^6$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, C₂F₄, and CF₃X (X = H, Cl, Br, I, CN). Details of the input data and adjustment are given in (1). Input included a calorimetric link to NF₃(g) and CF₄(g) plus an equilibrium link to C₂F₆(g) and C₂N₂(g). The calorimetric study (2) gave $\Delta H_f^\circ = -824.4 \pm 0.6$ kcal/mol at 298.15 K for the reaction $3\text{CF}_3\text{CN(g)} + 5\text{HF}_3\text{(g)} + 6\text{CF}_4\text{(g)} + 4\text{H}_2\text{(g)}$. Equilibrium data (3) in the range 865-925 K give ΔH_f° (3rd law) = 10.59 and ΔH_f° (2nd law) = 10.59 $\pm$ 0.20 kcal/mol at 298.15 K for the reaction $\text{C}_2\text{F}_6\text{(g)} + \text{C}_2\text{N}_2\text{(g)} + 2\text{CF}_3\text{CN(g)}$. The entropy difference, ΔS_f° (2nd law) = ΔS_f° (3rd law), is 0.0 $\pm$ 1.5 gibbs/mol. Deviations between the selected ΔH_f° and the two observations are 1.37 and 0.15 kcal/mol, respectively, both considerably less than the overall uncertainties including those in auxiliary values of ΔH_f° . Subsequent to the adjustment, Curtutt and Sinke (4) reported $\Delta H_f^\circ = -197.6 \pm 0.9$ kcal/mol from a calorimetric study of CF₃CN(g) + 1.25 O₂(g) + 1.5 H₂O(l) + 2 CO₂(g) + 0.5 N₂(g) + 3 HF(120 H₂O). Their result of $\Delta H_f^\circ = -118.4 \pm 1.2$ kcal/mol is confirmation of the selected value.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction data by Danford and Livingston (5) and from microwave data by Sheridan and Gordy (6) and Thomas et al. (7). These studies are in substantial agreement except for a difference of about 0.04 Å in the C-C bond distance. We adopt the results of Thomas et al. (7) since they are based on data for several isotopic species. Principal moments of inertia are $I_A = 14.676 \times 10^{-39}$ and $I_B = I_C = 28.482 \times 10^{-39} \text{ g cm}^2$. Vibrational frequencies are taken from the assignments of Edgell and Potter (8). All values except ν_9 are from infrared spectra of the vapor phase. Raman spectra of the liquid provide ν_9 and confirm the infrared data. Similar assignments have been given by Janz and Wait (9) based on spectra of Wait and Jenz (10).

Face and Bobka (11) used low temperature calorimetric data to derive the entropy of the ideal gas at the normal boiling point of 205.47 K. The experimental value of 65.01 $\pm$ 0.2 gibbs/mol is in good agreement with 65.03 gibbs/mol obtained from this table. The largest uncertainty in Cp° and S° probably arises from neglect of anharmonicity and rotational distortion. Uncertainty in the entropy is estimated to vary from 0.1 to 0.5 gibbs/mol over the range 300 to 1000°K. Discussions of the neglect of anharmonicity are given on the tables for CClF₃(g) and CF₄(g).

References

1. A. N. Syverud, Quarterly Technical Report AFRL-TR-69-187, Aug., 1969.
2. L. C. Walker, The Dow Chemical Co., personal communication, June, 1969.
3. D. J. Perette, The Dow Chemical Co., personal communication, June, 1969.
4. J. L. Curtutt and G. C. Sinke, presented at the 24th Annual Calorimetry Conference, Portsmouth, New Hampshire, October, 1969.
5. M. D. Danford and R. L. Livingston, J. Amer. Chem. Soc. **77**, 2944 (1955).
6. J. Sheridan and W. Gordy, J. Chem. Phys. **20**, 591 (1952).
7. L. F. Thomas, J. S. Heeks and J. Sheridan, Z. Elektrochem. **61**, 935 (1957).
8. W. F. Edgell and R. M. Potter, J. Chem. Phys. **24**, 80 (1956).
9. G. J. Janz and S. C. Wait, J. Chem. Phys. **28**, 1766 (1957).
10. S. C. Wait and G. J. Janz, J. Chem. Phys. **28**, 1554 (1957).
11. E. L. Pace and R. J. Bobka, J. Chem. Phys. **35**, 454 (1961).

C₂F₃N

Tetrafluoroethylene (C₂F₄)

(Ideal Gas)

GFW = 100.0159

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^c	ΔG ^f	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	10.562	55.830	86.157	-3.003	-156.579	-156.579	INFINITE
200	15.563	64.734	73.329	-3.033	-157.127	-157.127	337.722
300	18.230	71.678	64.734	-3.033	-157.369	-157.369	165.890
400	19.287	71.797	61.679	-3.036	-157.400	-157.400	100.561
500	21.665	77.731	52.469	-2.105	-157.363	-157.363	79.696
600	25.531	87.377	41.005	-6.867	-157.253	-157.253	51.246
700	29.611	95.033	29.759	-12.219	-157.123	-157.123	36.931
800	30.310	98.327	21.842	-15.016	-157.052	-157.052	32.163
1000	28.858	101.339	83.463	17.876	-156.974	-156.974	28.350
1100	26.292	104.111	85.216	20.784	-156.896	-156.896	25.232
1200	23.824	106.959	88.513	24.710	-156.818	-156.818	20.438
1300	20.924	109.959	92.461	28.710	-156.740	-156.740	15.127
1400	18.157	113.073	96.061	32.740	-156.661	-156.661	10.416
1500	15.350	116.244	99.316	36.784	-156.584	-156.584	6.357
1600	13.052	119.469	102.139	40.845	-156.507	-156.507	2.926
1700	10.925	122.749	104.565	44.925	-156.430	-156.430	0.000
1800	9.318	126.073	106.603	49.025	-156.353	-156.353	-7.818
1900	8.009	129.344	108.351	53.140	-156.276	-156.276	-15.547
2000	6.925	132.565	110.726	57.270	-156.199	-156.199	-23.180
2100	6.025	135.749	112.747	61.410	-156.122	-156.122	-30.723
2200	5.359	138.889	114.453	65.560	-156.045	-156.045	-38.180
2300	4.869	141.914	115.810	69.720	-155.968	-155.968	-45.561
2400	4.500	144.854	116.842	73.890	-155.891	-155.891	-52.880
2500	4.221	147.735	117.611	78.070	-155.814	-155.814	-60.157
2600	4.000	150.569	118.169	82.260	-155.737	-155.737	-67.396
2700	3.825	153.265	118.565	86.460	-155.660	-155.660	-74.596
2800	3.693	155.854	118.842	90.670	-155.583	-155.583	-81.756
2900	3.593	158.354	119.031	94.890	-155.506	-155.506	-88.876
3000	3.509	160.780	119.142	99.120	-155.429	-155.429	-95.956
3100	3.433	163.154	119.180	103.360	-155.352	-155.352	-102.996
3200	3.367	165.484	119.154	107.610	-155.275	-155.275	-109.996
3300	3.309	167.771	119.061	111.870	-155.198	-155.198	-116.956
3400	3.255	170.014	118.901	116.140	-155.121	-155.121	-123.876
3500	3.205	172.124	118.661	120.420	-155.044	-155.044	-130.756
3600	3.159	174.104	118.351	124.710	-154.967	-154.967	-137.596
3700	3.117	175.954	117.981	129.010	-154.890	-154.890	-144.396
3800	3.078	177.684	117.561	133.320	-154.813	-154.813	-151.156
3900	3.042	179.304	117.091	137.640	-154.736	-154.736	-157.876
4000	3.009	180.814	116.581	141.970	-154.659	-154.659	-164.556
4100	2.979	182.214	116.031	146.310	-154.582	-154.582	-171.196
4200	2.951	183.514	115.441	150.660	-154.505	-154.505	-177.806
4300	2.925	184.714	114.811	155.020	-154.428	-154.428	-184.386
4400	2.901	185.814	114.141	159.390	-154.351	-154.351	-190.926
4500	2.878	186.814	113.431	163.770	-154.274	-154.274	-197.426
4600	2.856	187.714	112.681	168.160	-154.197	-154.197	-203.886
4700	2.835	188.514	111.891	172.560	-154.120	-154.120	-210.306
4800	2.815	189.214	111.061	176.970	-154.043	-154.043	-216.686
4900	2.796	189.814	110.191	181.390	-153.966	-153.966	-223.026
5000	2.778	190.314	109.281	185.820	-153.889	-153.889	-229.326
5100	2.761	190.714	108.331	190.260	-153.812	-153.812	-235.586
5200	2.745	191.014	107.341	194.710	-153.735	-153.735	-241.806
5300	2.730	191.214	106.311	199.170	-153.658	-153.658	-247.986
5400	2.716	191.314	105.241	203.640	-153.581	-153.581	-254.126
5500	2.703	191.314	104.131	208.120	-153.504	-153.504	-260.226
5600	2.691	191.214	102.981	212.610	-153.427	-153.427	-266.286
5700	2.680	191.014	101.791	217.110	-153.350	-153.350	-272.306
5800	2.670	190.714	100.561	221.620	-153.273	-153.273	-278.286
5900	2.661	190.314	99.291	226.140	-153.196	-153.196	-284.226
6000	2.653	189.814	97.981	230.670	-153.119	-153.119	-290.126

June 30, 1962; June 30, 1963; Mar. 31, 1964; Sept. 30, 1964; June 30, 1969

TETRAFLUOROETHYLENE (C₂F₄)

(IDEAL GAS)

GFW = 100.0159

Point Group D_{2h}ΔH_f^o = -156.6 ± 0.7 kcal/molS^o_{298.15} = 71.678 ± 0.1 gibbs/molΔH_f^o_{298.15} = -157.4 ± 0.7 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω ₁ , cm ⁻¹	ω ₂ , cm ⁻¹	ω ₃ , cm ⁻¹	ω ₄ , cm ⁻¹
1872 (1)	1340 (1)	1337 (1)	1337 (1)
778 (1)	551 (1)	218 (1)	218 (1)
394 (1)	406 (1)	1186 (1)	1186 (1)
190 (1)	508 (1)	558 (1)	558 (1)

Bond Distance: C-F = 1.313 Å C-C = 1.313 Å

Bond Angle: F-C-F = 114°

Product of the Moments of Inertia: I_AI_BI_C = 1.5877 × 10⁻¹¹³ g³ cm⁶

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₃X (X = H, Cl, Br, I, CF₃) and C₂F₄. Details of the input data and the adjustment are given in (1). In this case, the selected ΔH_f^o corresponds to the weighted average of three calorimetric studies (2, 3) which may be reduced to the following:

Reference	Reaction	ΔH _f ^o _{298.15} kcal/mol	ΔH _f ^o kcal/mol
(2)	C ₂ F ₄ (g) + CF ₄ (g) + C(graphite)	-65.4 ± 0.5	-157.6 ± 0.6
(2)	C ₂ F ₄ (g) + 2H ₂ (g) + 4HF(50 H ₂ O) + 2C(graphite)	-150.9 ± 1.2	-156.2 ± 1.3
(3)	C ₂ F ₄ (g) + 4Na(c) + 4NaF(c) + 2C(graphite)	-392.9 ± 1.3	-157.2 ± 1.4

Amorphous carbon was formed in all three calorimetric reactions and separate combustions were made to refer the observed product to the standard state of graphite. Other calorimetric studies (4, 5, 6) are omitted because of apparent uncertainties in the reductions to the standard-state reactions.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction data by Karle (7), Broun (8) and Young (9). The resulting structures differ in minor respects, particularly in the exact location of the two carbons. Values from Karle (7) are adopted since they are intermediate between the others. Values from Young (9) and Broun (8) correspond to changes of ± 2.4% in the product of the moments of inertia. Principal moments of inertia for the adopted structure are I_A = 15.30 × 10⁻³⁹, I_B = 25.46 × 10⁻³⁹ and I_C = 40.76 × 10⁻³⁹ g cm². Vibrational fundamentals are those selected by Shimanouchi (10) from the data of Mann (11), Monfils (12) and Nielsen (13).

Furukawa (14) reported low-temperature calorimetric data from which the ideal gas entropy may be derived as 64.54 ± 0.09 gibbs/mol at 197.53°K. The calculated entropy from this table is also 64.54 eu. The range in values of I_AI_BI_C corresponds to an entropy change of ± 0.022 eu.

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFRL Contract Nr. F04611-67-C-0009, Dow Chemical Co., July, 1969.
2. C. Neugebauer and J. L. Margrave, J. Phys. Chem. **60**, 1318 (1956).
3. V. F. Kolesov, I. D. Zenkov and S. M. Skuratov, Russ. J. Phys. Chem. (English translation) **36**, 45 (1962).
4. H. C. Dous, Ind. Eng. Chem. **47**, 1445 (1955).
5. F. W. Kirkbridge and F. G. Davidson, Nature **174**, 79 (1954).
6. H. von Wartenberg and J. G. Schiefer, Z. Anorg. Allg. Chem. **278**, 326 (1955).
7. I. L. Karle and J. Karle, J. Chem. Phys. **18**, 963 (1950).
8. T. Broun and R. L. Livingston, J. Am. Chem. Soc. **74**, 6084 (1952).
9. J. A. Young, Dissertation Abstracts **15**, 460 (1956).
10. T. Shimanouchi, U. S. Nat. Bur. Stand. NSRDS-NBS **6**, 25 (1967).
11. D. E. Mann, N. Acquista and E. K. Plyler, J. Res. Nat. Bur. Stand. **52**, 67 (1954).
12. A. Monfils and J. Duchesne, J. Chem. Phys. **18**, 1415 (1950).
13. J. R. Nielsen, H. Claassen and D. C. Smith, J. Chem. Phys. **18**, 812 (1950).
14. G. T. Furukawa, R. McCoskey and M. L. Reilly, J. Res. Nat. Bur. Stand. **51**, 69 (1953).

C₂F₄

Hexafluoroethane (C₂F₆)

(Ideal Gas)

GF_W = 138.0127

T, °K	C _P ⁰	S ⁰	-(C _P ⁰ - H ₂₉₈ ⁰)/T	H ⁰ - H ₂₉₈ ⁰	ΔH _F ⁰	Log K _P
0	0.000	INFINITE	-	4.081	-319.207	INFINITE
100	12.700	59.332	97.852	3.852	-320.331	666.276
200	19.703	70.413	81.548	2.287	-320.962	335.944
298	25.432	79.368	79.368	0.000	-321.200	220.433
300	25.528	79.526	79.368	0.047	-321.203	210.902
400	30.006	87.513	80.427	2.634	-321.216	160.478
500	33.255	94.576	82.565	6.007	-321.104	125.383
600	35.542	100.855	85.100	9.453	-320.910	101.097
700	37.117	106.503	90.117	13.009	-320.613	87.293
800	38.177	111.603	94.617	16.660	-320.240	75.293
900	39.150	116.067	93.018	20.744	-320.140	63.072
1000	39.791	120.226	95.534	24.692	-319.859	55.301
1100	40.263	124.041	97.954	28.695	-319.578	48.949
1200	40.652	127.522	100.500	32.750	-319.297	43.060
1300	41.000	130.722	103.000	36.860	-319.021	37.765
1400	41.375	133.670	105.636	40.928	-318.746	33.359
1500	41.719	136.419	108.661	45.057	-318.480	32.043
1600	41.941	139.394	109.643	49.203	-318.219	29.144
1700	42.161	141.600	110.726	53.385	-317.961	26.396
1800	42.358	143.997	112.020	57.609	-317.707	23.890
1900	42.538	146.562	113.579	61.717	-317.467	22.289
2000	42.697	148.712	115.758	65.906	-317.227	20.463
2100	42.821	150.761	117.376	70.107	-316.992	19.413
2200	42.920	152.689	118.735	74.332	-316.768	17.315
2300	43.000	154.449	120.330	78.585	-316.550	15.155
2400	43.065	156.083	121.908	82.739	-316.334	14.694
2500	43.120	157.613	123.322	86.960	-316.128	13.542
2600	43.166	159.063	124.692	91.185	-315.930	12.480
2700	43.200	160.439	126.020	95.413	-315.739	11.506
2800	43.225	161.763	127.300	99.640	-315.550	10.616
2900	43.248	163.038	128.563	103.879	-315.372	9.734
3000	43.264	164.264	129.781	108.116	-315.204	8.943
3100	43.276	165.440	130.966	112.355	-315.039	8.202
3200	43.286	166.572	132.120	116.592	-314.884	7.506
3300	43.293	167.660	133.240	120.829	-314.735	6.853
3400	43.297	168.706	134.340	125.066	-314.597	6.244
3500	43.299	169.713	135.409	129.333	-314.468	5.666
3600	43.299	170.687	136.452	133.581	-314.343	5.121
3700	43.297	171.622	137.470	137.831	-314.229	4.605
3800	43.293	172.523	138.459	142.081	-314.125	4.116
3900	43.286	173.393	139.439	146.334	-314.027	3.653
4000	43.276	174.237	140.400	150.587	-313.936	3.213
4100	43.261	175.058	141.321	154.841	-313.857	2.795
4200	43.243	175.853	142.213	159.090	-313.788	2.397
4300	43.222	176.623	143.070	163.334	-313.729	2.016
4400	43.198	177.368	143.900	167.566	-313.675	1.655
4500	43.171	178.090	144.700	171.792	-313.623	1.309
4600	43.141	178.784	145.477	176.019	-313.580	0.978
4700	43.108	179.450	146.232	180.246	-313.545	0.661
4800	43.072	180.089	146.967	184.473	-313.515	0.356
4900	43.034	180.706	147.683	188.691	-313.557	0.065
5000	42.994	181.304	148.380	192.900	-313.563	0.214
5100	42.951	181.877	149.070	197.107	-313.581	0.482
5200	42.905	182.426	149.743	201.314	-313.601	0.761
5300	42.856	182.953	150.393	205.521	-313.631	1.053
5400	42.804	183.459	151.022	209.728	-313.670	1.369
5500	42.750	183.944	151.634	213.935	-313.719	1.702
5600	42.694	184.409	152.226	218.142	-313.777	2.056
5700	42.636	184.854	152.800	222.350	-313.844	2.436
5800	42.576	185.279	153.357	226.557	-313.919	2.841
5900	42.514	185.684	153.898	230.764	-313.999	3.274
6000	42.450	186.070	154.424	234.971	-314.084	3.736

Sept. 30, 1965; June 30, 1969

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
1228 (1)	1117 (1)	376 (2)
807 (1)	714 (1)	1251 (2)
348 (1)	1243 (2)	573 (2)
Torsion	619 (2)	220 (2)

Bond Distances: C-F = 1.32 Å C-C = 1.56 Å
 Bond Angle: C-C-F = 109.5 ± 1.5°
 Product of the Moments of Inertia: I_AI_BI_C = 6.007 × 10⁻¹¹³ g³ cm⁶
 Reduced Moment of Inertia: I_{red} = 7.32 × 10⁻³⁹ g cm²
 Barrier to Internal Rotation: V = 3.96 kcal/mol

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₃X (X = H, Cl, Br, I, CF₃) and C₂F₄. Details of the input data and the adjustment are given in (1). Data pertinent to C₂F₆ are summarized below. Calorimetric data (2) for the reaction of C₂F₆ with potassium were omitted from the adjustment due to insufficient characterization of the products.

Source	Method	Reaction	ΔH _{F298} ⁰ , kcal/mol
(2)	Calorimetric	3C ₂ F ₆ (g) + 2NF ₃ (g) → 6CF ₃ (g) + N ₂ (g)	-311.6 ± 3.0
(3)	Calorimetric	2C ₂ F ₆ (g) + 5NF ₃ (g) → 6CF ₃ (g) + 4N ₂ (g)	-321.3 ± 1.2
(4)	Equilibrium	2C ₂ F ₆ (g) + C ₂ F ₄ (g) → C ₂ F ₈ (g)	-824.4 ± 0.6
(5)	Equilibrium	C ₂ F ₆ (g) + Br ₂ (g) → 2CBrF ₃ (g)	-322.2 ± 1.8
(6, 7)	Kinetic	C ₂ F ₆ (g) + 2CF ₃ (g)	3.30 ± 0.7
			97.6 ± 6

Heat Capacity and Entropy

The adopted molecular structure was derived from electron-diffraction data by Swick and Karle (8). The vibrational frequencies are from the assignment of Carney et al. (9), who reviewed the extensive spectral data. Shimanouchi (10) has selected the same frequencies. Low-temperature calorimetric data were used by Pace and Aton (11) to derive a value for the entropy of the ideal gas of 69.88 ± 0.20 gibbs/mol at 194.87°K. This value is used to fix the barrier to internal rotation at 3960 cal/mol. Thermodynamic functions are calculated from these parameters, using hindered internal rotation in place of a torsional vibration.

An uncertainty of ±0.2 gibbs/mol in the third-law entropy corresponds to a variation in the barrier to internal rotation of about ±700 cal/mol. This range easily includes the barrier of 4300 cal/mol derived by Karle (12) from analysis of the electron-diffraction data (8). Uncertainty in the entropy of this table should not exceed 0.5 gibbs at 1000°K.

References

- A. N. Syverud, Quarterly Tech. Report T-0009-20-63 under AFPRP Contract Nr. F04611-67-C-0009, Dow Chemical Co., July, 1969.
- G. C. Sinke, J. Phys. Chem. **70**, 1326 (1966).
- L. C. Walker, Dow Chemical Co., Midland, Mich., personal communication, June, 1969.
- D. J. Perette, Dow Chemical Co., Midland, Mich., personal communication, June, 1969.
- J. W. Coomber and E. Whittle, Trans. Faraday Soc. **63**, 1394 (1967).
- E. Techukow-Roux, J. Chem. Phys. **43**, 2251 (1965).
- F. W. Kirkbride and F. G. Davidson, Nature **174**, 79 (1954).
- D. A. Swick and I. L. Karle, J. Chem. Phys. **23**, 1499 (1955).
- R. A. Carney, E. A. Plotrowski, A. G. Meister, J. H. Braun and F. F. Cleveland, J. Mol. Spectrosc. **21**, 209 (1961).
- T. Shimanouchi, U. S. Nat. Bur. Stand. NBS-RS-NBS 6, 29 (1967).
- E. L. Pace and J. G. Aton, J. Am. Chem. Soc. **70**, 566 (1948).
- J. Karle, J. Chem. Phys. **45**, 4199 (1966).

CCH Radical (C₂H)
(Ideal Gas)

GFW = 25.0303

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	6.000	∞	∞	2.248	113.268	113.268	INFINITE
100	6.989	41.186	56.717	1.531	113.535	110.699	241.931
200	7.978	42.452	50.422	0.800	113.768	109.466	317.462
298	8.968	43.553	49.553	.000	114.000	108.568	376.739
300	8.985	49.608	49.554	.016	114.002	108.630	76.223
400	9.555	52.276	49.912	.846	114.092	101.491	55.452
500	10.234	54.495	50.613	1.941	114.100	99.339	42.994
600	10.716	56.404	51.423	2.989	114.042	95.190	34.673
700	11.141	58.089	52.257	4.082	113.934	92.056	28.741
800	11.523	59.602	53.082	5.214	113.797	88.941	24.297
900	11.907	60.979	53.884	6.384	113.637	85.841	20.685
1000	12.176	62.246	54.658	7.588	113.458	82.761	18.087
1100	12.453	63.420	55.402	8.820	113.291	79.699	15.834
1200	12.701	64.514	56.116	10.079	113.110	76.654	13.941
1300	12.925	65.540	56.802	11.359	112.921	73.629	12.377
1400	13.129	66.505	57.461	12.662	112.735	70.614	11.023
1500	13.317	67.417	58.094	13.985	112.547	67.608	9.850
1600	13.492	68.282	58.704	15.325	112.358	64.615	8.824
1700	13.656	69.105	59.292	16.683	112.174	61.637	7.924
1800	13.813	69.880	59.859	18.054	111.991	58.670	7.123
1900	13.964	70.641	60.407	19.445	111.813	55.714	6.409
2000	14.109	71.361	60.937	20.849	111.639	52.765	5.766
2100	14.250	72.053	61.450	22.267	111.471	49.828	5.186
2200	14.386	72.719	61.997	23.694	111.305	46.902	4.658
2300	14.519	73.362	62.430	25.147	111.147	43.971	4.178
2400	14.648	73.982	62.898	26.602	110.992	41.054	3.739
2500	14.773	74.583	63.353	28.073	110.843	38.140	3.334
2600	14.893	75.165	63.797	29.557	110.699	35.235	2.962
2700	15.008	75.729	64.228	31.052	110.560	32.333	2.617
2800	15.119	76.277	64.649	32.558	110.426	29.439	2.298
2900	15.224	76.809	65.059	34.075	110.298	26.552	2.001
3000	15.324	77.327	65.459	35.603	110.174	23.664	1.724
3100	15.418	77.831	65.850	37.140	110.055	20.784	1.445
3200	15.506	78.322	66.232	38.685	109.938	17.906	1.223
3300	15.589	78.800	66.606	40.241	109.823	15.029	.995
3400	15.665	79.267	66.971	41.804	109.713	12.160	.782
3500	15.736	79.722	67.329	43.374	109.602	9.289	.580
3600	15.801	80.166	67.680	44.951	109.495	6.425	.390
3700	15.861	80.600	68.023	46.534	109.386	3.564	.211
3800	15.915	81.023	68.360	48.123	109.280	.712	.041
3900	15.963	81.438	68.690	49.716	109.172	-2.146	.120
4000	16.007	81.842	69.013	51.315	109.065	-4.995	.273
4100	16.046	82.238	69.311	52.919	108.955	-7.850	.419
4200	16.080	82.625	69.601	54.520	108.843	-10.693	.556
4300	16.110	83.004	69.894	56.134	108.728	-13.542	.688
4400	16.136	83.374	70.250	57.748	108.612	-16.383	.814
4500	16.158	83.737	70.584	59.361	108.492	-19.227	.934
4600	16.177	84.093	70.917	60.974	108.368	-22.043	1.048
4700	16.192	84.481	71.122	62.596	108.242	-24.895	1.158
4800	16.203	84.782	71.404	64.216	108.109	-27.724	1.242
4900	16.212	85.116	71.680	65.837	107.973	-30.552	1.363
5000	16.219	85.444	71.952	67.454	107.832	-33.380	1.459
5100	16.223	85.765	72.220	69.080	107.686	-36.210	1.552
5200	16.224	86.080	72.483	70.703	107.532	-39.027	1.640
5300	16.224	86.389	72.743	72.325	107.375	-41.839	1.725
5400	16.221	86.692	72.998	73.947	107.211	-44.651	1.807
5500	16.217	86.990	73.250	75.569	107.039	-47.464	1.886
5600	16.212	87.282	73.498	77.191	106.863	-50.273	1.942
5700	16.205	87.569	73.742	78.811	106.679	-53.083	2.005
5800	16.196	87.851	73.983	80.432	106.488	-55.884	2.106
5900	16.187	88.127	74.220	82.051	106.291	-58.670	2.173
6000	16.177	88.399	74.454	83.669	106.087	-61.475	2.239

Dec. 31, 1966; Mar. 31, 1967

CCH Radical (C₂H)
(Ideal Gas)

GFW = 25.0303



Point Group [C_{∞v}]
ΔH_f^o = [113.3 ± 7] kcal/mol
ΔH_f^o_{298.15} = [114 ± 7] kcal/mol

S_{298.15}^o = [49.55 ± 1.3] gibbs/mol

Electronic Levels and Quantum Weights

ε ₁ , cm ⁻¹	g ₁
0	(2)
[9000]	(4)

Vibrational Frequencies and Degeneracies

ω _i , cm ⁻¹
[1920] (1)
[640] (2)
[3220] (1)

Bond Distance: C-C = [1.207]Å
Bond Angles: C-C-H = [180°]
Rotational Constant: B₀ = [1.475]cm⁻¹
C-H = [1.061]Å
σ = 1

Heat of Formation

The heat of formation of C₂H(g) is not well established; however, we can place reliable upper and lower limits on the value.

T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Academic Press, New York, 1958, gives an upper limit for the C-H bond dissociation energy in acetylene, D(HCC-H) 4121 kcal. This was obtained from the fact that ultraviolet light of 121 kcal/mol energy causes acetylene to form diacetylene and hydrogen; assuming that this process occurs through the CCH radical, the light energy is equated with D(HCC-H). This value of D(HCC-H) gives an upper limit for ΔH_f^o₂₉₈(CCH,g) 4123 kcal/mol.

A lower limit for D(HCC-H) is obtained from a consideration of the C-H bond dissociation energies in ethylene and ethane, D(C₂H₃-H) = 103 kcal and D(C₂H₅-H) = 98 kcal. The heats of formation of the C₂H₃ and C₂H₅ radicals and their parent compounds are taken from S. W. Benson, J. Chem. Educ. 42, 502 (1965). The vibrational frequency of the C-H stretch increases steadily from ethane to ethylene and acetylene. Similarly we expect the bond strength to increase, and so D(HCC-H) > 103 kcal; this yields ΔH_f^o₂₉₈(CCH,g) > 105 kcal/mol.

F. H. Coats and R. C. Anderson, J. Am. Chem. Soc. 79, 1340 (1957), obtained several values for ΔH_f^o₂₉₈(CCH,g) from mass-spectroscopic measurements; their values range from 110 kcal/mol to 153 kcal/mol, but they chose to adopt 112 ± 3 kcal/mol.

Our adopted value of ΔH_f^o₂₉₈(CCH,g), 114 ± 7 kcal/mol, is 2 kcal smaller than that estimated by W. Tsang,

S. H. Bauer and M. Comperthwaite, J. Chem. Phys. 35, 1768 (1962).

Heat Capacity and Entropy

The molecule is assumed to be linear; the bond lengths are assumed to be the same as in acetylene and were taken from L. E. Sutton, "Interatomic Distances Supplement," Special Publication No. 18, The Chemical Society, London, 1965.

The vibrational frequencies are those estimated by M. N. Flooster and T. B. Reed, J. Chem. Phys. 31, 66 (1959). It should be noted that the values of the free energy function given by Flooster and Reed are incorrect due to the neglect of the electronic contributions.

The electronic levels, x²Σ⁺ and a²Π, were estimated by analogy with those of CN(g) which is isoelectronic; this assumption holds very well in the parent molecules HCC and HCN (O. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., New York, 1966). The molecule C₂H₂, which is also isoelectronic with CCH, is predicted to have a ²Π ground state by Herzberg, loc. cit.



Chloroacetylene (C₂HCl)

GFW = 60.48327

Point Group C_{2v} $\Delta H_f^\circ = [50.9 \pm 10] \text{ kcal/mol}$  $S_{298.15}^\circ = 57.811 \text{ gibbs/mol}$ $\Delta H_f^\circ_{298.15} = [51.1 \pm 10] \text{ kcal/mol}$

Ground State Quantum Weight = 1

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	Kcal/mol	ΔG°	Log Kp
0	∞.000	∞.000	INFINITE	2.4817	50.896	50.896	INFINITE
100	7.828	46.738	67.777	- 2.104	50.854	49.599	- 108.616
200	10.774	53.935	58.935	- 1.174	50.963	48.506	- 53.004
300	12.982	57.811	51.811	∞.000	51.100	47.270	- 34.650
400	13.015	57.892	51.812	.028	51.102	47.246	- 34.419
500	14.394	61.840	58.341	1.400	51.224	45.942	- 25.102
600	15.971	68.007	60.587	4.452	51.352	43.271	- 15.761
700	17.791	72.738	63.057	7.753	51.426	40.594	- 11.091
800	17.988	74.772	64.248	9.472	51.421	39.261	- 9.534
900	17.746	76.653	65.394	11.229	51.151	37.934	- 8.291
1000	18.061	78.329	66.493	13.019	51.088	36.617	- 7.275
1100	18.595	81.391	68.555	16.680	50.916	35.007	- 6.430
1200	19.482	87.585	73.021	26.215	50.578	31.702	- 5.716
1300	18.992	84.080	70.449	20.446	50.796	31.407	- 5.456
1400	19.161	85.311	71.340	22.354	50.721	30.736	- 5.287
1500	19.422	87.585	73.021	26.215	50.578	27.587	- 3.945
1600	19.559	88.639	73.816	28.185	50.501	26.272	- 3.022
1700	19.663	89.645	74.562	30.126	50.427	24.998	- 2.732
1800	19.759	90.607	75.322	32.097	50.355	23.736	- 2.470
1900	19.814	91.412	76.731	36.065	50.202	22.400	- 2.231
2000	19.981	93.260	77.402	38.060	50.123	19.942	- 1.816
2100	20.042	94.077	78.053	40.061	50.043	18.683	- 1.633
2200	20.097	94.854	78.685	42.068	49.960	17.432	- 1.465
2300	20.142	95.558	79.294	44.080	49.872	16.192	- 1.310
2400	20.182	96.184	79.894	46.097	49.787	14.936	- 1.166
2500	20.213	97.067	80.474	48.119	49.695	13.694	- 1.032
2600	20.271	97.753	81.039	50.144	49.600	12.452	∞.007
2700	20.306	98.419	81.580	52.173	49.508	11.217	∞.001
2800	20.339	99.064	82.125	54.205	49.420	9.983	∞.002
2900	20.367	99.690	82.648	56.240	49.295	8.749	∞.579
3000	20.393	100.299	83.156	58.278	49.186	7.524	∞.884
3100	20.418	100.890	83.656	60.319	49.071	6.297	∞.393
3200	20.441	101.466	84.143	62.362	48.953	5.074	∞.308
3300	20.462	102.024	84.619	64.404	48.824	3.828	∞.228
3400	20.482	102.572	85.084	66.456	48.702	2.652	∞.153
3500	20.500	103.104	85.539	68.503	48.568	1.444	∞.081
3600	20.517	103.623	85.985	70.554	48.431	.234	∞.013
3700	20.533	104.129	86.421	72.607	48.289	- 2.971	∞.052
3800	20.548	104.624	86.846	74.661	48.141	- 6.103	∞.013
3900	20.562	105.109	87.268	76.716	47.987	- 9.288	∞.011
4000	20.575	105.582	87.679	78.773	47.830	- 12.457	∞.007
4100	20.587	106.044	88.082	80.831	47.667	- 15.633	∞.008
4200	20.599	106.487	88.477	82.891	47.499	- 18.809	∞.009
4300	20.610	106.910	88.855	84.951	47.322	- 21.982	∞.010
4400	20.620	107.374	89.246	87.013	47.148	- 25.157	∞.011
4500	20.629	107.799	89.621	89.075	46.966	- 28.332	∞.012
4600	20.638	108.216	89.988	91.138	46.778	- 31.508	∞.013
4700	20.647	108.625	90.350	93.203	46.583	- 34.683	∞.014
4800	20.655	109.024	90.725	95.268	46.382	- 37.858	∞.015
4900	20.663	109.419	91.055	97.338	46.182	- 41.033	∞.016
5000	20.670	109.806	91.398	99.400	45.973	- 44.208	∞.017
5100	20.677	110.185	91.736	101.468	45.757	- 47.383	∞.018
5200	20.683	110.558	92.069	103.536	45.538	- 50.558	∞.019
5300	20.689	110.924	92.379	105.603	45.312	- 53.733	∞.020
5400	20.695	111.284	92.719	107.673	45.090	- 56.908	∞.021
5500	20.701	111.638	93.037	109.743	44.844	- 60.083	∞.022
5600	20.706	111.986	93.350	111.814	44.602	- 63.258	∞.023

Dec. 31, 1968





GFN = 44.02867

(IDEAL GAS)

MONOFLUOROACETYLENE (C_2HF)

Point Group $C_{\infty v}$

$\Delta H_f^\circ = [30 \pm 15] \text{ kcal/mol}$

$\Delta H_f^\circ = [30 \pm 15] \text{ kcal/mol}$

$S_{298.15}^\circ = 55.33 \pm 0.01 \text{ gibbs/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega, \text{ cm}^{-1}$

3160 (1)

2250 (1)

1060 (1)

580 (2)

367 (2)

C-C = 1.198 Å

C-H = 1.053 Å

C-C-H = 180°

σ = 1

Heat of Formation

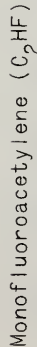
The heat of formation is estimated by assuming that the C-C bond strength is the average of those in C_2F_2 (113 kcal) and C_2H_2 (229 kcal). Combining the average value (171 kcal) with the heats of formation of CF and CH from the JANAF Tables, yields $\Delta H_f^\circ(C_2HF, g) = 30 \pm 15 \text{ kcal/mol}$.

Heat Capacity and Entropy

G. R. Hunt and M. K. Wilson, J. Chem. Phys. 34, 1301 (1961), and J. K. Brown and J. K. Tyler, Proc. Chem. Soc. (London) 1961, 13 (1961), have reported the infrared spectrum and have assigned the fundamental frequencies. The frequencies used in the present table are median values of the two sets and are generally within 5 cm^{-1} of each set.

The molecule has been shown to be linear by J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 59, 2661 (1963), who reported the rotational constant B_0 .

The electronic ground state is assumed to be $^1\Sigma$ by analogy with C_2H_2 .



GFN = 44.02867

(Ideal Gas)

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{300})/T$	$H^\circ - H^\circ_{300}$	ΔH°	ΔG°	Log Kp
0	-0.00	.000	INFINITE	-2.737	29.834	29.834	INFINITE
100	7.591	44.539	64.942	-2.030	29.786	28.618	-45.544
200	10.404	50.753	56.412	-1.132	29.877	27.420	-29.964
298	12.505	55.329	55.329	-1.000	30.000	26.188	-19.197
300	12.536	55.407	55.407	-0.923	30.002	26.164	-19.061
400	13.707	59.215	55.840	1.350	30.105	24.849	-13.588
500	14.952	62.425	56.844	2.791	30.154	23.553	-10.295
600	15.370	65.199	58.011	4.313	30.155	22.232	-8.098
700	16.159	67.845	59.216	5.900	30.115	20.915	-5.530
800	17.005	70.425	60.593	7.521	29.978	19.601	-3.000
900	17.894	73.048	62.066	9.176	29.891	18.301	-0.484
1000	18.825	75.732	63.750	10.962	29.803	17.009	3.717
1100	19.800	78.471	65.556	12.788	29.715	15.724	3.124
1200	20.819	81.273	67.485	14.658	29.627	14.450	2.432
1300	21.874	84.139	69.527	16.577	29.540	13.174	1.651
1400	22.966	87.065	71.683	18.549	29.453	11.922	0.792
1500	24.095	89.125	73.947	20.682	29.366	10.668	1.554
1600	25.262	90.338	76.323	22.975	29.279	9.416	1.866
1700	26.467	91.700	78.811	25.425	29.192	8.174	1.051
1800	27.709	93.215	81.405	27.938	29.105	6.946	0.185
1900	28.987	94.887	84.114	29.704	29.018	5.705	-0.556
2000	30.300	96.614	86.841	29.897	28.931	4.478	-0.889
2100	31.647	98.394	89.586	31.666	28.844	3.256	-0.339
2200	33.029	100.221	92.349	33.637	28.757	2.033	-0.202
2300	34.445	102.094	95.124	35.811	28.670	0.811	-0.035
2400	35.895	104.011	97.911	38.188	28.583	-0.411	0.140
2500	37.379	105.971	100.711	39.600	28.523	-1.598	
2600	38.895	107.971	103.536	41.041	28.428	-2.799	-0.235
2700	40.443	109.999	106.366	43.607	28.325	-4.001	-0.324
2800	42.023	112.045	109.161	46.292	28.219	-5.194	-0.481
2900	43.635	114.109	111.925	49.006	28.111	-6.382	-0.613
3000	45.279	116.189	114.666	51.749	28.002	-7.575	-0.552
3100	46.955	118.274	117.421	54.521	27.902	-8.759	-0.617
3200	48.665	120.364	120.171	57.324	27.799	-9.938	-0.679
3300	50.409	122.459	122.918	60.156	27.696	-11.120	-0.700
3400	52.187	124.559	125.665	63.027	27.592	-12.290	-0.700
3500	54.000	126.664	128.411	65.938	27.486	-13.463	-0.841
3600	55.847	128.774	131.158	68.889	27.379	-14.629	-0.888
3700	57.729	130.889	133.905	71.879	27.271	-15.790	-0.933
3800	59.645	132.999	136.652	74.908	27.165	-16.943	-0.979
3900	61.596	135.104	139.400	77.977	27.057	-18.100	-1.015
4000	63.581	137.204	142.148	81.085	26.943	-19.251	-1.052
4100	65.599	139.299	144.896	84.233	26.829	-20.405	-1.088
4200	67.649	141.389	147.644	87.421	26.715	-21.543	-1.121
4300	69.731	143.474	150.392	90.648	26.601	-22.679	-1.153
4400	71.845	145.554	153.140	93.915	26.486	-23.817	-1.183
4500	73.991	147.629	155.888	97.221	26.371	-24.958	-1.212
4600	76.169	149.699	158.636	100.567	26.256	-26.087	-1.239
4700	78.379	151.764	161.384	103.915	26.141	-27.211	-1.265
4800	80.621	153.824	164.132	107.263	26.026	-28.337	-1.290
4900	82.895	155.879	166.880	110.611	25.911	-29.467	-1.316
5000	85.200	157.929	169.628	113.959	25.796	-30.591	-1.336
5100	87.536	160.000	172.376	117.307	25.681	-31.680	-1.358
5200	89.903	162.061	175.124	120.655	25.566	-32.780	-1.376
5300	92.301	164.112	177.872	124.003	25.451	-33.879	-1.398
5400	94.730	166.153	180.620	127.351	25.336	-34.978	-1.415
5500	97.189	168.184	183.368	130.699	25.221	-36.064	-1.433
5600	99.678	170.205	186.116	134.047	25.106	-37.156	-1.450
5700	102.197	172.216	188.864	137.395	25.000	-38.245	-1.466
5800	104.745	174.217	191.612	140.743	24.894	-39.337	-1.482
5900	107.322	176.208	194.360	144.091	24.789	-40.432	-1.492
6000	109.929	178.189	197.108	147.439	24.683	-41.527	-1.502
6100	112.566	180.160	199.856	150.787	24.578	-42.624	-1.511
6200	115.233	182.121	202.604	154.135	24.472	-43.721	-1.519
6300	117.930	184.072	205.352	157.483	24.367	-44.818	-1.526
6400	120.657	186.013	208.100	160.831	24.261	-45.915	-1.532
6500	123.414	187.944	210.848	164.179	24.156	-47.012	-1.538
6600	126.191	189.865	213.596	167.527	24.050	-48.109	-1.543
6700	128.998	191.776	216.344	170.875	23.945	-49.206	-1.548
6800	131.835	193.677	219.092	174.223	23.840	-50.303	-1.553
6900	134.702	195.568	221.840	177.571	23.734	-51.400	-1.558
7000	137.600	197.449	224.588	180.919	23.629	-52.497	-1.563
7100	140.528	199.320	227.336	184.267	23.523	-53.594	-1.568
7200	143.486	201.181	230.084	187.615	23.418	-54.691	-1.573
7300	146.474	203.032	232.832	190.963	23.312	-55.788	-1.578
7400	149.492	204.873	235.580	194.311	23.207	-56.885	-1.583
7500	152.540	206.704	238.328	197.659	23.101	-57.982	-1.588
7600	155.618	208.525	241.076	201.007	23.000	-59.079	-1.593
7700	158.726	210.336	243.824	204.355	22.894	-60.176	-1.598
7800	161.864	212.137	246.572	207.703	22.789	-61.273	-1.603
7900	165.032	213.928	249.320	211.051	22.683	-62.370	-1.608
8000	168.230	215.709	252.068	214.399	22.578	-63.467	-1.613
8100	171.458	217.480	254.816	217.747	22.472	-64.564	-1.618
8200	174.716	219.241	257.564	221.095	22.367	-65.661	-1.623
8300	178.004	221.002	260.312	224.443	22.261	-66.758	-1.628
8400	181.322	222.753	263.060	227.791	22.156	-67.855	-1.633
8500	184.670	224.494	265.808	231.139	22.050	-68.952	-1.638
8600	188.048	226.225	268.556	234.487	21.945	-70.049	-1.643
8700	191.456	227.946	271.304	237.835	21.840	-71.146	-1.648
8800	194.894	229.657	274.052	241.183	21.734	-72.243	-1.653
8900	198.362	231.358	276.800	244.531	21.629	-73.340	-1.658
9000	201.860	233.049	279.548	247.879	21.523	-74.437	-1.663
9100	205.388	234.730	282.296	251.227	21.418	-75.534	-1.668
9200	208.946	236.401	285.044	254.575	21.312	-76.631	-1.673
9300	212.534	238.062	287.792	257.923	21.207	-77.728	-1.678
9400	216.152	239.713	290.540	261.271	21.101	-78.825	-1.683
9500	219.800	241.354	293.288	264.619	21.000	-79.922	-1.688
9600	223.478	242.985	296.036	267.967	20.894	-81.019	-1.693
9700	227.186	244.606	298.784	271.315	20.789	-82.116	-1.698
9800	230.924	246.217	301.532	274.663	20.683	-83.213	-1.703
9900	234.692	247.818	304.280	278.011	20.578	-84.310	-1.708
10000	238.490	249.409	307.028	281.359	20.472	-85.407	-1.713

Dec. 31, 1967





Acetylene (C₂H₂)
(Ideal Gas) Mol. Wt. = 26.038

MOL. WT. = 26.038

(IDEAL GAS)

ACETYLENE (C₂H₂)

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f ^o	Log K _p
0	7.000	INFINITE	2.393	54.325	INFINITE
100	7.505	28.213	1.838	54.325	1.8146
200	8.010	26.993	1.000	54.190	36.644
298	10.539	46.004	0.000	54.190	36.644
300	10.571	46.069	0.020	54.189	36.399
400	12.095	48.438	1.135	54.138	26.534
500	13.114	51.139	2.410	54.064	20.682
600	13.931	56.604	50.319	53.961	16.687
700	14.615	56.605	51.377	53.637	13.662
800	15.239	56.798	52.432	53.707	11.764
900	15.801	62.625	53.464	53.573	10.155
1000	16.316	64.317	54.466	53.430	8.656
1100	16.789	65.895	55.434	53.333	7.795
1200	17.221	67.375	56.366	53.228	6.913
1300	17.613	68.769	57.269	53.128	6.168
1400	17.968	70.087	58.139	53.041	5.531
1500	18.291	71.338	58.977	52.961	4.979
1600	18.592	72.528	59.787	52.887	4.497
1700	18.865	73.663	60.570	52.823	4.072
1800	19.085	74.747	61.327	52.765	3.695
1900	19.262	75.785	62.061	52.714	3.359
2000	19.504	76.760	62.772	52.670	3.055
2100	19.654	77.736	63.462	52.631	2.782
2200	19.833	78.656	64.132	52.594	2.532
2300	20.004	79.551	64.783	52.564	2.306
2400	20.151	80.396	65.416	52.535	2.100
2500	20.282	81.221	66.032	52.510	1.906
2600	20.404	82.019	66.631	52.486	1.730
2700	20.519	82.791	67.216	52.466	1.566
2800	20.625	83.540	67.785	52.448	1.415
2900	20.726	84.265	68.341	52.429	1.274
3000	20.820	84.969	68.884	52.413	1.142
3100	20.910	85.654	69.414	52.399	1.019
3200	20.996	86.319	69.932	52.385	0.903
3300	21.078	86.966	70.438	52.369	0.795
3400	21.154	87.596	70.934	52.356	0.693
3500	21.225	88.211	71.418	52.340	0.597
3600	21.297	88.810	71.893	52.325	0.506
3700	21.367	89.394	72.356	52.307	0.420
3800	21.431	89.965	72.814	52.291	0.339
3900	21.489	90.522	73.261	52.272	0.262
4000	21.557	91.067	73.699	52.252	0.189
4100	21.615	91.600	74.130	52.231	0.119
4200	21.670	92.122	74.552	52.206	0.053
4300	21.728	92.632	74.966	52.179	0.010
4400	21.782	93.133	75.374	52.151	0.071
4500	21.835	93.623	75.774	52.120	0.129
4600	21.883	94.103	76.167	52.087	0.183
4700	21.935	94.574	76.554	52.052	0.236
4800	21.985	95.037	76.934	52.013	0.286
4900	22.036	95.490	77.308	51.973	0.335
5000	22.077	95.936	77.676	51.930	0.381
5100	22.129	96.374	78.038	51.881	0.426
5200	22.174	96.804	78.395	51.832	0.468
5300	22.219	97.227	78.746	51.780	0.509
5400	22.263	97.642	79.093	51.724	0.549
5500	22.309	98.051	79.434	51.663	0.587
5600	22.349	98.454	79.770	51.600	0.624
5700	22.393	98.850	80.101	51.534	0.659
5800	22.433	99.239	80.428	51.463	0.693
5900	22.474	99.624	80.750	51.390	0.726
6000	22.521	100.001	81.067	51.313	0.758

March 31, 1961

ΔH_f^o = 54.33 ± 0.19 kcal. mole⁻¹
Point Group D_{∞h}
ΔH_f^o 298.15 = 54.19 ± 0.19 kcal. mole⁻¹
S_{298.15} = 48.004 cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω _e , cm. ⁻¹
3373.7 (1)
1973.8 (1)
3281.9 (1)
611.6 (2)
729.3 (2)

Rotational Constant B₀ = 1.17684 ± 0.00016 cm.⁻¹ σ = 2

Ground State Multiplicity = 1

Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm.⁻¹):

X ₁₁ = -24.08	X ₂₂ = -7.92	X ₃₄ = -9.06	D ₀ = 2.19 X 10 ⁻⁶
X ₁₂ = -16.94	X ₂₃ = -1.38	X ₅₅ = -5.73	ε ₄₄ = 1.1
X ₁₃ = -99.01	X ₂₄ = -6.15	X ₄₄ = 5.38	ε ₅₅ = 2.49
X ₁₄ = -16.46	X ₂₅ = -0.85	X ₄₅ = -12.65	
X ₁₅ = -11.75	X ₃₃ = -25.69	X ₅₅ = -2.27	

Values of α_i not available.

Heat of Formation

Taken from D. D. Wagman, J. E. Kilpatrick, K. S. Pitzer, and P. D. Rossini, J. Research Natl. Bureau Standards 55, 467 (1945).

Heat Capacity and Entropy

J. S. Gordon (private communication, February, 1961) has used the constants listed above to calculate C_p from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954). The constants are from E. E. Ball and H. H. Nielsen, J. Chem. Phys. 18, 1382 (1950) and H. C. Allen, E. D. Tidwell, and E. K. Plyler, J. Research Natl. Bureau Standards 57, 213 (1956). Heat capacities below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.



Ethylene (C₂H₄)

(Ideal Gas)

Mol. Wt. = 28.05418

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	Log K _p
0	∞	∞	∞	∞	∞
100	7.952	43.125	1.719	14.578	INFINITE
200	8.451	48.721	5.267	14.434	- 31.544
298	10.250	52.396	11.974	15.227	- 16.638
300	10.292	52.459	12.019	16.338	- 11.974
400	12.679	55.745	22.520	17.352	- 11.018
500	14.933	58.821	34.372	18.319	- 9.499
600	16.889	61.721	47.433	21.008	- 7.652
700	18.574	64.454	61.618	22.788	- 6.114
800	20.020	67.051	76.911	24.548	- 4.838
900	21.280	69.548	93.272	26.284	- 3.713
1000	22.443	71.974	110.665	28.031	- 2.713
1100	23.527	74.360	129.066	30.373	- 1.834
1200	24.590	76.736	148.491	32.334	- 1.069
1300	25.636	79.109	168.941	34.889	- 0.466
1400	26.666	81.480	190.416	37.122	- 0.000
1500	26.285	83.846	212.917	38.266	- 0.575
1600	26.794	83.399	236.452	40.246	- 1.261
1700	27.242	85.037	261.033	42.237	- 2.061
1800	27.636	86.721	286.661	44.248	- 2.961
1900	27.986	88.451	313.337	46.278	- 3.961
2000	28.296	89.125	341.062	48.204	- 5.061
2100	28.571	90.940	369.837	50.132	- 6.261
2200	28.818	92.275	399.662	52.114	- 7.561
2300	29.036	93.901	430.537	54.163	- 8.961
2400	29.226	95.908	462.462	56.284	- 10.461
2500	29.414	98.297	495.437	58.479	- 12.061
2600	29.575	101.065	529.462	60.749	- 13.761
2700	29.721	104.211	564.537	63.189	- 15.561
2800	29.853	107.746	600.662	65.789	- 17.461
2900	30.073	111.671	637.837	68.449	- 19.461
3000	30.083	101.425	674.434	71.169	- 21.561
3100	30.184	102.413	70.688	73.947	- 23.761
3200	30.276	103.373	80.413	76.782	- 26.061
3300	30.359	104.215	81.123	79.574	- 28.461
3400	30.436	105.040	81.813	82.326	- 30.961
3500	30.510	105.856	82.499	85.046	- 33.561
3600	30.577	106.657	83.167	87.726	- 36.261
3700	30.638	107.446	83.821	90.366	- 39.061
3800	30.694	108.215	84.463	92.966	- 41.961
3900	30.746	108.966	85.094	95.526	- 44.961
4000	30.797	110.190	85.710	97.921	- 48.061
4100	30.843	110.951	86.317	101.003	- 51.261
4200	30.886	111.695	86.912	104.080	- 54.561
4300	30.926	112.422	87.497	107.152	- 57.961
4400	30.964	113.135	88.076	110.219	- 61.461
4500	30.999	113.830	88.650	113.273	- 65.061
4600	31.032	114.512	89.191	116.314	- 68.761
4700	31.063	115.180	89.737	119.345	- 72.561
4800	31.092	115.834	90.274	122.366	- 76.461
4900	31.120	116.477	90.801	125.377	- 80.461
5000	31.146	117.104	91.322	128.379	- 84.561
5100	31.171	117.721	91.834	131.372	- 88.761
5200	31.194	118.327	92.337	134.357	- 93.061
5300	31.216	118.921	92.833	137.333	- 97.461
5400	31.236	119.505	93.321	140.301	- 101.961
5500	31.256	120.078	93.803	143.261	- 106.561
5600	31.275	120.641	94.277	146.213	- 111.261
5700	31.292	121.195	94.745	149.158	- 116.061
5800	31.308	121.740	95.205	152.096	- 120.961
5900	31.325	122.275	95.657	155.027	- 125.961
6000	31.340	122.802	96.108	157.952	- 131.061

Dec. 31, 1960; Sept. 30, 1965

ETHYLENE (C₂H₄)

(IDEAL GAS)

MOL. WT. = 28.05418

Point Group D_{2h}ΔH_f° 0 = 14.58 ± 0.07 kcal. mole⁻¹ΔH_f° 298.15 = 12.54 ± 0.07 kcal. mole⁻¹S° 298.15 = 52.396 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
3026.4 (1)	3026.5 (1)	3105.5 (1)	3105.5 (1)
1622.9 (1)	1222.0 (1)	826.0 (1)	826.0 (1)
1342.2 (1)	949.3 (1)	2986.7 (1)	2986.7 (1)
1023.0 (1)	943.0 (1)	1443.5 (1)	1443.5 (1)

Bond Distance: H-C = 1.086 Å C-C = 1.337 Å

Bond Angle: H-C-H = 117° 22' H-C-C = 121° 19'

Product of the Moments of Inertia: I_AI_BI_C = 5.4466 X 10⁻¹¹⁷ g.³ cm.⁶

σ = 4

Heat of Formation.

The heat of combustion of ethylene was measured by F. D. Rossini and J. W. Knowlton, *J. Res. Natl. Bur. Std.* **19**, 249 (1937). From the value, ΔH_f° 298.15 = -337.28 ± 0.07 kcal. mole⁻¹ for the reaction C₂H₄(g) + 3 O₂(g) = 2 CO₂(g) + 2 H₂O(l), the heat of formation (ΔH_f° 298.15) for C₂H₄(g) was derived to be 12.54 ± 0.07 kcal. mole⁻¹. The values of ΔH_f° 298.15 for CO₂(g) and H₂O(l) used for calculation were obtained from F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and Irving Jaffe, "Selected Values of Chemical Thermodynamic Properties", Circular of the National Bureau of Standards 500, 1952.

Heat Capacity and Entropy.

The molecular structure, bond distances and angles were obtained from H. C. Allen, Jr. and E. K. Plyler, *J. Am. Chem. Soc.* **80**, 2673 (1958). The vibrational frequencies were taken from W. L. Smith and I. M. Mills, *J. Chem. Phys.* **40**, 2095 (1964). Eight of the twelve frequencies were reported by R. L. Arnett and B. L. Crawford, *J. Chem. Phys.* **19**, 118 (1950); B. L. Crawford, J. E. Lancaster and R. Inskip, *J. Chem. Phys.* **21**, 678 (1953); B. P. Stoicheff, *J. Chem. Phys.* **21**, 755 (1953); T. Feldman, J. Romanko and H. L. Welsh, *Can. J. Phys.* **34**, 737 (1956); and H. C. Allen and E. K. Plyler, loc. cit. O. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., New York, 1945, also reported the vibrational frequencies for ethylenes as 3019.3 (1), 1623.3 (1), 1342.4 (1), 825.0 (1), 3272.3 (1), 1050 (1), 949.2 (1), 943 (1), 3105.5 (1), 995 (1), 2989.5 (1) and 1443.5 (1) which are very close to the values adopted. The infrared and Raman spectra of ethylene before 1945 have been summarized by O. Herzberg, loc. cit. The molecular structure of ethylene was also determined by L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **27**, 1414 (1957). Their results, r_{C-H} = 1.085 Å, r_{C-C} = 1.334 Å and X_{H-C-H} = 116° are in excellent agreement with the values adopted. The three principal moments of inertia are I_A = 0.5762 X 10⁻³⁹, I_B = 2.7999 X 10⁻³⁹ and I_C = 3.3761 X 10⁻³⁹ g. cm.²



T, °K.	C _p ^o	C _v ^o	S ^o	-(H ^o -H ₂₉₈ ^o)/T	-(H ^o -H ₂₉₈ ^o)/T	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	7.956	48.444	66.457	1.801	10.694	9.587	8.563	INFINITE
200	8.772	59.006	78.157	2.860	11.576	8.563	6.640	18.670
300	11.449	80.056	93.056	4.000	12.350	8.563	5.104	25.319
400	14.013	98.127	98.056	5.021	12.599	3.107	2.263	
500	16.493	111.004	98.548	5.958	13.514	.201	-1.110	
600	18.823	125.575	98.589	6.793	14.264	3.719	-1.625	
700	20.929	139.099	98.882	7.490	14.861	7.373	-2.685	
800	22.743	150.612	99.287	8.064	15.330	11.119	-3.471	
900	24.311	160.612	99.766	8.547	15.686	14.922	-4.076	
1000	25.615	169.602	100.250	8.951	15.951	18.764	-4.556	
1100	26.747	177.477	100.727	9.286	16.129	22.631	-4.946	
1200	27.747	184.428	101.197	9.567	16.260	26.512	-5.267	
1300	28.615	190.507	101.659	9.791	16.353	30.404	-5.537	
1400	29.367	195.838	102.109	9.964	16.404	34.294	-5.765	
1500	30.047	200.438	102.549	10.097	16.428	38.189	-5.961	
1600	30.671	204.366	102.976	10.197	16.428	42.078	-6.131	
1700	31.247	207.667	103.391	10.264	16.404	45.957	-6.277	
1800	31.779	210.367	103.791	10.300	16.353	49.837	-6.407	
1900	32.266	212.507	104.176	10.318	16.280	53.708	-6.521	
2000	32.713	214.104	104.544	10.318	16.189	57.576	-6.622	
2100	33.126	215.266	104.897	10.300	16.080	61.433	-6.713	
2200	33.508	216.000	105.236	10.264	15.959	65.288	-6.794	
2300	33.854	216.333	105.561	10.213	15.828	69.128	-6.867	
2400	34.168	216.266	105.876	10.148	15.686	72.969	-6.933	
2500	34.454	215.800	106.176	10.069	15.536	76.804	-6.994	
2600	34.713	214.933	106.461	9.977	15.379	80.622	-7.048	
2700	34.947	213.566	106.726	9.876	15.208	84.446	-7.098	
2800	35.158	211.700	106.976	9.757	15.028	88.256	-7.143	
2900	35.347	209.333	107.213	9.624	14.840	92.063	-7.186	
3000	35.513	206.466	107.433	9.477	14.640	95.872	-7.225	
3100	35.658	203.100	107.640	9.318	14.428	99.667	-7.260	
3200	35.786	199.233	107.833	9.148	14.204	103.466	-7.294	
3300	35.897	194.866	107.997	8.969	13.969	107.251	-7.325	
3400	35.993	190.000	108.133	8.780	13.726	111.037	-7.353	
3500	36.076	184.633	108.240	8.583	13.476	114.820	-7.380	
3600	36.148	178.766	108.318	8.376	13.213	118.597	-7.405	
3700	36.206	172.400	108.366	8.154	12.936	122.375	-7.429	
3800	36.252	165.533	108.383	7.918	12.646	126.148	-7.451	
3900	36.286	158.166	108.366	7.669	12.346	129.925	-7.472	
4000	36.309	150.300	108.318	7.407	12.036	133.696	-7.492	
4100	36.322	141.933	108.240	7.134	11.713	137.466	-7.510	
4200	36.326	133.066	108.133	6.850	11.376	141.226	-7.528	
4300	36.322	123.700	107.997	6.556	11.028	144.988	-7.545	
4400	36.309	113.833	107.833	6.250	10.669	148.755	-7.560	
4500	36.286	103.466	107.640	5.933	10.296	152.516	-7.575	
4600	36.252	92.600	107.433	5.597	9.913	156.272	-7.589	
4700	36.206	81.233	107.213	5.250	9.520	160.043	-7.603	
4800	36.148	69.366	106.976	4.893	9.113	163.806	-7.617	
4900	36.076	57.000	106.726	4.526	8.690	167.570	-7.629	
5000	36.000	44.133	106.461	4.148	8.253	171.333	-7.641	
5100	35.913	30.766	106.176	3.757	7.800	175.089	-7.653	
5200	35.818	16.900	105.876	3.354	7.333	178.851	-7.664	
5300	35.713	2.533	105.561	2.939	6.856	182.611	-7.675	
5400	35.597	-11.333	105.236	2.513	6.369	186.389	-7.686	
5500	35.471	-23.466	104.897	2.076	5.872	190.145	-7.695	
5600	35.336	-35.000	104.544	1.629	5.369	193.916	-7.705	
5700	35.193	-46.033	104.176	1.172	4.856	197.680	-7.714	
5800	35.040	-56.566	103.791	0.707	4.333	201.445	-7.723	
5900	34.878	-66.600	103.391	0.230	3.800	205.219	-7.733	
6000	34.707	-76.133	102.976	-0.257	3.257	209.001	-7.742	
6100	34.526	-85.166	102.549	-0.734	2.704	212.760	-7.749	

See 31, 1950; Sept. 30, 1965

Point group C_{2v}
ΔH_f^o 0 = -9.59 ± 0.15 kcal. mole⁻¹
ΔH_f^o 298.15 = 56.06 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies
 ω , cm.⁻¹ ω , cm.⁻¹

Bond Distances: C-H = 1.0802 Å C-O = 1.4363 Å C-C = 1.4726 Å
Bond Angle: H-C-H = 116° 51' H₂-C-C = 156° 51'
Product of the Moments of Inertia: I_AI_BI_C = 7.42336 X 10⁻¹¹⁶ g.³ cm.⁶

Heat of Formation.

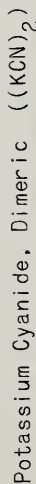
The heat of combustion of ethylene oxide (g) was determined by A. S. Fell and O. Fitcher, Trans. Faraday Soc. 51, 71 (1955) and R. S. Clegg and H. Hunt, J. Phys. Chem. 46, 1162 (1942), as -312.15 ± 0.14 and -312.55 ± 0.20 kcal. mole⁻¹, respectively. The corresponding value of ΔH_f^o 298.15 (C₂H₄O, g) was evaluated to be -12.58 ± 0.15 and -12.19 ± 0.22 kcal. mole⁻¹. The former value is adopted.

Heat Capacity and Entropy.

The vibrational frequencies were taken from R. C. Lord and B. Nollin, J. Chem. Phys. 24, 656 (1956). The infrared and Raman spectra of ethylene oxide have also been examined by J. W. Linnett, J. Chem. Phys. 6, 692 (1938) and H. W. Thompson and W. T. Cave, Trans. Faraday Soc., 47, 946 (1951). The vibrational frequencies assigned were slightly different from the ones reported by R. C. Lord and B. Nollin, loc. cit. As a result of analogies between ethylene oxide and ethylene imine, small changes of R. C. Lord and B. Nollin's assignment have been made by W. J. Potts, Spectrochim. Acta, 21, 511 (1965). The bond distances and angles were obtained from O. L. Cunningham, A. W. Boyd and W. D. Omlin, J. Chem. Phys. 17, 211 (1949). The investigation of the structure of ethylene oxide by electron diffraction was reported by P. C. Ackermann and J. E. Mayer, J. Chem. Phys. 4, 377 (1936) and M. Igereahli, Bull. Chem. Soc. Japan, 28, 330 (1953). The three principal moments of inertia are: I_A = 3.8052 X 10⁻³⁹, I_B = 3.2788 X 10⁻³⁹ and I_C = 5.9499 X 10⁻³⁹ g. cm.²

The calculated heat capacities (307.2 - 371.2°K.) are in good agreement with the experimentally measured ones reported by O. B. Kistiakowsky and W. W. Rice, J. Chem. Phys. 9, 616 (1940).





POTASSIUM CYANIDE, DIMERIC ((KCN)₂)

POTASSIUM CYANIDE, DIMERIC ((KCN)₂)

Mol. Wt. = 130.2397

(Ideal Gas)

(Ideal Gas)

Point Group [D_{2h}]
 $\Delta H_f^\circ 0 = [-2 \pm 10] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [-2 \pm 10] \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [89.15] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega_e, \text{cm.}^{-1}$	$\omega_e, \text{cm.}^{-1}$	$\omega_e, \text{cm.}^{-1}$
[240] (1)	[220] (1)	[2158] (1)
[130] (1)	[225] (1)	[2158] (1)
[205] (1)	[207] (1)	[2158] (1)
[130] (1)	[207] (1)	[2158] (1)

Bond Distance: K-C = [2.75] Å C-N = [1.16] Å
 Bond Angle: N-C-K = [140]° C-K-C = [100]° K-C-K = [80]°
 Product of the Moments of Inertia: $I_A I_B I_C = [2.94818 \times 10^{-112}] \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.
 $\Delta H_f^\circ 298.15 ((\text{KCN})_2, g)$ was calculated based on an estimated heat of dissociation, 40 kcal. mole⁻¹ for the reaction $(\text{KCN})_2(g) \rightarrow 2\text{KCN}(g)$, which was obtained by comparison with that for $(\text{NaCN})_2(g)$.

Heat Capacity and Entropy.

The molecular structure and bond angles were assumed to be the same as those for KCN(c) reported by J. M. Bljvoet and J. A. Lely, Rec. trav. chim. 52, 908 (1940). The C-N bond distance was assumed to be the same as that for KCN(g), and the K-C bond distance was assumed to be 10% longer than that in KCN(g). The vibrational frequencies were estimated by comparison with those for K₂P₂(g). The last six frequencies were adopted from the bending and asymmetric stretching frequencies for KCN(g). The three principal moments of inertia are: $I_A = 4.05745 \times 10^{-38}$, $I_B = 6.73551 \times 10^{-38}$ and $I_C = 1.079095 \times 10^{-37} \text{ g. cm.}^2$.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	Log K _p
0	0.000	INFINITE	5.924	1.962	INFINITE
100	18.534	63.656	4.758	3.147	6.879
200	26.353	89.153	4.000	4.807	3.597
300	26.371	89.316	0.049	3.588	
400	27.081	97.009	2.725	3.139	3.109
500	27.586	103.108	5.459	3.232	2.762
600	28.050	108.179	8.241	3.370	2.522
700	28.489	112.556	11.068	3.553	2.342
800	28.893	116.367	13.937	3.769	2.199
900	29.252	119.791	16.845	4.018	2.082
1000	29.565	122.890	19.786	4.305	1.981
1100	29.834	125.721	22.756	4.624	1.886
1200	30.064	128.327	25.752	4.974	1.794
1300	30.261	130.741	28.768	5.351	1.704
1400	30.429	132.990	31.803	5.752	1.615
1500	30.573	135.094	34.853	6.178	1.527
1600	30.697	137.072	37.917	6.629	1.440
1700	30.804	138.936	40.992	7.104	1.354
1800	30.897	140.689	44.077	7.604	1.268
1900	30.978	142.372	47.171	8.129	1.182
2000	31.050	143.993	50.273	8.679	1.096
2100	31.112	145.570	53.381	9.254	1.010
2200	31.167	147.108	56.495	9.854	0.924
2300	31.216	148.613	59.614	10.479	0.838
2400	31.260	149.664	62.738	11.129	0.752
2500	31.299	150.621	65.866	11.804	0.666
2600	31.334	151.549	68.998	12.504	0.580
2700	31.365	152.432	72.133	13.229	0.494
2800	31.394	153.274	75.271	13.979	0.408
2900	31.419	154.076	78.411	14.754	0.322
3000	31.443	154.841	81.554	15.554	0.236
3100	31.464	155.573	84.700	16.379	0.150
3200	31.483	156.272	87.847	17.229	0.064
3300	31.501	156.941	90.996	18.104	-0.022
3400	31.518	157.581	94.147	19.004	-0.108
3500	31.533	158.195	97.300	19.929	-0.194
3600	31.547	158.784	100.454	20.879	-0.280
3700	31.559	159.348	103.609	21.854	-0.366
3800	31.571	159.890	106.766	22.854	-0.452
3900	31.582	160.410	109.923	23.879	-0.538
4000	31.592	160.910	113.082	24.929	-0.624
4100	31.602	161.400	116.242	26.004	-0.710
4200	31.611	161.872	119.402	27.104	-0.796
4300	31.619	162.328	122.564	28.229	-0.882
4400	31.627	162.772	125.726	29.379	-0.968
4500	31.634	163.204	128.889	30.554	-1.054
4600	31.641	163.624	132.053	31.754	-1.140
4700	31.647	164.034	135.217	32.979	-1.226
4800	31.653	164.434	138.382	34.229	-1.312
4900	31.659	164.824	141.546	35.504	-1.398
5000	31.664	165.204	144.714	36.804	-1.484
5100	31.669	165.574	147.881	38.129	-1.570
5200	31.674	165.934	151.048	39.479	-1.656
5300	31.678	166.284	154.215	40.854	-1.742
5400	31.682	166.624	157.383	42.254	-1.828
5500	31.686	166.954	160.552	43.679	-1.914
5600	31.690	167.274	163.720	45.129	-2.000
5700	31.694	167.584	166.889	46.604	-2.086
5800	31.697	167.884	170.059	48.104	-2.172
5900	31.700	168.174	173.229	49.629	-2.258
6000	31.703	168.454	176.400	51.179	-2.344

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _P
0						
100	17.100	14.000	14.000	.000	- 13.415	9.633
200	17.200	14.106	14.000	.032	- 14.196	9.769
300	17.200	14.630	14.728	1.061	- 15.003	7.197
400	20.690	24.506	16.206	4.150	- 15.266	5.612
500	22.720	24.506	16.206	4.150	- 15.266	5.612
600	23.630	26.756	17.953	6.462	- 15.136	4.503
700	24.600	32.491	19.769	6.906	- 14.964	3.720
800	25.600	35.815	21.571	11.396	- 14.776	3.139
900	25.660	38.610	23.322	13.936	- 14.566	2.693
1000	26.070	41.535	25.009	16.525	- 14.395	2.342
1100	26.830	44.037	26.427	19.151	- 14.189	2.037
1200	26.770	46.352	28.175	21.411	- 13.977	1.625
1300	27.090	46.507	29.657	24.504	- 13.750	1.630
1400	27.390	50.525	31.077	27.228	- 13.508	1.466
1500	27.680	52.425	32.437	29.962	- 13.246	1.327
1600	27.940	54.221	33.743	32.764	- 12.970	1.206
1700	26.240	55.024	34.998	35.574	- 62.764	.763
1800	26.510	57.546	36.206	38.411	- 62.077	.174
1900	28.780	59.064	37.370	41.276	- 61.370	.346
2000	29.040	60.577	38.494	44.167	- 60.643	.614

December 31, 1960.

DILITHIUM DICARBIDE (Li₂C₂) (Solid)

Mol. Wt. = 37.902
ΔH_f⁰ 298.15 = -14.2 ± 2 kcal mole⁻¹
S_{298.15}⁰ = 14 ± 1 cal. deg.⁻¹ mole⁻¹

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

Monomagnesium Dicarbide (MgC₂)
(Solid) Mol. Wt. = 48.33

INTERIM TABLE

T, °K.	C _p ^a	S° ^b - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^c	ΔF _f ^d	Log K _p
0						
100	13.440	13.000	.000	21.000	20.270	- 14.857
200	13.490	13.063	.025	21.006	20.265	- 14.762
300	13.530	13.125	.081	21.060	20.266	- 10.908
400	13.567	13.187	.162	21.077	20.266	- 8.537
500	13.607	13.250	.273	21.094	20.266	- 6.949
600	13.649	13.313	.419	21.111	20.266	- 5.949
700	13.690	13.376	.606	21.128	20.266	- 5.053
800	13.730	13.439	.839	21.145	20.266	- 4.284
900	13.769	13.502	1.119	21.162	20.266	- 3.782
1000	13.809	13.565	1.452	21.179	20.266	- 3.382
1100	13.849	13.628	1.839	21.196	20.266	- 3.046
1200	13.889	13.691	2.281	21.213	20.266	- 2.769
1300	13.929	13.754	2.779	21.230	20.266	- 2.549
1400	13.969	13.817	3.332	21.247	20.266	- 2.371
1500	14.009	13.880	3.940	21.264	20.266	- 2.231
1600	14.049	13.943	4.603	21.281	20.266	- 2.121
1700	14.089	14.006	5.322	21.298	20.266	- 2.031
1800	14.129	14.069	6.095	21.315	20.266	- 1.959
1900	14.169	14.132	6.922	21.332	20.266	- 1.907
2000	14.209	14.195	7.805	21.349	20.266	- 1.865
2100	14.249	14.258	8.742	21.366	20.266	- 1.831
2200	14.289	14.321	9.735	21.383	20.266	- 1.803
2300	14.329	14.384	10.782	21.400	20.266	- 1.782
2400	14.369	14.447	11.885	21.417	20.266	- 1.766
2500	14.409	14.510	13.042	21.434	20.266	- 1.754

MONOMAGNESIUM DICARBIDE (MgC₂) (Solid)

Mol. Wt. = 48.33

ΔH_f^o 298.15 = 21 ± 5 kcal. mole⁻¹

S_{298.15} = 13 ± 2 cal. deg.⁻¹ mole⁻¹

Data from National Bureau of Standards Report No. 6828, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

CNC RADICAL (C₂N) (IDEAL GAS)

OPW = 38.029

Point Group D_{∞h}

ΔHf° = [131.9] kcal/mol

S°_{298.15} = [55 ± 2] gibbs/mol

ΔHf°_{298.15} = [133 ± 30] kcal/mol

Electronic Levels and Quantum Weights

ε ₁ , cm ⁻¹	g ₁
0	2
26.41	2
30338.53	4
34802.33	2

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	[1200] (1)	[321] (2)	[900] (1)

Bond Distance: C-N = 1.245 Å

Bond Angle: C-N-C = 180°

Rotational Constant: B₀ = 0.4535 cm⁻¹

σ = 2

Heat of Formation.

A. J. Merer and D. N. Trevis, Can. J. Phys. 44, 353 (1966), state that the observed bond length in CNC(g) indicates double-bonded CN links. The value of the C = N dissociation energy is derived as 147 kcal from the heat of combustion of n-butyl-isobutylidene emine determined by O. E. Coates and L. E. Sutton, J. Chem. Soc. 1187, (1948). However, due to possible extra binding energy from the unpaired electron, we assume here a slightly higher value of 160 kcal. This yields a ΔHf°₂₉₈(CNC,g) = 133 kcal/mol. It is also possible to calculate another value by assuming that the ratio of the heat of atomization (ΔH_{at}) of Si₂N to that of C₂N(g) is equal to the ratio of the dissociation energies of SiN(g) and CN(g); by this method ΔHf°₂₉₈(CNC,g) = 144 kcal/mol.

Heat Capacity and Entropy.

Merer and Trevis, loc. cit., have observed the ultraviolet absorption spectrum of the CNC radical. They have assigned the configuration, bond distance, and the electronic levels. In addition, they have derived w₀, the remaining frequencies are estimated by comparison with the T₁ state of C₂(g), which has been assigned by N. Weitzner and D. J. McLeod, J. Chem. Phys. 40, 1305 (1964), and J. Chem. Phys. 45, 3096 (1966).

Mar. 31, 1967

Cyanogen (C₂N₂)

(Ideal Gas) Mol. Wt. = 52.038

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	Log K _p
0	0.000	0.000	INFINITE	3.018	73.428	INFINITE
100	6.760	45.854	68.408	2.275	72.742	-158.670
200	11.690	52.663	58.976	1.267	73.659	-78.650
298	13.363	57.711	50.000	0.000	73.670	-52.128
300	13.390	57.795	49.925	-0.025	73.674	-51.794
400	14.771	61.876	58.260	1.487	74.107	-38.321
500	15.615	65.269	59.332	2.968	74.287	-30.213
600	16.405	68.178	60.549	4.565	74.415	-26.797
700	17.149	70.737	61.843	6.294	74.599	-24.923
800	17.851	73.028	63.100	7.992	74.554	-18.015
900	18.558	75.106	64.321	9.707	74.586	-15.751
1000	19.237	77.007	65.496	11.512	74.604	-13.939
1100	19.859	78.761	66.623	13.352	74.610	-12.457
1200	20.434	80.385	67.708	15.150	74.604	-11.177
1300	20.966	81.895	68.738	16.934	74.598	-10.177
1400	21.464	83.325	69.729	18.694	74.578	-9.281
1500	21.934	84.660	70.681	20.434	74.556	-8.505
1600	22.379	85.919	71.594	22.150	74.531	-7.826
1700	22.800	87.103	72.465	23.845	74.503	-7.232
1800	23.198	88.230	73.317	25.515	74.475	-6.695
1900	23.571	89.314	74.131	27.167	74.444	-6.220
2000	23.923	90.337	74.916	28.842	74.412	-5.792
2100	24.266	91.314	75.674	30.545	74.379	-5.405
2200	24.592	92.245	76.408	32.285	74.345	-5.052
2300	24.901	93.134	77.115	34.055	74.306	-4.732
2400	25.194	93.984	77.801	35.855	74.267	-4.436
2500	25.473	94.803	78.465	37.685	74.227	-4.167
2600	25.739	95.599	79.110	39.545	74.183	-3.919
2700	25.994	96.372	79.731	41.434	74.135	-3.689
2800	26.239	97.118	80.345	43.352	74.086	-3.473
2900	26.475	97.836	80.936	45.299	74.047	-3.273
3000	26.702	98.526	81.512	47.274	73.997	-3.086
3100	26.921	99.191	82.072	49.278	73.947	-2.914
3200	27.132	100.830	82.616	51.304	73.897	-2.750
3300	27.335	102.445	83.146	53.354	73.846	-2.591
3400	27.530	104.038	83.670	55.428	73.796	-2.436
3500	27.717	105.611	84.177	57.526	73.746	-2.284
3600	27.897	107.166	84.672	59.648	73.693	-2.131
3700	28.070	108.703	85.156	61.794	73.639	-1.979
3800	28.236	110.224	85.629	63.964	73.587	-1.826
3900	28.395	111.729	86.091	66.158	73.537	-1.673
4000	28.548	113.219	86.544	68.376	73.479	-1.520
4100	28.696	114.696	86.987	70.618	73.426	-1.367
4200	28.839	116.160	87.421	72.884	73.370	-1.214
4300	28.977	117.610	87.847	75.174	73.310	-1.061
4400	29.111	119.046	88.264	77.490	73.253	-0.908
4500	29.241	120.469	88.672	81.988	73.193	-0.755
4600	29.368	121.881	89.073	86.456	73.136	-0.602
4700	29.492	123.283	89.467	90.894	73.079	-0.449
4800	29.613	124.676	89.853	95.304	73.022	-0.296
4900	29.731	126.060	90.233	99.686	72.966	-0.143
5000	29.846	127.435	90.605	104.040	72.910	0.010
5100	29.959	128.800	90.971	108.366	72.853	0.157
5200	30.070	130.156	91.331	112.674	72.796	0.304
5300	30.179	131.503	91.685	116.964	72.739	0.451
5400	30.285	132.841	92.033	121.236	72.682	0.598
5500	30.389	134.169	92.375	125.490	72.625	0.745
5600	30.491	135.488	92.712	129.726	72.568	0.892
5700	30.591	136.798	93.045	133.944	72.511	1.039
5800	30.689	138.100	93.370	138.144	72.454	1.186
5900	30.785	139.394	93.691	142.326	72.397	1.333
6000	30.879	140.680	94.008	146.490	72.340	1.480

March 31, 1961

C₂N₂

MOL. WT. = 52.038

(IDEAL GAS)

CYANOGEN (C₂N₂)

ΔH°_f 298.15 = 73.87 ± 0.43 kcal. mole⁻¹
 S°_{298.15} = 57.71 cal. deg.⁻¹ mole⁻¹

ΔH°_f 0 = 73.428 kcal. mole⁻¹
 Point Group D_{∞h}

Vibrational Levels and Multiplicities

W, cm. ⁻¹
2328.5 (1)
850.6 (1)
214.9 (1)
507.2 (2)
240 (2)

Rotational constant B₀ = 0.15752 ± 0.00015 cm.⁻¹ CN distance = 1.157 Å CC distance = 1.380 Å σ = 2
 Moment of inertia = 1.776(g) × 10⁻³⁸ g. cm.²

Heat of Formation

J. W. Knowlton and E. J. Prosen, J. Research Natl. Bur. Standards 46, 489 (1951), report ΔH°_f 298.15 = -261.94 ± 0.43 kcal. for the reaction C₂N₂(g) + 2 O₂(g) → 2 CO₂(g) + N₂(g). When corrected for a change in the atomic weight of carbon, this becomes ΔH°_f 298.15 = -261.95 ± 0.43 kcal., whence ΔH°_f 298.15 for C₂N₂(g) is found to be 73.87 ± 0.43 kcal. mole⁻¹.

Heat Capacity and Entropy

A. Langseth and C. K. Møller, Acta Chem. Scand. 4, 725 (1950), determined the vibrational frequencies by Raman spectroscopy. C. K. Møller and B. P. Stoicheff, Can. J. Phys. 32, 625 (1954), determined B₀ by Raman spectroscopy and calculated the bond lengths listed above. These agree with lengths found from electron-diffraction measurements by Langseth and Møller, loc. cit., (CN distance = 1.15 Å, CC distance = 1.38 Å) and L. Pauling, H. D. Springall, and K. J. Palmer, J. Am. Chem. Soc. 61, 927 (1939) (CN distance = 1.16 ± 0.02 Å, CC distance = 1.37 ± 0.02 Å). From measurements reported by R. A. Ruehrwein and W. F. Glauque, J. Am. Chem. Soc. 81, 2940 (1959), S°_{298.15} is calculated by the third law to be 57.63 cal. deg.⁻¹ mole⁻¹, in satisfactory agreement with the value calculated here.

C₂N₂

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f kcal. mole ⁻¹	ΔF° _f	Log K _p
0	∞	∞	∞	∞	∞	INFINITE
100	16.175	59.048	104.034	- 1.982	- 3.207	7.009
200	23.539	73.050	85.231	- 4.499	- 4.479	3.692
298	25.737	82.932	82.932	- 2.264	- 2.100	3.692
300	25.762	83.091	82.932	- 2.097	- 5.054	3.682
400	26.716	90.647	83.056	- 2.676	- 5.948	3.250
500	27.339	96.678	85.918	- 3.346	- 6.586	2.879
600	27.867	101.710	88.142	- 3.614	- 7.196	2.621
700	28.306	106.055	90.000	- 3.887	- 7.783	2.377
800	28.776	109.856	92.595	- 4.136	- 8.346	2.154
900	29.155	113.268	94.706	- 4.203	- 8.869	2.049
1000	29.482	116.357	96.719	- 4.437	- 9.375	1.959
1100	29.763	119.181	98.655	- 4.700	- 9.861	1.881
1200	29.998	121.774	100.434	- 5.000	- 10.329	1.814
1300	30.206	124.191	102.191	- 5.1357	- 10.780	1.757
1400	30.381	126.436	103.843	- 5.1255	- 11.216	1.706
1500	30.530	128.537	105.420	- 5.1160	- 11.641	1.659
1600	30.659	130.512	106.927	- 51.070	- 12.059	1.615
1700	30.776	132.369	108.369	- 50.802	- 12.463	1.573
1800	30.866	134.135	109.753	- 50.486	- 12.853	1.532
1900	30.950	135.806	111.081	- 50.821	- 13.229	1.492
2000	31.024	137.396	112.357	- 50.746	- 13.593	1.453
2100	31.088	138.911	113.586	- 50.670	- 13.948	1.415
2200	31.146	140.359	114.764	- 50.595	- 14.294	1.378
2300	31.196	141.744	115.903	- 50.520	- 14.632	1.342
2400	31.241	143.073	117.017	- 50.472	- 14.963	1.307
2500	31.282	144.349	118.085	- 50.410	- 15.288	1.273
2600	31.318	145.577	119.119	- 50.357	- 15.608	1.240
2700	31.350	146.760	120.123	- 50.302	- 15.923	1.207
2800	31.380	147.900	121.093	- 50.262	- 16.233	1.175
2900	31.406	149.002	122.025	- 50.222	- 16.538	1.143
3000	31.431	150.067	122.933	- 50.191	- 16.838	1.111
3100	31.453	151.098	123.844	- 50.165	- 17.133	1.080
3200	31.472	152.097	124.762	- 50.149	- 17.423	1.049
3300	31.491	153.065	125.686	- 50.130	- 17.708	1.018
3400	31.508	154.006	126.579	- 50.147	- 17.988	0.987
3500	31.524	154.919	127.182	- 50.163	- 18.263	0.956
3600	31.538	155.807	127.964	- 50.192	- 18.533	0.925
3700	31.550	156.672	128.724	- 50.230	- 18.798	0.894
3800	31.563	157.513	129.465	- 50.265	- 19.058	0.863
3900	31.575	158.333	130.205	- 50.365	- 19.313	0.832
4000	31.585	159.133	130.918	- 50.457	- 19.563	0.801
4100	31.595	159.913	131.616	- 50.571	- 19.808	0.770
4200	31.603	160.674	132.297	- 50.670	- 20.048	0.739
4300	31.613	161.418	132.967	- 51.060	- 20.283	0.708
4400	31.621	162.145	133.622	- 51.060	- 20.513	0.677
4500	31.628	162.856	134.264	- 51.281	- 20.738	0.646
4600	31.635	163.551	134.893	- 51.535	- 20.958	0.615
4700	31.642	164.232	135.510	- 51.823	- 21.173	0.584
4800	31.648	164.898	136.115	- 52.143	- 21.383	0.553
4900	31.654	165.550	136.709	- 52.531	- 21.588	0.522
5000	31.659	166.190	137.293	- 52.955	- 21.788	0.491
5100	31.664	166.817	137.865	- 53.432	- 21.983	0.460
5200	31.668	167.432	138.426	- 53.960	- 22.173	0.429
5300	31.674	168.035	138.981	- 54.544	- 22.358	0.398
5400	31.678	168.627	139.524	- 55.219	- 22.538	0.367
5500	31.682	169.208	140.059	- 55.955	- 22.713	0.336
5600	31.686	169.779	140.585	- 56.763	- 22.883	0.305
5700	31.690	170.340	141.107	- 57.640	- 23.048	0.274
5800	31.694	170.891	141.617	- 58.590	- 23.208	0.243
5900	31.697	171.433	142.111	- 59.697	- 23.363	0.212
6000	31.700	171.966	142.605	- 60.857	- 23.513	0.181

Mar. 31, 1966

Heat of Formation.
The mass spectra of vapors from samples of NaCN have been observed by R. F. Porter, J. Chem. Phys. **35**, 318 (1961), at temperatures around 1000°K. The results indicate that the compound evaporates as NaCN(g) and Na₂(CN)₂(g). A comparison of relative ion currents produced by electron bombardment of NaCN vapors effusing from single - and double-oven-type Knudsen cells, yielded information on the partial pressures of monomer and dimer. Based on the partial pressures for NaCN(g) and (NaCN)₂(g) reported at temperatures, 903-1049°K., the vapor pressures of (NaCN)₂(g) over NaCN(l), 1078.2-1266.2°K., were calculated from the total vapor pressure measurements reported by C. K. Ingold, J. Chem. Soc. **123**, 885 (1923). By the second and third law methods, the values of ΔH°_f 298.15 (1 → dimer) were evaluated to be 38.89 and 38.21 kcal. mole⁻¹, respectively. Using the third law value, the heat of formation for (NaCN)₂(g) was evaluated.

Heat Capacity and Entropy.

The molecular structure, bond distances and C-Na-C bond angle were estimated by R. F. Porter, loc. cit. The vibrational frequencies were estimated by comparison with those for NaCl(g). The last six frequencies were the bending and asymmetric stretching frequencies for NaCN(g). The three principal moments of inertia are: I_A = 1.3570 X 10⁻³⁸, I_B = 5.1030 X 10⁻³⁸ and I_C = 6.4860 X 10⁻³⁸ g. cm.²

Point Group [D_{2h}]
S°_{298.15} = [82.93] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 1
ΔH°_f 0 = [-2.0 ± 3] kcal. mole⁻¹
ΔH°_f 298.15 = [-2.1 ± 3] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies			
ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
[295](1)	[290](1)	[2176](1)	[2176](1)
[175](1)	[290](1)	[2176](1)	[2176](1)
[250](1)	[239](1)	[2176](1)	[2176](1)
[170](1)	[239](1)	[2176](1)	[2176](1)

Bond Distances: N-C = [1.116] Å C-Na = [2.19] Å
Bond Angle: C-Na-C = [105]° N-C-Na = [75]° N-C-Na = [142.5]°
Product of the Moments of Inertia: I_AI_BI_C = [4.48269 X 10⁻¹¹³] g.³ cm.⁶
σ = [4]

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔHf° kcal/mol	ΔGf°	Log Kp
0	∞.000	INFINITE	- 2.503	67.538	67.538	INFINITE
100	7.456	46.046	- 1.799	67.868	65.375	- 142.877
200	9.209	51.783	- 0.961	68.200	62.755	- 68.575
298	10.292	55.677	∞.000	68.500	60.016	- 43.993
300	10.309	55.741	.019	68.505	59.963	- 43.683
400	11.024	58.819	56.092	68.720	57.079	- 31.187
500	11.722	61.364	68.869	68.867	54.150	- 23.669
600	12.243	63.549	74.829	68.933	51.198	- 18.649
700	12.620	65.270	79.731	68.976	48.287	- 12.372
800	13.056	67.189	83.676	68.911	45.428	- 8.250
900	13.377	68.745	86.657	68.852	42.535	- 10.280
1000	13.657	70.170	88.640	68.779	39.593	- 8.609
1100	13.903	71.483	89.975	68.691	36.657	- 7.243
1200	14.121	72.693	90.582	68.592	33.715	- 6.107
1300	14.315	73.800	91.460	68.487	30.770	- 5.157
1400	14.488	74.808	92.606	68.378	27.824	- 4.325
1500	14.641	75.693	93.939	68.262	24.880	- 3.614
1600	14.776	76.462	95.466	68.140	21.907	- 2.992
1700	14.896	77.120	97.188	68.013	18.963	- 2.459
1800	15.001	77.666	99.000	67.881	16.044	- 1.959
1900	15.093	79.429	100.912	67.745	13.143	- 1.486
2000	15.172	80.206	102.926	67.606	10.263	- 1.035
2100	15.241	80.948	104.941	67.462	7.428	- .783
2200	15.300	81.656	107.058	67.313	4.644	- .565
2300	15.350	82.339	109.278	67.159	1.864	- .374
2400	15.392	82.993	111.602	67.000	- 0.924	- .217
2500	15.428	83.623	114.037	66.836	- 3.887	- .094
2600	15.457	84.228	116.584	66.668	- 6.725	.565
2700	15.479	84.806	119.244	66.496	- 9.504	.774
2800	15.495	85.356	121.918	66.320	- 12.225	.946
2900	15.513	85.919	124.606	66.140	- 14.886	1.083
3000	15.524	86.446	127.307	65.956	- 17.488	1.187
3100	15.531	86.955	130.021	65.768	- 20.032	1.264
3200	15.534	87.436	132.749	65.575	- 22.518	1.314
3300	15.538	87.892	135.492	65.378	- 24.945	1.347
3400	15.538	88.330	138.250	65.176	- 27.316	1.364
3500	15.536	88.740	141.023	64.969	- 29.632	1.368
3600	15.533	89.128	143.811	64.756	- 31.894	1.361
3700	15.529	89.497	146.614	64.538	- 34.102	1.344
3800	15.523	89.847	149.432	64.315	- 36.256	1.318
3900	15.516	90.181	152.266	64.087	- 38.362	1.283
4000	15.509	90.513	155.117	63.854	- 40.418	1.239
4100	15.501	91.296	157.984	63.616	- 42.424	1.187
4200	15.493	92.010	160.866	63.372	- 44.380	1.127
4300	15.483	92.656	163.764	63.122	- 46.286	1.061
4400	15.474	93.230	166.688	62.866	- 48.142	0.980
4500	15.465	93.738	169.638	62.605	- 49.948	0.885
4600	15.455	94.177	172.614	62.339	- 51.704	0.778
4700	15.445	94.549	175.616	62.068	- 53.410	0.657
4800	15.434	94.856	178.644	61.792	- 55.066	0.524
4900	15.426	95.100	181.698	61.511	- 56.672	0.380
5000	15.416	95.364	184.778	61.225	- 58.228	0.228
5100	15.406	95.670	187.884	60.934	- 59.734	0.069
5200	15.397	95.920	191.016	60.638	- 61.190	- 0.106
5300	15.387	96.120	194.174	60.336	- 62.606	- 0.286
5400	15.377	96.269	197.358	60.029	- 63.972	- 0.476
5500	15.368	96.461	200.568	59.716	- 65.288	- 0.674
5600	15.358	96.618	203.804	59.398	- 66.554	- 0.878
5700	15.348	96.730	207.066	59.074	- 67.772	- 1.086
5800	15.338	96.800	210.354	58.745	- 68.944	- 1.296
5900	15.331	96.906	213.668	58.410	- 70.066	- 1.506
6000	15.323	97.017	217.008	58.069	- 71.138	- 1.716

June 30, 1968; Sept. 30, 1968

CCO RADICAL (C₂O)

(IDEAL GAS)

GFW = 40.0217

Point Group C_{∞v}

ΔHf° = 67.5 ± 15 kcal/mol

ΔHf°_{298.15} = 68.5 ± 15 kcal/mol

Electronic Levels and Quantum Weights

ε, e ⁻¹ cm ⁻¹	g _i
0	3
[4050]	[2]
[6450]	[1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
1074 (1)
381 (2)
1978 (1)

Bond Distance: C-C = [1.160] Å

Bond Angle: C-C-O = [180]°

Rotational Constant: B₀ = [0.408475] cm⁻¹

σ = 1

Heat of Formation

The adopted heat of formation, ΔHf°_{298.15} (C₂O, g) = 68.5 kcal/mol, was calculated from the heat of reaction ΔHf°₂₉₈ = 65.5 kcal/mol for C₂O₂(g) = C₂O(g) + CO(g) using all JANAF functions (dated Sept. 30, 1965). The value of ΔHf° was obtained from the third law calculation of the equilibrium constant (Kp = 3.3 x 10⁻⁶ atm at 1060°K) which was determined in the studies of decomposition rate of C₂O₂(g) by H. B. Palmer and W. D. Cross, Carbon 3, 475 (1956).

M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, J. Chem. Phys. 43, 3745 (1965), have observed the photo-dissociation of C₂O near 5000 Å, which corresponds to a minimum of 57 kcal/mol for C₂O(g) → C(g) + CO(g). This yields ΔHf°₂₉₈(C₂O, g) ≤ 87 kcal/mol, which was not adopted because the irradiation was not monochromatic and thus possibly contained all wavelengths below 5000 Å.

Heat Capacity and Entropy

Jacox et al., loc. cit., have observed three vibrational fundamentals in the infrared spectrum by matrix isolation, and suggested a linear structure with 3 Σ_g ground state for the CCO radical (g). They also estimated the bond distances C-C = 1.160 Å and C-O = 1.279 Å based on the structural analogy between the carbon suboxide and the CCO radical. The principal moment of inertia is 8.825 x 10⁻³³ g cm². K. D. Bayes, J. Am. Chem. Soc. 85, 1730 (1963), has predicted that the 1Δ and 1Σ states lie respectively 0.5 and 0.8 eV above the ground state. These two electronic states have been included in the tabulation.

T, °K	Cp°	S°	gibbs/mol -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	-0.00	INFINITE	-	2.482	185.431	INFINITE	
100	7.972	46.238	65.872	1.922	181.767	-109.832	
200	9.953	52.409	57.519	-1.022	137.086	-149.800	
298	10.901	56.553	56.553	-0.000	137.000	-96.971	
300	10.917	56.620	56.553	.020	132.199	-96.307	
400	11.651	59.869	56.551	1.115	127.113	-93.462	
500	12.259	62.539	57.881	2.349	122.264	-93.462	
600	12.729	64.817	58.819	3.599	117.291	-92.723	
700	13.105	66.909	59.821	4.892	112.334	-92.073	
800	13.403	68.579	60.807	6.218	107.408	-91.408	
900	13.651	70.171	61.761	7.569	102.504	-90.729	
1000	13.851	71.619	62.635	8.944	97.626	-90.037	
1100	13.984	72.945	63.549	10.335	92.779	-89.333	
1200	14.109	74.167	64.384	11.740	87.960	-88.620	
1300	14.212	75.301	65.161	13.156	83.184	-87.981	
1400	14.298	76.357	65.882	14.582	78.401	-87.329	
1500	14.372	77.336	66.559	16.015	73.600	-86.666	
1600	14.438	78.276	67.186	17.456	68.940	-86.000	
1700	14.498	79.153	68.034	18.903	64.334	-85.334	
1800	14.557	79.993	68.675	20.356	59.783	-84.666	
1900	14.616	80.772	69.291	21.814	55.287	-84.000	
2000	14.677	81.523	69.894	23.279	50.748	-83.334	
2100	14.743	82.241	70.455	24.750	46.162	-82.666	
2200	14.815	82.928	71.007	26.228	41.533	-82.000	
2300	14.893	83.589	71.540	27.713	36.866	-81.334	
2400	14.980	84.224	72.055	29.204	32.166	-80.666	
2500	15.074	84.838	72.559	30.709	27.431	-80.000	
2600	15.178	85.431	73.038	32.222	22.661	-79.334	
2700	15.289	86.006	73.508	33.745	17.866	-78.666	
2800	15.409	86.564	73.964	35.280	13.044	-78.000	
2900	15.535	87.107	74.408	36.827	8.196	-77.334	
3000	15.669	87.638	74.840	38.387	3.227	-76.666	
3100	15.808	88.152	75.261	39.961	-1.728	-76.000	
3200	15.951	88.656	75.672	41.549	-6.666	-75.334	
3300	16.098	89.149	76.073	43.151	-11.582	-74.666	
3400	16.247	89.632	76.465	44.766	-16.444	-74.000	
3500	16.398	90.105	76.848	46.391	-21.266	-73.334	
3600	16.548	90.569	77.222	48.048	-26.044	-72.666	
3700	16.698	91.024	77.589	49.710	-30.786	-72.000	
3800	16.848	91.472	77.949	51.387	-35.494	-71.334	
3900	16.999	91.911	78.301	53.079	-40.166	-70.666	
4000	17.149	92.343	78.647	54.785	-44.800	-70.000	
4100	17.294	92.768	78.986	56.505	-49.400	-69.334	
4200	17.433	93.185	79.319	58.238	-53.966	-68.666	
4300	17.516	93.596	79.646	59.983	-58.494	-68.000	
4400	17.633	94.000	79.968	61.741	-62.986	-67.334	
4500	17.742	94.398	80.284	63.509	-67.444	-66.666	
4600	17.843	94.789	80.595	65.289	-71.866	-66.000	
4700	17.936	95.173	80.901	67.074	-76.250	-65.334	
4800	18.022	95.552	81.203	68.876	-80.600	-64.666	
4900	18.099	95.924	81.499	70.682	-84.914	-64.000	
5000	18.168	96.291	81.792	72.495	-89.186	-63.334	
5100	18.230	96.651	82.079	74.315	-93.420	-62.666	
5200	18.283	97.006	82.363	76.141	-97.614	-62.000	
5300	18.339	97.354	82.643	77.972	-101.766	-61.334	
5400	18.397	97.697	82.918	79.807	-105.886	-60.666	
5500	18.456	98.035	83.190	81.645	-109.966	-60.000	
5600	18.423	98.366	83.458	83.484	-113.994	-59.334	
5700	18.440	98.693	83.722	85.329	-117.974	-58.666	
5800	18.452	98.913	83.983	87.174	-121.906	-58.000	
5900	18.458	99.139	84.241	89.019	-125.786	-57.334	
6000	18.458	99.639	84.495	90.865	-129.614	-56.666	

Mar. 31, 1967

Point Group C_{2v}
S°_{298.15} = 56.55 gibbs/mol
ΔH°₀ = 145.6 ± 7 kcal/mol
ΔH°_{298.15} = 147 ± 7 kcal/mol

Electronic Levels and Quantum Weights

ε _i , cm ⁻¹	g _i
0	1
(13000)	(6)
20085	2

Vibrational Frequencies and Degeneracies

ω _i , cm ⁻¹	g _i
853 (1)	1
300 (2)	2
1742 (1)	1

Bond Distances: C-C = [1.28] Å
Bond Angle: C-C-Si = 180°
C-Si = [1.75] Å

Rotational Constant: B₀ = [0.2012] cm⁻¹
σ = 1

Heat of Formation.

The selected value is an average based on the equilibrium data summarized below. Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor equilibria over the systems SiC-graphite¹, SiC-silicon² and boron-carbon-silicon³. Third law analysis of the partial pressures of C₂Si and Si lead to the concordant values 146.7, 149.0 and 146.0 kcal/mol. Although the drifts all suggest that the entropy of C₂Si may be about 3.5 eu less than tabulated, this is of doubtful significance because the uncertainty bands are so large. The low condensation coefficient suggested by Drowart⁴ may also be involved. Rates of free evaporation reported by Voronin⁴ lead to apparent pressures which are smaller by a factor of 1/30, thus confirming the existence of a low evaporation coefficient. The adopted value of ΔH°₂₉₈ = 147 ± 7 kcal/mol includes allowance for the unlikely possibility that the entropy may be in error by up to 3.5 eu.

Source	Method	Reaction	Range, T°K	No. of Points	ΔH° ₂₉₈ (kcal/mol)	Drift (eu)
Drowart (1958)	"	A	2149-2316	7	31±9	36.98
Drowart (1960)	"	B	1935-2160	4	189±10	194.8
Verhaegen (1964)	"	A	2166-2344	5	30±16	36.31
		B	2310(α) = Si(1) + C ₂ Si(g)			
						3.5±4.1
						3.3±4.9
						3.9±7.2
						146.7
						149.0
						146.0

Heat Capacity and Entropy.

The known molecular constants are from the assignments of Walther and McLeod⁵. These authors observed the infrared spectrum, emission spectrum and visible absorption spectrum of C₂Si in matrix isolation. The matrix data allowed more certain assignment of the A-X band system of the gas as observed by Klean⁶ and McKellar⁷. Walther concluded that this system probably involves transitions between a 1Σ⁺ ground state and a 1Π excited state. The two stretching frequencies were observed in the matrix infrared spectrum, whereas the bending mode, 300 cm⁻¹, was derived solely from the analysis of the A-X band system. The analysis presumed a linear unsymmetrical structure for the molecule.

A 3Π excited state is assumed to lie 7000 cm⁻¹ below the 1Π state, which presumably arises from the same molecular orbital configuration. The effect of the estimated level is to increase the entropy by about 0.2 and 1.8 eu at 3000 and 6000°K. Bond distances are estimated by comparison with those in Si₂, C₂ and C₃. The moment of inertia is 13.91 x 10⁻³⁹ g cm².

References.

1. J. Drowart, G. DeWaele and M. G. Inghram, J. Chem. Phys. **29**, 1015 (1958).
2. J. Drowart and O. DeWaele, pp. 16-25 in Silicon Carbide, Edited by J. R. O'Connor and J. Smilens, Pergamon Press, New York, 1960.
3. G. Verhaegen, F. E. Stafford and J. Drowart, J. Chem. Phys. **40**, 1622 (1964).
4. N. I. Voronin, N. L. Makarov and B. P. Yudin, Izvest. v Obl. Khim. Silykatov 1 Okladov, Akad. Nauk SSSR, Sb. Statei 1955-1956.
5. F. Walther, Jr., and D. McLeod, Jr., J. Chem. Phys. **41**, 235 (1964).
6. B. Klean, Astrophys. J. **123**, 62 (1956).
7. A. McKellar, J. Roy. Astron. Soc. Canada **41**, 147 (1947).

Point Group D_{∞h}D_{∞h}S_{298.15} = 56.7 ± 3 gibbs/molΔH_f⁰ = 194 ± 4 kcal/molC₃ΔH_f⁰ = 196 ± 4 kcal/mol

Ground State Quantum Weight = [1]

Carbon, Triatomic (C₃)

(Ideal Gas) GFW = 36.03345

T, °K	Cp ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log Kp
0	∞	∞	INFINITE	-	193.945	193.945	INFINITE
100	10.148	46.107	65.054	-1.895	190.272	-415.816	-
200	9.527	52.484	57.515	-1.906	185.516	-402.605	-
298	9.020	56.677	53.677	-1.906	180.317	-387.176	-
300	9.015	56.733	53.677	-1.912	180.220	-131.290	-
400	8.462	59.318	57.029	-1.912	174.928	-95.576	-
500	8.173	61.338	57.694	-1.818	166.111	-69.622	-
600	8.049	63.029	58.485	-1.750	155.909	-59.861	-
700	8.029	65.518	59.208	-1.716	145.103	-49.674	-
800	10.153	65.852	59.597	-1.716	135.915	-42.048	-
900	10.448	67.065	60.680	-1.716	126.774	-36.127	-
1000	10.711	68.179	61.679	-1.716	117.685	-31.402	-
1100	10.943	69.241	62.641	-1.716	108.642	-27.546	-
1200	11.149	70.273	63.573	-1.716	99.642	-24.381	-
1300	11.332	71.272	64.479	-1.716	90.682	-21.635	-
1400	11.495	72.241	65.358	-1.716	81.762	-19.324	-
1500	11.642	73.181	66.216	-1.716	72.882	-17.325	-
1600	11.775	74.091	67.054	-1.716	64.042	-15.581	-
1700	11.896	74.979	67.873	-1.716	55.242	-14.066	-
1800	12.006	75.843	68.679	-1.716	46.482	-12.666	-
1900	12.104	76.685	69.464	-1.716	37.762	-11.473	-
2000	12.202	77.505	70.236	-1.716	29.082	-10.384	-
2100	12.290	78.301	71.000	-1.716	20.442	-9.305	-
2200	12.371	79.071	71.749	-1.716	11.842	-8.245	-
2300	12.448	79.816	72.484	-1.716	3.282	-7.201	-
2400	12.520	80.536	73.204	-1.716	-5.318	-6.166	-
2500	12.588	81.231	73.909	-1.716	-11.858	-5.142	-
2600	12.652	81.901	74.599	-1.716	-18.482	-4.128	-
2700	12.712	82.546	75.274	-1.716	-25.192	-3.124	-
2800	12.769	83.166	75.934	-1.716	-31.882	-2.130	-
2900	12.823	83.761	76.579	-1.716	-38.552	-1.146	-
3000	12.877	84.331	77.209	-1.716	-45.202	-0.172	-
3100	12.927	84.876	77.824	-1.716	-51.832	0.802	-
3200	12.974	85.396	78.424	-1.716	-58.442	1.726	-
3300	13.020	85.891	79.009	-1.716	-65.032	2.600	-
3400	13.064	86.361	79.579	-1.716	-71.602	3.424	-
3500	13.106	86.806	80.134	-1.716	-78.152	4.200	-
3600	13.146	87.226	80.674	-1.716	-84.682	4.926	-
3700	13.184	87.621	81.199	-1.716	-91.192	5.602	-
3800	13.222	88.001	81.709	-1.716	-97.682	6.226	-
3900	13.258	88.356	82.204	-1.716	-104.152	6.800	-
4000	13.293	88.686	82.684	-1.716	-110.602	7.324	-
4100	13.326	89.001	83.149	-1.716	-117.032	7.800	-
4200	13.358	89.291	83.599	-1.716	-123.442	8.226	-
4300	13.389	89.556	84.034	-1.716	-129.832	8.600	-
4400	13.419	89.796	84.454	-1.716	-136.202	8.926	-
4500	13.450	90.011	84.859	-1.716	-142.552	9.200	-
4600	13.478	90.201	85.249	-1.716	-148.882	9.426	-
4700	13.505	90.366	85.624	-1.716	-155.192	9.600	-
4800	13.532	90.506	85.984	-1.716	-161.482	9.726	-
4900	13.558	90.621	86.329	-1.716	-167.752	9.800	-
5000	13.583	90.711	86.659	-1.716	-174.002	9.826	-
5100	13.608	90.776	86.974	-1.716	-180.232	9.800	-
5200	13.632	90.816	87.274	-1.716	-186.442	9.726	-
5300	13.654	90.841	87.559	-1.716	-192.632	9.600	-
5400	13.677	90.851	87.829	-1.716	-198.802	9.426	-
5500	13.698	90.846	88.084	-1.716	-204.942	9.200	-
5600	13.719	90.816	88.324	-1.716	-211.052	8.926	-
5700	13.739	90.761	88.549	-1.716	-217.132	8.600	-
5800	13.760	90.681	88.759	-1.716	-223.182	8.226	-
5900	13.780	90.576	88.954	-1.716	-229.202	7.800	-
6000	13.799	90.446	89.134	-1.716	-235.192	7.324	-

Dec. 31, 1960, Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	
1225 (1)	
615 (2)	
2040 (1)	

The contribution of the doubly degenerate bending frequency was approximated by direct summation of the following levels (cm⁻¹): 0, 63.5, 132.7, 207.4, 286.5, 370.5, 459.2, and 650 x n where n = 1 to 76. The contribution to each function due to these levels was doubled to account for the degeneracy.

Bond Distance: C-C = 1.277 Å

Bond Angle: C-C-C = 180°

Rotational Constant: B₀ = 0.4305 cm⁻¹

σ = 2

Heat of Formation

Drowart et al. (1) have measured mass spectrometrically the ion intensity ratio C₃⁺/C⁺ as a function of temperature from 1800 to 2700°K. We derive from a 2nd law analysis of their data ΔH_{f,2000} = 185.2 ± 3.3 kcal, and S₂₀₀₀ = 74.9 ± 2.8 eu by calculation of the absolute pressure from the vapor pressure of monatomic carbon and a relative ionization cross-section ratio of 2.3. The entropy uncertainty includes 1.3 eu for uncertainty in the absolute pressure. Several earlier mass-spectrometric determinations (2, 3, 4) are in reasonable agreement. The absolute magnitude of the pressure is also confirmed by the work of Thorn and Winslow (5) who measured the total pressure of all species over graphite as 1.2 to 4.8 x 10⁻⁷ atm. at 2400°K.

Subtracting the JANAF values for C and C₂ we obtain C₃ = 5.4 x 10⁻⁸ to 2.2 x 10⁻⁷ atm., which compares with Drowart's value of 3.3 x 10⁻⁸ to 1.3 x 10⁻⁷ atm. The 2nd law heat of formation is reported (3) to be ΔH₂₄₀₀ = 184.4 but the range is only 80°K. It does, however, confirm the magnitude of the mass-spectrometric values for both heat and entropy. We have adopted a heat of formation within the uncertainty limits of Drowart's measurements which with the adopted functions yields pressures in the 2000-3000°K range consistent with the measurements. We were not able to generate functions which agree exactly with the 2nd law entropies, since even direct summation over only the observed levels of the bending frequency gives an entropy which is already too large.

Heat Capacity and Entropy

The stretching frequencies are from Merer (6), Weltner et al. (7) and Weltner and McLeod (8). The bending frequency and its harmonics are from Gausset et al. (9) and Merer (6). The rotational constant and bond distance are from Gausset et al. (9).

As indicated briefly above, the calculated entropy of C₃ gas is higher than the experimental value even when a summation is performed only over the observed first six levels of the bending frequency. Treatment of the vibration as a harmonic oscillator or as an anharmonic oscillator gives values considerably higher. Straus and Thiele (10) have also calculated functions based on a quartic potential function which still yields values several units higher than the experiments. In order to reduce the entropy to the approximate range of the measurements we have made the assumption that the potential function is of an unusual form above the sixth vibrational level. We assume that the large amplitude of the bending vibration causes a drastic change in the function, possibly due to the increasing repulsion between carbon atoms, as the amplitude increases. Thus, we assume a very steeply rising potential above the sixth vibrational level. We have chosen to represent this part of the potential by a harmonic oscillator of 650 cm⁻¹. The choice of 650 cm⁻¹ is arbitrary, but is not unreasonable for a bending vibration, and yields functions which approximate the experimental data.

In order to explain the observed spectrum of C₃O, a molecule with a bending frequency of 63 cm⁻¹, Smith and Barrett (11) have proposed that potential maxima occur in the bending potential away from linearity. Thus, the adoption of an unusual potential function for C₃ bending may be justifiable. We do not claim that our functions are necessarily correct but only that they include all known facts and satisfy the experimental equilibrium observations. Further investigation of the carbon vapor pressure and of the higher vibrational levels of C₃ is desirable.

References

1. J. Drowart, R. P. Burns, G. Delahria, and M. G. Inghram, *J. Chem. Phys.* **31**, 1131 (1959).
2. W. A. Chupka and M. G. Inghram, *J. Phys. Chem.* **59**, 100 (1955).
3. W. A. Chupka and M. G. Inghram, *J. Chem. Phys.* **21**, 371 and 1313, (1953).
4. R. E. Honig, *J. Chem. Phys.* **22**, 126 (1954).
5. R. J. Thorn and G. H. Winslow, *J. Chem. Phys.* **26**, 186 (1957).
6. A. J. Merer, *Can. J. Phys.* **45**, 4103 (1967).
7. W. Weltner, P. N. Walsh and C. L. Angel, *J. Chem. Phys.* **40**, 1299 (1964).
8. W. Weltner and D. McLeod, *J. Chem. Phys.* **40**, 1305 (1964).
9. L. Gausset, G. Herzberg, A. Lagerqvist, and B. Rosen, *Astrophys. J.* **142**, 45 (1965).
10. H. L. Straus and E. Thiele, *J. Chem. Phys.* **46**, 2473 (1967).
11. W. H. Smith and J. J. Barrett, *J. Chem. Phys.* **51**, 1475 (1969).

(Crystal) Mol. Wt. = 143.95945

TETRALUMINUM TRICARBIDE (Al₄C₃) (CRYSTAL)

MOL. WT. = 143.95945

Dec. 31, 1960; June 30, 1963; Sept. 30, 1965

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	+0.00	INFINITE	3.936	-50.354	-50.354	INFINITE
100	7.099	24.808	3.728	-50.612	-50.170	109.641
200	19.622	11.759	23.579	-51.250	-49.512	54.102
298	27.912	21.264	21.264	-51.550	-48.602	35.624
300	28.035	21.437	21.265	-51.554	-48.585	35.302
400	33.104	30.269	22.434	-51.598	-47.581	25.696
500	36.064	37.997	24.792	-51.594	-46.579	20.359
600	38.050	44.787	27.568	-51.642	-45.575	16.600
700	39.479	50.734	30.459	-51.786	-44.553	13.909
800	40.518	56.000	33.413	-52.000	-43.512	11.800
900	41.411	60.907	36.433	-52.272	-42.419	10.300
1000	42.099	65.307	38.834	-52.801	-40.552	8.682
1100	42.669	69.346	41.426	-52.931	-38.322	7.613
1200	43.150	73.080	43.911	-53.004	-36.077	6.570
1300	43.563	76.541	46.288	-53.114	-33.864	5.557
1400	43.922	79.773	48.568	-53.252	-31.664	4.597
1500	44.239	82.834	50.752	-53.335	-29.497	4.268
1600	44.521	85.698	52.848	-53.407	-27.028	3.692
1700	44.774	88.405	54.860	-53.464	-24.755	3.182
1800	44.999	90.957	56.799	-53.509	-22.732	2.732
1900	45.204	93.410	58.659	-53.547	-20.191	2.332
2000	45.406	95.734	60.455	-53.571	-17.909	1.957
2100	45.562	97.953	62.188	-53.584	-15.626	1.626
2200	45.710	100.076	63.863	-53.593	-13.345	1.326
2300	45.848	102.109	65.493	-53.598	-11.073	1.057
2400	45.982	104.065	67.099	-53.598	-8.773	0.813
2500	46.106	105.955	68.557	-53.598	-6.450	0.587
2600	46.222	107.755	70.000	-53.548	-4.211	0.354
2700	46.330	109.502	71.469	-53.521	-1.896	0.157
2800	46.430	111.210	72.968	-53.481	0.481	0.000
2900	46.522	112.819	74.298	-53.452	2.852	1.272
3000	46.606	114.398	75.522	-53.400	5.205	2.338

$$\Delta H_f^0 = -50.35 \pm 1.6 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 298.15 = -51.55 \pm 1.6 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = \text{Unknown}$$

$$S_{298.15} = 21.26 \pm 0.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = [2500]^\circ \text{K.}$$

Heat of Formation.

The $\Delta H_f^0 298.15 = -51.55 \pm 1.6 \text{ kcal. mole}^{-1}$ is the average value of $\Delta H_f^0 298.15 = -49.7 \pm 1.2 \text{ kcal. mole}^{-1}$ by R. C. King and G. T. Armstrong, National Bureau of Standards Report No. 8504 (1964) and that of $\Delta H_f^0 298.15 = -53.4 \pm 2.0 \text{ kcal. mole}^{-1}$ by A. D. Mah, United States Bureau of Mines, Report No. 6415 (1964). Both measured the heat of reaction $\text{Al}_4\text{C}_3(\text{c}) + 6\text{O}_2(\text{g}) \rightarrow 2\text{Al}_2\text{O}_3(\text{c}, \infty) + 3\text{CO}_2(\text{g})$ and used their $\Delta H_f^0 298.15$ and the $\Delta H_f^0 298.15$ of $\text{Al}_2\text{O}_3(\text{c})$ and $\text{CO}_2(\text{g})$ to calculate the $\Delta H_f^0 298.15$ of $\text{Al}_4\text{C}_3(\text{c})$. The $\Delta H_f^0 298.15$ measured by King and Armstrong was $-1033.3 \pm 1.1 \text{ kcal. mole}^{-1}$, the $\Delta H_f^0 298.15$ measured by Mah was $-1029.6 \pm 1.9 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The low temperature heat capacities, 18-390°K., were measured by W. G. Saba and G. T. Furukawa, National Bureau of Standards Report 7587, July 1, 1962. The high temperature heat capacities, 275-1173°K., were measured by A. C. Victor, W. R. Thurber, and T. B. Douglas, National Bureau of Standards Report 7437, January 1, 1962. These two sets of heat capacity data were joined smoothly and extrapolated to 2000°K. by W. G. Saba and G. T. Furukawa, loc. cit. The values of C_p above 2000°K. were estimated by extrapolation graphically. $S_{298.15}$ was reported by W. G. Saba and G. T. Furukawa, loc. cit., using $S_{298.15}^0(\text{extrap.}) = 0.013 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Temperature.

T_m was estimated by O. Ruff and E. Jellinek, Z. anorg. u. allgem. Chem. 97, 312 (1916).

Dimagnesium Tricarbide (Mg_2C_3)

(Solid) Mol. Wt. = 84.67

INTERIM TABLE

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0							
100	22.410	24.7000	24.000	.000	19.000	17.729	- 12.995
200	22.500	24.139	24.000	.042	19.008	17.721	- 12.909
300	22.580	31.105	24.929	2.470	19.478	17.223	- 9.410
400	27.280	37.019	28.772	5.124	19.901	18.808	- 7.258
500	28.250	42.084	28.912	7.903	20.224	15.918	- 5.797
600	29.490	50.395	33.288	13.687	20.528	14.425	- 3.931
700	29.940	53.895	35.385	16.659	20.518	13.682	- 3.317
800	30.340	57.071	37.397	19.873	18.171	13.257	- 2.867
900	30.700	59.979	39.320	22.728	18.056	12.972	- 2.577
1000	31.030	62.685	41.005	25.912	15.850	12.649	- 2.093
1100	31.350	65.185	42.580	28.911	15.852	12.642	- 2.092
1200	31.650	67.495	44.580	32.081	15.852	13.134	- 2.050
1300	31.950	69.889	46.182	35.281	44.966	17.304	- 2.521
1400	32.240	71.760	47.718	38.471	44.485	21.436	- 2.928
1500	32.520	73.460	50.404	41.679	43.488	25.543	- 3.294
1600	32.800	75.000	52.980	44.800	42.488	29.649	- 3.654
1700	33.070	77.371	55.986	48.268	42.488	33.860	- 4.016
1800	33.350	79.074	53.279	51.590	42.297	37.870	- 4.116
1900	33.620	80.706	54.587	54.938	41.704	41.856	- 4.335
2000	33.880	82.260	55.952	58.713	41.068	45.811	- 4.531
2100	34.150	83.760	57.280	62.513	40.470	49.511	- 4.731
2200	34.420	85.249	58.108	65.143	39.827	53.439	- 4.868
2300	34.690	86.859	59.220	68.598	39.165	57.314	- 5.010

DIMAGNESIUM TRICARBIDE (Mg_2C_3)

(Solid)

Mol. Wt. = 84.67

$\Delta H^\circ_f 298.15 = 19 \pm 8 \text{ kcal. mole}^{-1}$

$S^\circ_{298.15} = 24 \pm 3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

(Ideal Gas)

GFN = 68.03225

T, °K	Cp°	S° - (C°-H° ₂₉₈)/T	ΔH° kcal/mol	Log Kp
0	10.525	51.586	23.138	19.111
100	13.367	67.345	22.933	52.277
200	16.010	65.959	22.680	27.328
298	16.010	65.959	22.380	19.219
300	16.052	66.058	22.375	19.119
400	16.313	67.102	21.944	17.957
500	16.436	67.806	21.884	17.657
600	16.436	68.148	21.884	17.657
700	16.436	68.148	21.884	17.657
800	16.436	68.148	21.884	17.657
900	16.436	68.148	21.884	17.657
1000	16.436	68.148	21.884	17.657
1100	16.436	68.148	21.884	17.657
1200	16.436	68.148	21.884	17.657
1300	16.436	68.148	21.884	17.657
1400	16.436	68.148	21.884	17.657
1500	16.436	68.148	21.884	17.657
1600	16.436	68.148	21.884	17.657
1700	16.436	68.148	21.884	17.657
1800	16.436	68.148	21.884	17.657
1900	16.436	68.148	21.884	17.657
2000	16.436	68.148	21.884	17.657
2100	16.436	68.148	21.884	17.657
2200	16.436	68.148	21.884	17.657
2300	16.436	68.148	21.884	17.657
2400	16.436	68.148	21.884	17.657
2500	16.436	68.148	21.884	17.657
2600	16.436	68.148	21.884	17.657
2700	16.436	68.148	21.884	17.657
2800	16.436	68.148	21.884	17.657
2900	16.436	68.148	21.884	17.657
3000	16.436	68.148	21.884	17.657
3100	16.436	68.148	21.884	17.657
3200	16.436	68.148	21.884	17.657
3300	16.436	68.148	21.884	17.657
3400	16.436	68.148	21.884	17.657
3500	16.436	68.148	21.884	17.657
3600	16.436	68.148	21.884	17.657
3700	16.436	68.148	21.884	17.657
3800	16.436	68.148	21.884	17.657
3900	16.436	68.148	21.884	17.657
4000	16.436	68.148	21.884	17.657
4100	16.436	68.148	21.884	17.657
4200	16.436	68.148	21.884	17.657
4300	16.436	68.148	21.884	17.657
4400	16.436	68.148	21.884	17.657
4500	16.436	68.148	21.884	17.657
4600	16.436	68.148	21.884	17.657
4700	16.436	68.148	21.884	17.657
4800	16.436	68.148	21.884	17.657
4900	16.436	68.148	21.884	17.657
5000	16.436	68.148	21.884	17.657
5100	16.436	68.148	21.884	17.657
5200	16.436	68.148	21.884	17.657
5300	16.436	68.148	21.884	17.657
5400	16.436	68.148	21.884	17.657
5500	16.436	68.148	21.884	17.657
5600	16.436	68.148	21.884	17.657
5700	16.436	68.148	21.884	17.657
5800	16.436	68.148	21.884	17.657
5900	16.436	68.148	21.884	17.657
6000	16.436	68.148	21.884	17.657

Dec. 31, 1960; Sept. 30, 1965; June 30, 1968

(IDEAL GAS)

CARBON SUBOXIDE (C₃O₂)

GFN = 68.03225

Point Group D_{∞h}

ΔH_f⁰ = -23.14 ± 0.44 kcal/mol

S_{298.15}° = 65.959 ± 0.2 gibbs/mol

ΔH_f⁰ = -22.38 ± 0.44 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω ₁ , cm ⁻¹	ω ₂ , cm ⁻¹	ω ₃ , cm ⁻¹
2200 (1)	2258 (1)	550 (2)
830 (1)	1573 (1)	63 (2)
	577 (2)	

Bond Distances: C-C = 1.28 Å C-O = 1.16 Å

Bond Angles: C-C-C = 180° O-C-C = 180°

Rotational Constant: B₀ = 0.073206 cm⁻¹

σ = 2

Heat of Formation

Kybett et al. (1) have determined the heat of combustion of the liquid form under its own pressure using the sample from the heat capacity determinations (2).

The average of four determinations gave ΔH_f⁰₂₉₈(l) = -28.03 ± 0.24 kcal/mol; the authors report -29.03 due to an arithmetic error. The sample was 99.98 mole percent pure. McDougall et al. (2) measured ΔH_f⁰₃₀ = 6.421 ± 0.012 kcal/mol from which we calculate ΔH_f⁰₂₉₈ = 5.65 ± 0.2 kcal/mol. Thus the heat of formation of the gas is found to be -22.38 ± 0.44 kcal/mol.

Heat Capacity and Entropy

There has been considerable controversy as to the configuration of this molecule and the assignment of its vibrational frequencies. However, the evidence seems fairly conclusive for the linearity of the molecule from the work of Lafferty et al. (3) and Miller et al. (4). The rotational constant adopted here is that found by Lafferty et al. (3) and the vibrational frequencies are those reported by Miller et al. (4), except for ν₇ which is taken from Miller et al. (5) and Borgers (2). The low frequency ν_u mode is confirmed by the work of McDougall et al. (2), who measured the low temperature entropy of C₃O₂(c) and (l) and also the heat of vaporization. From a comparison of the entropy calculated statistically and that measured, they conclude ν₇ = 63.2 cm⁻¹. The values adopted are confirmed by third law analysis of the vapor pressure data of McDougall et al. (5) which indicate a heat of vaporization in fair agreement with their calorimetric value. The drift in the third law analysis indicates that the entropy of the solid is too low or that of the gas is too high by 1 eu. Alternatively as systematic error in the pressure measurements could have caused this deviation.

The bond distances are taken from the electron diffraction experiments of Livingston et al. (6) and are in good accord with the adopted rotational constant.

References

1. B. D. Kybett, G. K. Johnson, C. K. Barker and J. L. Hargrave, J. Phys. Chem. **69**, 3603 (1965).
2. L. A. McDougall and J. E. Kilpatrick, J. Chem. Phys. **42**, 2111 (1965).
3. W. J. Lafferty, A. G. Haki and E. K. Plyler, J. Chem. Phys. **40**, 224 (1964).
4. F. A. Miller and W. G. Fateley, Spectrochim. Acta **20**, 753 (1964).
5. F. A. Miller, D. H. Lemmon and R. E. Witkowski, Spectrochim. Acta **21**, 1709-16 (1965).
6. R. L. Livingston and C. H. Rao, J. Am. Chem. Soc. **81**, 285 (1959).
7. T. R. Borgers, Ph.D. Thesis, University of California, Berkeley, 1961.

Carbon, Tetratomic (C₄)
(Ideal Gas)

GFW = 48.0446

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	Log Kp
0	0.000	0.000	INFINITE	-2.579	230.429	INFINITE
100	7.138	44.875	63.489	-1.861	231.071	228.687
200	9.153	50.553	68.523	-1.400	231.559	229.229
298	11.592	54.544	71.300	-1.000	232.000	229.662
300	12.031	54.618	71.300	-1.022	232.006	229.662
400	13.780	58.333	75.038	-1.318	232.316	229.662
500	15.057	61.552	76.026	-1.763	232.487	229.662
600	16.045	64.368	76.026	-2.320	232.532	229.662
700	16.831	66.923	76.026	-3.005	232.477	229.662
800	17.463	69.213	76.026	-3.781	232.357	229.662
900	17.973	71.300	76.026	-4.600	232.182	229.662
1000	18.367	73.216	76.026	-5.442	231.976	229.662
1100	18.725	74.985	76.026	-6.300	231.741	229.662
1200	19.003	76.627	76.026	-7.163	231.483	229.662
1300	19.234	78.157	76.026	-8.000	231.200	229.662
1400	19.426	79.590	76.026	-8.800	230.900	229.662
1500	19.588	80.938	76.026	-9.561	230.604	229.662
1600	19.724	82.204	76.026	-10.278	230.290	229.662
1700	19.841	83.404	76.026	-10.950	229.972	229.662
1800	19.942	84.541	76.026	-11.580	229.645	229.662
1900	20.028	85.621	76.026	-12.163	229.316	229.662
2000	20.104	86.650	76.026	-12.700	228.983	229.662
2100	20.169	87.633	76.026	-13.190	228.648	229.662
2200	20.227	88.573	76.026	-13.640	228.308	229.662
2300	20.278	89.473	76.026	-14.050	227.962	229.662
2400	20.324	90.337	76.026	-14.420	227.612	229.662
2500	20.364	91.167	76.026	-14.750	227.262	229.662
2600	20.400	91.967	76.026	-15.040	226.904	229.662
2700	20.432	92.737	76.026	-15.290	226.548	229.662
2800	20.461	93.481	76.026	-15.500	226.187	229.662
2900	20.488	94.199	76.026	-15.680	225.821	229.662
3000	20.512	94.894	76.026	-15.830	225.451	229.662
3100	20.533	95.567	76.026	-15.960	225.076	229.662
3200	20.553	96.219	76.026	-16.070	224.699	229.662
3300	20.571	96.852	76.026	-16.160	224.315	229.662
3400	20.588	97.467	76.026	-16.230	223.929	229.662
3500	20.603	98.064	76.026	-16.290	223.537	229.662
3600	20.617	98.644	76.026	-16.340	223.142	229.662
3700	20.630	99.209	76.026	-16.380	222.740	229.662
3800	20.642	99.760	76.026	-16.410	222.335	229.662
3900	20.653	100.296	76.026	-16.440	221.924	229.662
4000	20.663	100.819	76.026	-16.460	221.510	229.662
4100	20.673	101.329	76.026	-16.480	221.099	229.662
4200	20.682	101.828	76.026	-16.490	220.681	229.662
4300	20.690	102.314	76.026	-16.500	220.255	229.662
4400	20.698	102.790	76.026	-16.510	219.827	229.662
4500	20.705	103.255	76.026	-16.520	219.394	229.662
4600	20.712	103.710	76.026	-16.530	218.958	229.662
4700	20.718	104.156	76.026	-16.540	218.519	229.662
4800	20.724	104.592	76.026	-16.550	218.076	229.662
4900	20.730	105.019	76.026	-16.560	217.630	229.662
5000	20.735	105.438	76.026	-16.570	217.183	229.662
5100	20.740	105.849	76.026	-16.580	216.733	229.662
5200	20.745	106.252	76.026	-16.590	216.280	229.662
5300	20.749	106.647	76.026	-16.600	215.824	229.662
5400	20.753	107.035	76.026	-16.610	215.365	229.662
5500	20.757	107.416	76.026	-16.620	214.904	229.662
5600	20.761	107.790	76.026	-16.630	214.440	229.662
5700	20.765	108.157	76.026	-16.640	213.973	229.662
5800	20.768	108.516	76.026	-16.650	213.503	229.662
5900	20.771	108.873	76.026	-16.660	213.030	229.662
6000	20.774	109.223	76.026	-16.670	212.554	229.662

Dec. 31, 1960; Dec. 31, 1969

CARBON, TETRATOMIC (C₄)

(IDEAL GAS)

GFW = 48.0446

Point Group [D_{2h}]

ΔH°_f = 230.4 ± 8 kcal/mol

S°_{298.15} = 54.5 ± 4.0 gibbs/mol

ΔH°_f 298.15 = 232 ± 8 kcal/mol

Ground State Configuration [1Σ]

Vibrational Frequencies and Degeneracies

ω _i , cm ⁻¹	
[2150] (1)	
[950] (1)	
[1700] (1)	
[550] (2)	
[550] (2)	

Bond distance: C-C = [1.28] Å

Bond Angle: C-C-C = [180°]

Rotational Constant: B₀ = [0.17132] cm⁻¹

σ = 2

Heat of Formation

The heat of formation is obtained from the mass-spectrometric results of Drowart et al. (1) who obtained ΔH°_f 2400 = 226 ± 7 kcal/mol. This was obtained from a 2nd law analysis of the ion intensity ratio C₄⁺/C⁺ over a temperature range of 2200-2700°K. The absolute pressure, obtained from a knowledge of the monatomic carbon vapor pressure and an estimated ionization cross-section ratio of 4.96, yields a 2nd law entropy at 2400°K of 90.5 ± 3 eu. The uncertainty in the ionization cross-section ratio is probably no more than a factor of two which gives an overall entropy uncertainty of 4.5 eu. The heats of formation at temperatures other than 2400°K depend on the functions adopted, for a discussion of these see below.

Heat Capacity and Entropy

The molecular properties of C₄ are all estimated. We have chosen a set of functions which is consistent with the mass-spectrometric observations of Drowart et al. (1). The thermodynamic functions of C₄ were first estimated by Pitzer and Clementi (2) but the basis for this estimate has completely changed. Originally they were calculated by analogy with C₃, C₃O₂ and CO₂, but the discovery of very low bending frequencies in C₃ and C₃O₂ complicated the picture by raising the calculated entropies significantly. Sandborn (3) has correlated the bending force constants in several related triatomics and has estimated the vibrational frequencies in C₄ and C₅. These vibrational frequencies yield high entropies outside the limits of the second law determination. Since these frequencies are estimates based on a basically triatomic correlation we have chosen to adopt two bending frequencies of 550 cm⁻¹ rather than the 200 cm⁻¹ and 440 cm⁻¹ estimated by Sandborn. In addition we have assumed that the ground state arising from a π² term is ¹Σ and not ³Σ as assumed by Pitzer and Clementi. The basis for both these changes is to make the functions conform to the only available measured data. Use of the present table will yield values for the vapor pressure of C₄ in excellent agreement with the measurements in the 2000-3000°K range. Outside this range they provide only a general indication of the variation since they may not correspond to the real situation.

The stretching frequencies are from Sandborn (3) and the bond length is estimated from C₃.

References

1. J. Drowart, R. P. Burns, G. DeMaría and M. G. Inghram, J. Chem. Phys. **31**, 1131 (1959).
2. K. S. Pitzer and E. Clementi, J. Am. Chem. Soc. **81**, 4477 (1959).
3. R. H. Sandborn, J. Chem. Phys. **49**, 4219 (1968).



Tetramethylsilane (Si(CH₃)₄)
(Ideal Gas) Mol. Wt. = 88.230

INTERIM TABLE

T, °K.	cal. mole ⁻¹ deg. ⁻¹		kcal. mole ⁻¹		Log K _p
	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o
0					
100					
200					
300	33.240	66.300	66.300	0.000	- 35.456
400	33.240	66.305	66.301	0.061	- 35.232
500	33.240	66.310	66.306	0.122	- 35.008
600	33.240	66.317	66.313	0.184	- 34.784
700	33.240	66.326	66.322	0.246	- 34.560
800	33.240	66.336	66.332	0.308	- 34.336
900	33.240	66.347	66.343	0.370	- 34.112
1000	33.240	66.359	66.355	0.432	- 33.888
1100	33.240	66.372	66.368	0.494	- 33.664
1200	33.240	66.386	66.382	0.556	- 33.440
1300	33.240	66.401	66.397	0.618	- 33.216
1400	33.240	66.416	66.412	0.680	- 32.992
1500	33.240	66.432	66.428	0.742	- 32.768
1600	33.240	66.448	66.444	0.804	- 32.544
1700	33.240	66.464	66.460	0.866	- 32.320
1800	33.240	66.481	66.477	0.928	- 32.096
1900	33.240	66.498	66.494	1.000	- 31.872
2000	33.240	66.516	66.512	1.062	- 31.648
2100	33.240	66.534	66.530	1.124	- 31.424
2200	33.240	66.552	66.548	1.186	- 31.200
2300	33.240	66.570	66.566	1.248	- 30.976
2400	33.240	66.588	66.584	1.310	- 30.752
2500	33.240	66.606	66.602	1.372	- 30.528
2600	33.240	66.624	66.620	1.434	- 30.304
2700	33.240	66.642	66.638	1.496	- 30.080
2800	33.240	66.660	66.656	1.558	- 29.856
2900	33.240	66.678	66.674	1.620	- 29.632
3000	33.240	66.696	66.692	1.682	- 29.408
3100	33.240	66.714	66.710	1.744	- 29.184
3200	33.240	66.732	66.728	1.806	- 28.960
3300	33.240	66.750	66.746	1.868	- 28.736
3400	33.240	66.768	66.764	1.930	- 28.512
3500	33.240	66.786	66.782	1.992	- 28.288
3600	33.240	66.804	66.800	2.054	- 28.064
3700	33.240	66.822	66.818	2.116	- 27.840
3800	33.240	66.840	66.836	2.178	- 27.616
3900	33.240	66.858	66.854	2.240	- 27.392
4000	33.240	66.876	66.872	2.302	- 27.168
4100	33.240	66.894	66.890	2.364	- 26.944
4200	33.240	66.912	66.908	2.426	- 26.720
4300	33.240	66.930	66.926	2.488	- 26.496
4400	33.240	66.948	66.944	2.550	- 26.272
4500	33.240	66.966	66.962	2.612	- 26.048
4600	33.240	66.984	66.980	2.674	- 25.824
4700	33.240	67.002	66.998	2.736	- 25.600
4800	33.240	67.020	67.016	2.798	- 25.376
4900	33.240	67.038	67.034	2.860	- 25.152
5000	33.240	67.056	67.052	2.922	- 24.928
5100	33.240	67.074	67.070	2.984	- 24.704
5200	33.240	67.092	67.088	3.046	- 24.480
5300	33.240	67.110	67.106	3.108	- 24.256
5400	33.240	67.128	67.124	3.170	- 24.032
5500	33.240	67.146	67.142	3.232	- 23.808
5600	33.240	67.164	67.160	3.294	- 23.584
5700	33.240	67.182	67.178	3.356	- 23.360
5800	33.240	67.200	67.196	3.418	- 23.136
5900	33.240	67.218	67.214	3.480	- 22.912
6000	33.240	67.236	67.232	3.542	- 22.688
6100	33.240	67.254	67.250	3.604	- 22.464
6200	33.240	67.272	67.268	3.666	- 22.240
6300	33.240	67.290	67.286	3.728	- 22.016
6400	33.240	67.308	67.304	3.790	- 21.792
6500	33.240	67.326	67.322	3.852	- 21.568
6600	33.240	67.344	67.340	3.914	- 21.344
6700	33.240	67.362	67.358	3.976	- 21.120
6800	33.240	67.380	67.376	4.038	- 20.896
6900	33.240	67.398	67.394	4.100	- 20.672
7000	33.240	67.416	67.412	4.162	- 20.448
7100	33.240	67.434	67.430	4.224	- 20.224
7200	33.240	67.452	67.448	4.286	- 20.000
7300	33.240	67.470	67.466	4.348	- 19.776
7400	33.240	67.488	67.484	4.410	- 19.552
7500	33.240	67.506	67.502	4.472	- 19.328
7600	33.240	67.524	67.520	4.534	- 19.104
7700	33.240	67.542	67.538	4.596	- 18.880
7800	33.240	67.560	67.556	4.658	- 18.656
7900	33.240	67.578	67.574	4.720	- 18.432
8000	33.240	67.596	67.592	4.782	- 18.208
8100	33.240	67.614	67.610	4.844	- 17.984
8200	33.240	67.632	67.628	4.906	- 17.760
8300	33.240	67.650	67.646	4.968	- 17.536
8400	33.240	67.668	67.664	5.030	- 17.312
8500	33.240	67.686	67.682	5.092	- 17.088
8600	33.240	67.704	67.700	5.154	- 16.864
8700	33.240	67.722	67.718	5.216	- 16.640
8800	33.240	67.740	67.736	5.278	- 16.416
8900	33.240	67.758	67.754	5.340	- 16.192
9000	33.240	67.776	67.772	5.402	- 15.968
9100	33.240	67.794	67.790	5.464	- 15.744
9200	33.240	67.812	67.808	5.526	- 15.520
9300	33.240	67.830	67.826	5.588	- 15.296
9400	33.240	67.848	67.844	5.650	- 15.072
9500	33.240	67.866	67.862	5.712	- 14.848
9600	33.240	67.884	67.880	5.774	- 14.624
9700	33.240	67.902	67.898	5.836	- 14.400
9800	33.240	67.920	67.916	5.898	- 14.176
9900	33.240	67.938	67.934	5.960	- 13.952
10000	33.240	67.956	67.952	6.022	- 13.728

December 31, 1960.

Tetramethylsilane (Si(CH₃)₄) (Ideal Gas)

Mol. Wt. = 88.230
ΔH_f^o 298.15 = [-68.5] kcal. mole⁻¹
S_{298.15}^o = 86.300 cal. deg.⁻¹ mole⁻¹
Point Group T_d

Heat of Formation. ΔH_f^o 298.15 was estimated.

Heat Capacity and Entropy. C_p and S_{298.15} were taken from G. Janz, Y. Mikawa, and P. Behnke, private communication, March 16, 1960.

Tetracarbon Dinitride (C₄N₂)

(Ideal Gas) Mol. Wt. = 76.06

C₄N₂

MOL. WT. = 76.06

(IDEAL GAS)

TETRACARBON DINITRIDE (C₄N₂)

T, °K.	C _p	S° - (F°-H ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	1.000	51.900	126.341	126.341	126.341	10.71117
100	17.205	51.766	126.957	126.957	126.957	10.71117
200	20.528	69.314	127.500	127.500	127.500	89.486
300	20.576	69.441	127.509	127.509	127.509	66.919
400	20.576	69.441	127.509	127.509	127.509	66.919
500	22.152	60.692	126.363	126.363	126.363	51.651
600	25.370	65.407	124.616	124.616	124.616	42.290
700	26.391	69.397	124.776	124.776	124.776	35.594
800	27.255	72.503	124.853	124.853	124.853	30.551
900	27.686	75.492	124.940	124.940	124.940	26.551
1000	28.617	79.216	125.072	125.072	125.072	23.532
1100	29.141	101.969	125.072	125.072	125.072	20.959
1200	29.562	104.524	125.072	125.072	125.072	16.624
1300	29.975	106.907	125.072	125.072	125.072	17.017
1400	30.378	109.133	125.072	125.072	125.072	15.116
1500	30.752	111.237	125.072	125.072	125.072	13.412
1600	30.773	113.215	125.072	125.072	125.072	12.935
1700	30.972	115.067	125.072	125.072	125.072	11.920
1800	31.145	116.863	125.072	125.072	125.072	11.000
1900	31.285	118.593	125.072	125.072	125.072	10.116
2000	31.406	120.159	125.072	125.072	125.072	9.439
2100	31.541	121.695	125.072	125.072	125.072	8.770
2200	31.642	123.165	125.072	125.072	125.072	8.162
2300	31.732	124.574	125.072	125.072	125.072	7.606
2400	31.814	125.926	125.072	125.072	125.072	7.100
2500	31.884	127.228	125.072	125.072	125.072	6.632
2600	31.946	128.478	125.072	125.072	125.072	6.201
2700	32.006	129.685	125.072	125.072	125.072	5.802
2800	32.056	130.849	125.072	125.072	125.072	5.432
2900	32.106	131.972	125.072	125.072	125.072	5.066
3000	32.156	133.064	125.072	125.072	125.072	4.706
3100	32.197	134.119	125.072	125.072	125.072	4.466
3200	32.222	135.142	125.072	125.072	125.072	4.165
3300	32.255	136.134	125.072	125.072	125.072	3.920
3400	32.285	137.093	125.072	125.072	125.072	3.673
3500	32.312	138.033	125.072	125.072	125.072	3.436
3600	32.337	138.944	125.072	125.072	125.072	3.216
3700	32.361	139.830	125.072	125.072	125.072	3.009
3800	32.382	140.693	125.072	125.072	125.072	2.812
3900	32.403	141.535	125.072	125.072	125.072	2.612
4000	32.421	142.356	125.072	125.072	125.072	2.446
4100	32.436	143.158	125.072	125.072	125.072	2.278
4200	32.453	143.936	125.072	125.072	125.072	2.119
4300	32.470	144.702	125.072	125.072	125.072	1.965
4400	32.486	145.448	125.072	125.072	125.072	1.820
4500	32.497	146.179	125.072	125.072	125.072	1.680
4600	32.509	146.893	125.072	125.072	125.072	1.546
4700	32.521	147.592	125.072	125.072	125.072	1.421
4800	32.532	148.277	125.072	125.072	125.072	1.300
4900	32.542	148.948	125.072	125.072	125.072	1.183
5000	32.552	149.608	125.072	125.072	125.072	1.071
5100	32.561	150.250	125.072	125.072	125.072	0.964
5200	32.569	150.883	125.072	125.072	125.072	0.861
5300	32.577	151.503	125.072	125.072	125.072	0.763
5400	32.585	152.112	125.072	125.072	125.072	0.666
5500	32.592	152.710	125.072	125.072	125.072	0.577
5600	32.599	153.297	125.072	125.072	125.072	0.489
5700	32.606	153.875	125.072	125.072	125.072	0.404
5800	32.612	154.442	125.072	125.072	125.072	0.323
5900	32.616	154.996	125.072	125.072	125.072	0.249
6000	32.624	155.538	125.072	125.072	125.072	0.186

March 31, 1961

ΔH_f⁰ = 126.3 ± 0.2 kcal. mole⁻¹
 ΔF_f⁰ 298.15 = 127.5 ± 0.2 kcal. mole⁻¹
 S_{298.15} = 69.31 ± 0.02 cal. deg.⁻¹ mole⁻¹

Point Group D_{∞h}

Vibrational Levels and Multiplicities

ω cm. ⁻¹	ω cm. ⁻¹	ω cm. ⁻¹
2290 (1)	2241 (1)	283 (2)
2119 (1)	1154 (1)	472 (2)
692 (1)	504 (2)	107 (2)

Bond Distances C≡N 1.14 Å C-C 1.37 Å C≡C 1.19 Å

Moment of Inertia I = 61.85 × 10⁻³⁹ g. cm.² σ = 2

Heat of Formation

O. T. Armstrong and S. Marantz, J. Phys. Chem. **64**, 1776 (1960), measured the heat of combustion of the liquid for which they obtain a ΔH_f⁰ 298.15 of 120.6 kcal. mole⁻¹ using 94.05 kcal. mole⁻¹ for ΔH_f⁰ 298.15 of CO₂(g). They calculate the ΔH_f⁰ 298.15 of C₄N₂(g) with a ΔH_{vap} taken from A. J. Saggione, J. Org. Chem. **22**, 1171 (1957).

Heat Capacities and Entropies

Bond lengths determined by P. A. Miller and R. B. Hannan Jr., J. Chem. Phys. **21**, 110 (1953) from X-ray diffraction measurements on the solid. The vibrational frequencies were observed in the infra red and Raman by F. A. Miller, R. B. Hannan Jr., and L. R. Cousins, J. Chem. Phys. **23**, 2127 (1955).

C₄N₂

Carbon, Pentatomic (C₅)

GFW = 60.05575

Point Group [D_{3h}]Point Group [D_{3h}] $\Delta H_f^\circ = 232.4 \pm 6 \text{ kcal/mol}$ $\Delta H_f^\circ = 232.4 \pm 6 \text{ kcal/mol}$ $S_{298.15}^\circ = 57.6 \pm 4 \text{ gibbs/mol}$ $\Delta H_f^\circ = 234 \pm 6 \text{ kcal/mol}$ Ground State Configuration [1²]

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	ω_i , cm ⁻¹
[1320] (1)	[550] (2)
[770] (1)	[550] (2)
[2210] (1)	[550] (2)
[1430] (1)	

Bond Distance: C-C = [1.28] Å

Bond Angle: C-C-C = [180°]

Rotational Constant = B₀ = [0.085652] cm⁻¹

σ = 2

Heat of Formation

The heat of formation is obtained from the mass-spectrometric results of Drowart et al. (1) who obtained $\Delta H_f^\circ = 230 \pm 5 \text{ kcal/mol}$. This was obtained from a 2nd law analysis of the ion intensity ratio C_5^+/C^+ over a temperature range of 2200-2700°K. The absolute pressure, obtained from a knowledge of the monatomic carbon vapor pressure and an estimated ionization cross-section ratio of 6.3, yields a 2nd law entropy at 2400°K of $103.7 \pm 2 \text{ eu}$. The uncertainty in the ionization cross-section ratio is probably no more than a factor of two which gives an overall entropy uncertainty of $\pm 3.5 \text{ eu}$. The heats of formation at temperatures other than 2400°K depend on the functions adopted, for a discussion of these see below.

Heat Capacity and Entropy

The molecular properties of C₅ are all estimated. We have chosen a set of functions which is consistent with the mass-spectrometric observations of Drowart et al. (1). The thermodynamic functions of C₅ were first estimated by Pitzer and Clementi (2) but the basis for this estimate has completely changed. Originally they were calculated by analogy with C₄, C₃, and CO₂, but the discovery of very low bending frequencies in C₄ and C₃ complicated the picture by raising the calculated entropies significantly. Sandborn (3) has correlated the bending force constants in several related triatomics and has estimated the vibrational frequencies in C₄ and C₅. These vibrational frequencies yield high entropies outside the limits of the second law determination. Since these frequencies are estimates, based on a basically triatomic correlation we have chosen to adopt three doubly degenerate bending frequencies of 550 cm⁻¹ in place of the 130 cm⁻¹, 330 cm⁻¹ and 520 cm⁻¹ frequencies estimated by Sandborn. The basis for this change is to make the functions conform to the only available measured data. Use of the present tables will yield values for the vapor pressures of C₄ in excellent agreement with the measurements in the 2000-3000°K range. Outside this range they provide only a general indication of the variation since they may not correspond to the real situation.

The stretching frequencies are from Sandborn (3) and the bond length is estimated equal to that in C₃.

References

1. J. Drowart, R. P. Burns, G. DeMaria, M. G. Inghram, J. Chem. Phys. **31**, 1131 (1959).
2. K. S. Pitzer and E. Clementi, J. Am. Chem. Soc. **81**, 4477 (1959).
3. R. H. Sandborn, J. Chem. Phys. **43**, 4219 (1965).

T, °K	Cp ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log Kp
0	∞	∞	∞	2.847	232.413	232.413	INFINITE
100	7.232	6.6215	2.148	2.847	232.413	232.413	INFINITE
200	10.915	57.814	59.032	2.148	232.413	232.413	INFINITE
298	14.611	57.806	60.000	2.148	232.413	232.413	INFINITE
300	14.668	57.806	60.000	2.148	232.413	232.413	INFINITE
400	17.184	62.484	58.414	1.628	234.378	213.534	116.670
500	18.964	66.520	59.640	3.440	234.595	208.295	91.046
600	20.318	70.102	61.091	5.407	234.672	203.023	73.951
700	21.385	73.317	62.612	7.494	234.634	197.753	61.741
800	22.239	76.231	64.135	9.677	234.529	192.493	52.587
900	22.927	78.861	65.659	11.936	234.346	187.243	45.449
1000	23.484	81.337	67.079	14.258	234.138	182.021	39.771
1100	23.900	83.597	68.079	16.630	233.895	176.819	35.131
1200	24.314	85.657	68.828	19.043	233.628	171.646	31.261
1300	24.624	87.456	69.374	21.490	233.330	166.490	27.990
1400	24.863	89.000	70.371	23.966	233.026	161.367	25.190
1500	25.101	91.215	71.571	26.466	232.706	156.259	22.767
1600	25.284	93.091	72.925	28.985	232.375	151.166	20.688
1700	25.424	94.578	74.437	31.522	232.042	146.101	18.793
1800	25.529	95.837	76.007	34.073	231.698	141.056	17.127
1900	25.598	96.823	77.640	36.637	231.352	136.033	15.647
2000	25.638	97.583	78.342	39.212	231.009	131.025	14.318
2100	25.654	98.084	79.001	41.794	230.651	126.041	13.117
2200	25.658	98.434	80.589	44.389	230.289	121.058	12.026
2300	25.653	98.736	82.111	46.989	229.929	116.111	11.033
2400	25.640	98.983	83.581	49.595	229.560	111.167	10.123
2500	25.619	99.184	84.992	52.207	229.192	106.238	9.287
2600	25.584	99.348	86.359	54.825	228.815	101.328	8.517
2700	25.538	99.481	87.687	57.447	228.437	96.426	7.805
2800	25.481	99.583	88.973	60.073	228.058	91.550	7.146
2900	25.416	99.656	90.210	62.703	227.668	86.682	6.533
3000	25.349	99.699	91.401	65.336	227.274	81.826	5.961
3100	25.278	99.713	92.546	67.972	226.882	76.988	5.428
3200	25.205	99.708	93.641	70.612	226.482	72.159	4.928
3300	25.129	99.683	94.696	73.253	226.073	67.331	4.459
3400	25.052	99.638	95.709	75.897	225.662	62.537	4.020
3500	24.972	99.573	96.684	78.544	225.244	57.733	3.605
3600	24.889	99.498	97.619	81.192	224.822	52.956	3.215
3700	24.804	99.413	98.514	83.842	224.392	48.190	2.846
3800	24.718	99.318	99.369	86.493	223.958	43.442	2.498
3900	24.632	99.213	100.184	89.147	223.517	38.701	2.169
4000	24.545	99.098	100.959	91.801	223.071	33.969	1.866
4100	24.458	98.973	101.694	94.455	222.617	29.235	1.588
4200	24.372	98.838	102.390	97.108	222.154	24.537	1.327
4300	24.286	98.693	103.046	99.773	221.683	19.831	1.086
4400	24.200	98.538	103.663	102.432	221.207	15.139	0.872
4500	24.114	98.373	104.240	105.093	220.721	10.453	0.680
4600	24.028	98.198	104.778	107.754	220.229	5.793	0.525
4700	23.942	98.013	105.278	110.417	219.732	1.139	0.403
4800	23.856	97.818	105.740	113.080	219.220	-3.499	0.319
4900	23.770	97.613	106.163	115.744	218.704	-8.137	0.261
5000	23.684	97.398	106.546	118.408	218.178	-12.759	0.219
5100	23.598	97.173	106.890	121.074	217.643	-17.394	0.185
5200	23.512	96.937	107.200	123.740	217.099	-21.994	0.157
5300	23.426	96.793	108.311	126.407	216.542	-26.574	0.132
5400	23.340	96.638	109.391	129.074	215.979	-31.150	0.109
5500	23.254	96.473	110.446	131.742	215.409	-35.723	0.087
5600	23.168	96.308	111.478	134.410	214.820	-40.287	0.069
5700	23.082	96.133	112.488	137.079	214.220	-44.854	0.054
5800	23.000	95.948	113.478	139.748	213.618	-49.391	0.041
5900	22.914	95.753	114.448	142.418	213.003	-53.900	0.030
6000	22.828	95.548	115.398	145.088	212.378	-58.441	0.021

Dec. 31, 1960; Dec. 31, 1969

Calcium (Ca)

(Reference State) GFW = 40.08

(REFERENCE STATE)

Ca

0 to 721°K Crystal alpha
721 to 1112°K Crystal beta
1112 to 1767.4°K Liquid
1767.4 to 6000°K Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

T, °K	C _p	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG_f°	Log Kp
0	.000	.000	INFINITE	-	1.371	.000	.000
100	5.652	7.516	15.163	-	1.595	.000	.000
200	8.536	9.932	9.932	.000	.000	.000	.000
298	6.279	9.932	9.932	.000	.000	.000	.000
300	6.283	9.971	9.932	.012	.000	.000	.000
400	6.432	11.802	10.181	.649	.000	.000	.000
500	6.495	13.245	10.654	1.295	.000	.000	.000
600	6.522	14.432	11.188	1.946	.000	.000	.000
700	6.532	15.438	11.725	2.599	.000	.000	.000
800	6.524	16.772	12.283	3.592	.000	.000	.000
900	6.784	17.775	12.638	4.444	.000	.000	.000
1000	9.314	18.728	13.379	5.349	.000	.000	.000
1100	9.844	19.681	13.907	6.307	.000	.000	.000
1200	7.200	22.131	14.508	9.099	.000	.000	.000
1300	7.200	22.707	15.154	9.819	.000	.000	.000
1400	7.200	23.281	15.713	10.539	.000	.000	.000
1500	7.200	23.737	16.232	11.259	.000	.000	.000
1600	7.200	24.202	16.715	11.979	.000	.000	.000
1700	7.200	24.639	17.169	12.699	.000	.000	.000
1800	4.982	25.925	17.973	50.313	.000	.000	.000
1900	4.982	46.185	19.452	50.812	.000	.000	.000
2000	5.008	46.451	20.795	51.312	.000	.000	.000
2100	5.030	46.696	22.023	51.811	.000	.000	.000
2200	5.061	46.931	23.150	52.318	.000	.000	.000
2300	5.101	47.156	24.189	52.826	.000	.000	.000
2400	5.153	47.375	25.150	53.339	.000	.000	.000
2500	5.219	47.586	26.043	53.857	.000	.000	.000
2600	5.299	47.792	26.876	54.383	.000	.000	.000
2700	5.386	47.994	27.654	54.918	.000	.000	.000
2800	5.511	48.193	28.384	55.463	.000	.000	.000
2900	5.644	48.388	29.071	56.020	.000	.000	.000
3000	5.796	48.582	29.718	56.592	.000	.000	.000
3100	5.968	48.775	30.330	57.180	.000	.000	.000
3200	6.159	48.967	30.909	57.786	.000	.000	.000
3300	6.370	49.160	31.459	58.413	.000	.000	.000
3400	6.600	49.353	31.983	59.061	.000	.000	.000
3500	6.848	49.548	32.482	59.733	.000	.000	.000
3600	7.113	49.745	32.958	60.431	.000	.000	.000
3700	7.394	49.944	33.415	61.156	.000	.000	.000
3800	7.688	50.145	33.852	61.910	.000	.000	.000
3900	7.995	50.348	34.273	62.695	.000	.000	.000
4000	8.312	50.555	34.677	63.510	.000	.000	.000
4100	8.636	50.768	35.067	64.357	.000	.000	.000
4200	8.966	50.976	35.443	65.237	.000	.000	.000
4300	9.300	51.191	35.807	66.151	.000	.000	.000
4400	9.635	51.409	36.159	67.097	.000	.000	.000
4500	9.969	51.629	36.500	68.078	.000	.000	.000
4600	10.300	51.852	36.832	69.091	.000	.000	.000
4700	10.626	52.077	37.154	70.137	.000	.000	.000
4800	10.944	52.304	37.467	71.216	.000	.000	.000
4900	11.254	52.532	37.772	72.326	.000	.000	.000
5000	11.553	52.763	38.070	73.466	.000	.000	.000
5100	11.841	52.995	38.360	74.636	.000	.000	.000
5200	12.115	53.227	38.644	75.834	.000	.000	.000
5300	12.376	53.460	38.921	77.059	.000	.000	.000
5400	12.622	53.694	39.192	78.309	.000	.000	.000
5500	12.852	53.928	39.456	79.583	.000	.000	.000
5600	13.067	54.161	39.719	80.879	.000	.000	.000
5700	13.265	54.394	39.974	82.195	.000	.000	.000
5800	13.447	54.627	40.225	83.531	.000	.000	.000
5900	13.613	54.858	40.471	84.884	.000	.000	.000
6000	13.763	55.088	40.712	86.253	.000	.000	.000

Calcium, Alpha (Ca, α)

GFW = 40.08

Ca

$$\Delta H_f^\circ = 0 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = 0 \text{ kcal/mol}$$

$$\Delta H_t^\circ = 0.220 \pm 0.05 \text{ kcal/mol}$$

$$\Delta H_s^\circ_{298.15} = 42.85 \pm 0.3 \text{ kcal/mol}$$

$$S^\circ_{298.15} = 9.93 \pm 0.06 \text{ gibbs/mol}$$

$$T_t = 721 \pm 2^\circ\text{K}$$

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacity data of Griffel et al. (1), 1.8° to 4.2°K, Roberts (2), 1.5° to 20°K, and Clusius and Vaughan (3), 10° to 200°K, were fit with polynomial expressions. Up to 20°K the three sets fit the adopted curve within ± 61 with a maximum deviation of 14%. This is considered excellent agreement since the heat capacity is only 0.35 gibbs/mol at 20°K. From 20° to 200°K the data of Clusius were within $\pm 1\%$ of the adopted polynomial. The data of Gunther (4), 22° to 62°K, generally deviated from the adopted curve by 10%. The polynomial fit of the data of Clusius was arranged to be linear in temperature at high temperatures and was extrapolated to 298°K. The data of Eastman et al. (5), 67° to 293°K, were consistently high by 5.8 to 91 over the whole range. The extrapolation of the heat capacity to 6.28 gibbs/mol at 298°K is further justified by comparison with the heat capacity of magnesium, which is almost identical to that of calcium over the whole range, if its temperature scale is multiplied by 0.75.

The heat capacity between 298° and 721°K was obtained by forcing a polynomial of the type $H = aT^2 + bT + c + d/T$ through 298° with a slope of 6.28 and also through a value of $H_{721} = 2736$ cal, and making a good fit of the adopted low temperature enthalpies. The choice of $H_{721} = 2736$ cal was made, since Zalesinski and Zulinsky (6), Jauch (7), and Eastman et al. (8) were in essential agreement in the beta-phase at this temperature. The enthalpy of transition was subtracted to give the adopted value. The individual measurements of Jauch (7) were not available, but the value at 720°K could be read from a small plot with reasonable accuracy; Eastman et al. (8) gave only an equation for their data. There is no question that reliable measurements of the heat capacity and enthalpy are needed in the range 200° to 700°K.

Transition Data

The temperature of transition was that reported by Peterson and Fattore (9) and confirmed by Chiodi et al. (10). Earlier reports on impure specimens ranged from 718° to 737°K and were not considered. The heat of transition was measured by Chiodi et al. (10) using an adiabatic high temperature calorimeter, and is in agreement with that reported by Kubaschewski (11) of 0.24 ± 0.04 kcal from enthalpy data.

Sublimation Data

See Ca(g) for details.

References:

1. M. Griffel, R. W. Vest and J. F. Smith, J. Chem. Phys. **27**, 1267 (1957).
2. L. M. Roberts, Proc. Phys. Soc. (London), **70B**, 738 (1957).
3. K. Clusius and J. V. Vaughan, J. Amer. Chem. Soc. **52**, 4686 (1930).
4. P. Gunther, Ann. Physik **51**, 828 (1916).
5. E. D. Eastman and W. H. Rodebush, J. Amer. Chem. Soc. **40**, 489 (1918).
6. E. Zalesinski and R. Zulinsky, Bull. Intern. Acad. Polon. **1928A**, 479 (1928).
7. R. Jauch, Diplomarbeit, Techn. Hochschule Stuttgart, 1946. Quoted in Ref. 11.
8. E. D. Eastman, A. M. Williams and T. F. Young, J. Amer. Chem. Soc. **46**, 1178 (1924).
9. D. T. Peterson and V. G. Fattore, J. Phys. Chem. **65**, 2062 (1961).
10. P. Chiodi, G. J. Gartner, E. R. Stevens, and Y. Saito, J. Chem. Eng. Data **11**, 571 (1966).
11. O. Kubaschewski, Z. Elektrochem. **54**, 275 (1950).

Calcium, Beta (Ca. β)

(Crystal)

GFW = 40.08

T, °K	Cp ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	5.594	10.151	10.151	.000	.117	.052	.038
300	5.604	10.185	10.151	.010	.116	.051	.037
400	6.134	11.870	10.377	.597	.045	.036	.021
500	6.664	13.296	10.821	1.237	.059	.038	.015
600	7.194	14.558	11.341	1.930	.101	.026	.009
700	7.724	15.706	11.684	2.676	.194	.006	.002
800	8.254	16.772	12.829	3.475	.000	.000	.000
900	8.784	17.775	12.868	4.327	.000	.000	.000
1000	9.314	18.788	13.496	5.232	.000	.000	.000
1100	9.844	19.481	14.014	6.190	.000	.000	.000
1200	10.374	20.520	14.520	7.200	.132	.028	.028
1300	10.904	21.371	15.014	8.264	1.437	.299	.050
1400	11.434	22.199	15.498	9.381	1.041	.416	.063
1500	11.964	23.006	15.971	10.551	.591	.507	.074
1600	12.494	23.795	16.436	11.774	.088	.564	.077
1700	13.024	24.566	16.892	13.050	.468	.588	.076
1800	13.554	25.327	17.339	14.379	35.417	1.259	.153
1900	14.084	26.075	17.779	15.761	34.934	3.294	.379
2000	14.614	26.810	18.213	17.196	33.999	5.282	.577

CALCIUM, BETA (Ca)

(CRYSTAL)

GFW = 40.08

 ΔH°_f = unknown $\Delta H^\circ_{f, 298.15} = 10.15$ gibbs/mol $\Delta H^\circ_f = 0.220 \pm 0.05$ kcal/mol $\Delta H^\circ_m = 2.04 \pm 0.10$ kcal/molHeat of Formation
Obtained from that of α -Ca by adding ΔH° and the difference in $H^\circ_{721} - H^\circ_{298}$ for α - and β -Ca.

Heat Capacity and Entropy

The enthalpy at 721°K was fixed as described on the α -Ca table. The data of Jauch (1), and Zalesinski and Zulinski (2), and Eastman et al. (3) were then fitted by an equation of the form $H = a + bT + cT^2$ where $a = -1315$, $b = 4.014$ and $c = 0.00285$. The values of Jauch, read from a small graph, fit within 1% generally and within 2% maximum deviation; those of Zalesinski and Zulinski fit within 0.7% with the exception of the highest point which differed by 1.8%. The data of Eastman et al. vary from 3.6% high to 0.4% low. The entropy was obtained in a manner analogous to the heat of formation.

Transition Data

See the α -Ca table for details.

Melting Data

The melting point is that reported by Peterson and Fattore (4) and confirmed by Chioffi et al. (5). Earlier reports on less pure specimens ranged from 1083° to 1122°K. The heat of melting was measured by Chioffi et al. (5) using an adiabatic high temperature calorimeter, and is in agreement with that reported by Kubaschewski (6) of 2.07 ± 0.1 kcal/mol from enthalpy data.

References:

1. R. Jauch, Diplomarbeit, Techn. Hochschule Stuttgart, 1946. Quoted in Ref. 6.
2. E. Zalesinski and R. Zulinski, Bull. Intern. Acad. Polon. 1928A, 479 (1928).
3. E. D. Eastman, A. M. Williams and T. F. Young, J. Amer. Chem. Soc. 46, 1178 (1924).
4. D. T. Peterson and V. G. Fattore, J. Phys. Chem. 65, 2062 (1961).
5. P. Chioffi, G. J. Gartner, E. R. Stevens, and Y. Saito, J. Chem. Eng. Data 11, 571 (1966).
6. O. Kubaschewski, Z. Elektrochem. 54, 275 (1950).

Calcium (Ca)

(Liquid)

GFW = 40.08

CALCIUM (Ca)

(LIQUID)

GFW = 40.08

$$S_{298.15}^{\circ} = 12.105 \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} 298.15 = 2.606 \pm 0.1 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 2.04 \pm 0.10 \text{ kcal/mol}$$

$$T_m = 1112 \pm 2^{\circ}\text{K}$$

$$\Delta H_v^{\circ} = 36.9668 \text{ kcal/mol}$$

$$T_b = 1767.4 \pm 15^{\circ}\text{K}$$

Heat of Formation

Obtained from that of β -Ca by adding ΔH_m° and the difference between $H_{1112}^{\circ} - H_{298}^{\circ}$ for β -Ca and liquid.

Heat Capacity and Entropy

The heat capacity was derived as constant from the enthalpy values of R. Jauch, Diplomarbeit, Techn. Hochschule Stuttgart, 1946, quoted by O. Kubaschewski, Z. Elektrochem. 51, 275 (1950). The entropy was obtained in a manner analogous to the heat of formation.

Melting Data

See the β -Ca table for details.

Vaporization Data

T_b is calculated from the free energy crossovers of the Ca(l) and Ca(g) tables, and ΔH_v° is the difference between $\Delta H_f^{\circ} 1767.4$ for liquid and gas.

T, °K	Cp°	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	7.200	12.105	12.105	.000	2.606	1.958	1.435
300	7.200	12.109	12.105	.013	2.607	1.953	1.423
400	7.200	14.221	12.387	.733	2.690	1.723	1.941
500	7.200	15.627	12.921	1.453	2.764	1.473	1.644
600	7.200	17.140	13.518	2.173	2.833	1.208	1.440
700	7.200	18.250	14.117	2.893	2.907	.932	1.241
800	7.200	19.059	14.622	3.613	2.976	.657	1.047
900	7.200	20.559	15.245	4.333	2.865	.439	1.107
1000	7.200	20.818	15.765	5.053	2.310	.220	1.048
1100	7.200	21.504	16.256	5.773	2.072	.022	1.004
1200	7.200	22.131	16.720	6.493	.000	.000	.000
1300	7.200	22.507	17.176	7.613	.000	.000	.000
1400	7.200	22.781	17.622	8.133	.000	.000	.000
1500	7.200	23.737	17.968	8.653	.000	.000	.000
1600	7.200	24.202	18.344	9.373	.000	.000	.000
1700	7.200	24.639	18.701	10.093	.000	.000	.000
1800	7.200	25.039	19.049	10.813	36.483	2.742	.318
1900	7.200	25.439	19.389	11.533	36.483	2.742	.318
2000	7.200	25.409	19.682	12.253	36.453	4.832	.528
2100	7.200	26.160	19.982	12.973	36.235	6.891	.717
2200	7.200	26.495	20.271	13.693	36.019	8.950	.888
2300	7.200	26.825	20.546	14.413	35.800	10.950	1.042
2400	7.200	27.125	20.816	15.133	35.600	13.008	1.185
2500	7.200	27.415	21.074	15.853	35.398	15.039	1.314
2600	7.200	27.699	21.323	16.573	35.204	17.042	1.433
2700	7.200	27.969	21.564	17.293	35.019	19.048	1.542
2800	7.200	28.224	21.794	18.013	34.840	21.054	1.642
2900	7.200	28.464	22.028	18.733	34.661	23.061	1.736
3000	7.200	28.728	22.244	19.453	34.533	25.029	1.823

Dec. 31, 1968

Ca

Ground State Configuration $2s^2$

$$\Delta H_f^\circ = -25.0 \pm 3 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 57.7 \pm 0.2 \text{ gibbs/mol}$$

$$\Delta H_f^\circ_{298.15} = -25.0 \pm 3 \text{ kcal/mol}$$

Calcium Monochloride (CaCl)

$$GFW = 75.533$$

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	ΔH ^o	Log K _p
0	+0.000	+0.000	INFINITE	2.292	24.624	INFINITE
100	7.244	49.046	64.976	1.591	24.705	58.949
200	8.116	50.476	59.476	1.591	24.838	31.903
300	8.524	57.707	57.707	+0.000	25.000	22.944
400	8.529	57.760	57.707	-0.16	25.004	22.831
500	8.622	62.200	58.687	1.757	25.192	16.262
600	8.855	63.815	59.411	2.642	25.567	13.642
700	9.061	65.382	60.887	3.485	26.330	11.298
800	9.247	67.439	61.522	5.135	26.729	10.483
900	9.409	68.387	62.162	6.225	27.182	9.829
1000	9.528	69.247	62.768	7.127	27.686	9.284
1100	9.601	70.758	63.484	8.936	30.260	8.371
1200	9.671	71.717	64.212	10.751	30.555	8.006
1300	9.707	72.056	64.869	11.661	31.084	7.404
1400	9.710	72.483	65.355	12.532	31.586	6.846
1500	9.713	72.817	65.833	13.399	31.865	6.408
1600	9.716	73.129	66.314	14.261	32.122	6.014
1700	9.717	73.429	66.795	15.110	32.366	5.657
1800	9.718	73.717	67.268	15.945	32.592	5.332
1900	9.719	73.995	67.735	16.771	32.802	5.032
2000	9.720	74.261	68.198	17.591	33.000	4.763
2100	9.721	74.517	68.656	18.406	33.187	4.513
2200	9.722	74.764	69.109	19.216	33.363	4.281
2300	9.723	74.995	69.556	20.021	33.529	4.066
2400	9.724	75.217	69.999	20.821	33.686	3.871
2500	9.725	75.431	70.437	21.616	33.834	3.681
2600	9.726	75.637	70.871	22.406	33.973	3.507
2700	9.727	75.835	71.299	23.191	34.104	3.345
2800	9.728	76.025	71.723	23.971	34.227	3.192
2900	9.729	76.208	72.143	24.746	34.343	3.047
3000	9.730	76.384	72.559	25.516	34.452	2.912
3100	9.731	76.553	72.971	26.281	34.555	2.784
3200	9.732	76.716	73.379	27.041	34.653	2.662
3300	9.733	76.873	73.783	27.796	34.746	2.547
3400	9.734	77.025	74.183	28.546	34.834	2.437
3500	9.735	77.172	74.579	29.291	34.918	2.333
3600	9.736	77.315	74.971	30.031	35.000	2.233
3700	9.737	77.453	75.359	30.766	35.077	2.138
3800	9.738	77.587	75.745	31.500	35.150	2.047
3900	9.739	77.717	76.127	32.231	35.219	1.957
4000	9.740	77.843	76.505	32.957	35.284	1.876
4100	9.741	77.966	76.879	33.680	35.344	1.796
4200	9.742	78.086	77.249	34.400	35.400	1.718
4300	9.743	78.202	77.615	35.116	35.453	1.644
4400	9.744	78.315	77.977	35.829	35.503	1.570
4500	9.745	78.425	78.335	36.539	35.550	1.502
4600	9.746	78.532	78.689	37.245	35.594	1.435
4700	9.747	78.637	79.040	37.947	35.635	1.370
4800	9.748	78.740	79.387	38.645	35.673	1.307
4900	9.749	78.841	79.731	39.339	35.708	1.246
5000	9.750	78.940	80.071	40.030	35.740	1.186
5100	9.751	79.037	80.407	40.717	35.769	1.129
5200	9.752	79.132	80.740	41.401	35.796	1.073
5300	9.753	79.225	81.070	42.081	35.821	1.018
5400	9.754	79.316	81.396	42.757	35.844	0.963
5500	9.755	79.405	81.719	43.430	35.865	0.908
5600	9.756	79.492	82.039	44.100	35.884	0.853
5700	9.757	79.577	82.355	44.766	35.901	0.798
5800	9.758	79.660	82.668	45.429	35.916	0.743
5900	9.759	79.741	82.977	46.089	35.929	0.688
6000	9.760	79.820	83.283	46.746	35.941	0.633

June 30, 1970

Electronic Levels and Quantum Weights

State	ϵ_1 , cm ⁻¹	g_1
X ² _g ⁺	0	2
A ² _g ⁺	15093.3	2
B ² _g	16162.8	2
C ² _g	16850.6	2
D ² _g	26498.9	2
E ² _g	26574.7	2
F ² _g	31107.6	2
G ² _g	34266.4	2
H ² _g	35875	2
I ² _g	35700	2
J ² _g	36705	2
K ² _g	36710	2

$$\omega_e x_e = 1.31 \text{ cm}^{-1}$$

$$\omega_e = 369.8 \text{ cm}^{-1}$$

$$B_e = 0.1516 \text{ cm}^{-1}$$

$$a_e = 10.0071 \text{ cm}^{-1}$$

$$r_e = 2.439 \text{ \AA}$$

Heat of Formation

N. D. Potter (1) Investigated mass spectrometrically the gaseous equilibria among Ca, CaCl, and CaCl₂. Ion intensities were measured 2.5 eV above the ionization threshold. Using the equilibrium constants $K = I(\text{CaCl})^2 / I(\text{Ca}) I(\text{CaCl}_2)$ which we calculated from the reported ion intensities for the reaction $\text{Ca(g)} + \text{CaCl}_2(\text{g}) \rightleftharpoons 2\text{CaCl(g)}$ in the temperature range 1252°-1557°K, we obtain $\Delta H_f^\circ_{298} = 15.81 \text{ kcal/mol}$ by the third law method. The third law drift is $-2.8 \pm 3.5 \text{ eu}$. The heat of formation is derived as $\Delta H_f^\circ_{298}(\text{CaCl, g}) = -27.0 \text{ kcal/mol}$.

K. F. Zmbov (2) determined by mass spectrometry the heat of the above reaction as $24.4 \pm 1.3 \text{ kcal/mol}$ with a drift of $12.5 \pm 9.4 \text{ eu}$. This yields the heat of formation, $\Delta H_f^\circ_{298}(\text{CaCl, g}) = -22.7 \text{ kcal/mol}$.

D. L. Hildenbrand (2) also determined the equilibrium constants for the reaction (a) $\text{Ca(g)} + \text{CaCl}_2(\text{g}) \rightleftharpoons 2\text{CaCl(g)}$ and the reaction (b) $\text{Ca(g)} + \text{AlCl}_3(\text{g}) \rightleftharpoons \text{CaCl(g)} + \text{Al(g)}$ by mass spectrometry in the temperature range 1219-1353°K. Third law analysis of the reported equilibrium constants gives $\Delta H_f^\circ_{298} = 21.08 \text{ kcal/mol}$ and drift = $-1.4 \pm 1.8 \text{ eu}$ for reaction (a); and $\Delta H_f^\circ_{298} = 24.20 \text{ kcal/mol}$ and drift = $0.5 \pm 1.3 \text{ eu}$ for reaction (b). From third law $\Delta H_f^\circ_{298}$ of (a) and (b), we derived $\Delta H_f^\circ_{298}(\text{CaCl, g})$ as -24.4 and -23.3 kcal/mol , respectively, using all JANAF functions. Hildenbrand has also derived a corrected $D_0(\text{Ca-Cl}) = 95.0 \text{ kcal/mol}$ from a linear Birge-Sponer extrapolation of the ground state vibrational levels with correction for its ionicity. This corrected $D_0(\text{Ca-Cl})$ yields the heat of formation, $\Delta H_f^\circ_{298}(\text{CaCl, g}) = -23.9 \text{ kcal/mol}$.

Ryabova and Gurvich (3) reported $D_0(\text{Ca-Cl}) = 102 \pm 6 \text{ kcal/mol}$ from flame spectra studies. This leads to $\Delta H_f^\circ_{298}(\text{CaCl, g}) = -30.9 \text{ kcal/mol}$.

D. L. Hildenbrand (3) determined the dissociation energy of CaCl₂(g) by electron impact as $D_0(\text{CaCl-Cl}) = 5.04 \pm 0.02 \text{ eV}$ which, combined with JANAF $\Delta H_f^\circ_{298}$ of CaCl₂(g) and Cl(g) gives $\Delta H_f^\circ_{298}(\text{CaCl, g}) = -23.1 \text{ kcal/mol}$.

A weighted average, $\Delta H_f^\circ_{298}(\text{CaCl, g}) = -25 \pm 3 \text{ kcal/mol}$, is adopted in the tabulation.

Heat Capacity and Entropy

The vibrational constants (ω_e and $\omega_e x_e$), electronic levels and ground state configuration were taken from Herzberg (4). Morgan and Barrow (5) made rotational analysis of the C²H-X²g system and reported $B_e = 0.1516 \text{ cm}^{-1}$ and $r_e = 2.439 \text{ \AA}$ for the ground state. The value of q_e is calculated from the Morse potential function. The F and G states were reported by Schutte (6).

References

1. N. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. D. L. Hildenbrand, "Dissociation Energies and Chemical Bonding in the Alkaline-Earth Chlorides from Mass Spectrometric Studies," J. Chem. Phys., in press.
3. V. G. Ryabova and L. V. Gurvich, Teplofiz. Vysokikh Temp. Akad. Nauk SSSR 3, 652 (1965).
4. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc. New York, 1950.
5. E. Morgan and R. F. Barrow, Nature 185, 754 (1960).
6. D. L. Hildenbrand, CPTA Publication No. 189, Vol. 1 page 86, Aug. 1969.
7. K. F. Zmbov, Chem. Phys. Lett. 1, 191 (1969).
8. M. Schutte, Naturwiss. 40, 528 (1953).

Calcium Chloride (CaCl₂)

GFW = 110.986

(Crystal)

CALCIUM CHLORIDE (CaCl₂)

(CRYSTAL)

GFW = 110.986

 $\Delta H_f^\circ = -190.3 \pm 0.3 \text{ kcal/mol}$ $\Delta H_{298.15}^\circ = -190.2 \pm 0.3 \text{ kcal/mol}$ $\Delta H_m^\circ = 6.822 \pm 0.2 \text{ kcal/mol}$ $\Delta H_{298.15}^\circ = 77.5 \pm 2 \text{ kcal/mol}$ $S_{298.15}^\circ = 25.0 \pm 1 \text{ gibbs/mol}$ $T_m = 1045^\circ\text{K}$ CaCl₂

T, °K	C _p	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	11.666	8.508	39.406	3.678	-190.313	-190.313	INFINITE
200	16.099	18.296	26.558	3.090	-190.655	-186.609	407.434
298	17.413	25.000	25.000	1.652	-190.485	-182.610	199.546
300	17.430	25.108	25.001	1.652	-190.485	-182.610	131.067
400	18.080	30.222	25.694	1.411	-189.883	-174.961	130.204
500	18.440	34.288	27.021	3.639	-189.454	-171.267	74.461
600	18.650	37.682	28.523	5.495	-189.218	-167.641	61.063
800	19.340	43.139	31.524	6.292	-188.836	-164.250	43.726
900	19.640	45.456	32.954	11.251	-188.614	-157.001	38.125
1000	20.500	47.570	34.302	13.268	-188.396	-153.501	33.548
1100	21.260	49.557	35.600	17.253	-188.166	-150.073	29.407
1200	22.000	51.212	36.033	19.233	-188.100	-147.431	26.012
1300	22.600	52.712	36.033	19.233	-188.100	-147.431	23.745
1400	23.300	54.913	39.178	22.028	-188.429	-139.294	19.748
1500	24.000	56.544	40.282	24.393	-187.490	-135.812	18.092
1600	24.700	58.115	41.388	26.828	-186.863	-132.360	15.574
1800	26.100	61.105	43.379	31.808	-184.957	-124.957	13.741
1900	26.800	62.535	44.349	34.553	-184.957	-119.637	12.496
2000	27.500	63.928	45.294	37.268	-184.957	-114.350	

Heat of Formation

V. B. Parker (1) has selected the standard heat of formation as -190.2 kcal/mol which is adopted in the tabulation. The heat of formation was derived from two independent paths. The first path involves $\Delta H_f^\circ(\text{Ca}^{++}, \infty \text{H}_2\text{O}) = -129.74$ kcal/mol (1), $\Delta H_f^\circ(\text{Cl}^-, \infty \text{H}_2\text{O}) = -39.952$ kcal/mol (2) and the heat of solution of $\text{CaCl}_2(\text{c})$ in water (3, 4, 5, 6, 7). The second path involves the heats of reaction of $\text{Ca}(\text{c})$, $\text{CaO}(\text{c})$ and $\text{CaCl}_2(\text{c})$ in aqueous HCl solution (1, 8-20).

Heat Capacity and Entropy

Kelley and Moore (21) measured the low temperature heat capacities in the temperature range from 52.6° to 295.1°K and made an extrapolation to 0°K which yielded an entropy of 4.59 ± 0.4 eu at 50.12°K. We have adopted the measured heat capacities, but made our own extrapolation to 0°K by comparison with the measured heat capacities of $\text{BaCl}_2(\text{c})$ (22) and $\text{SrCl}_2(\text{c})$ (23) from 6° to 50°K. The extrapolation gives $S_{50}^\circ = 2.45 \pm 1$ eu, which is used in the table. Moore (24) measured high temperature enthalpy data from 403.7° to 1687°K by drop calorimetry. The low temperature heat capacities and high temperature enthalpy data are smoothly joined at 298°K. The deviations of the observed enthalpies from the adopted values are about 21 near 400-500°K and only a few tenths percent at higher temperatures. Dworkin and Bredig (25) determined drop-calorimetrically $H_{1045}^\circ - H_{298}^\circ = 14.3$ kcal/mol, which is in very good agreement with the adopted value of 14.2 kcal/mol.

Melting Data

The adopted melting point 1045°K was determined by T. V. Tokareva (26). Dworkin and Bredig determined the heat of fusion $\Delta H_{1045}^\circ = 6.78 \pm 0.1$ kcal/mol by drop calorimetry. Chiotti, Gartner, Stevens and Saito (27) also measured the heat of fusion $\Delta H_{1055}^\circ = 6.79 \pm 0.2$ kcal/mol in an adiabatic calorimeter. The adopted heat of fusion, 6.822 kcal/mol, is calculated from the difference between the observed relative enthalpy of the liquid and the adopted value for the crystal at the melting point.

Sublimation Data

The heat of sublimation is calculated from the heats of formation of $\text{CaCl}_2(\text{c})$ and $\text{CaCl}_2(\text{g})$.

References

1. V. B. Parker, U. S. Natl. Bur. Std. private communication, Jan. 7, 1969.
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. Pickering, J. Chem. Soc. 53, 875 (1888).
4. Samoilov, Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk 1952, 626.
5. Ditte, Compt. Rend. 85, 1103 (1877).
6. Baud, Ann. Chim. Phys. 1, 8 (1904).
7. Berthelot and Ilosvay, Ann. Chim. Phys. 23, 295 (1883).
8. Kapustinski and Samoilov, Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk 1950, 367.
9. P. Ehrlich, K. Feik and E. Koch, Z. Anorg. Allgem. Chem. 324, 113 (1963).
10. Vedenev, Zh. Fiz. Khim. 28, 1808 (1952).
11. Young, J. Amer. Chem. Soc. 65, 773 (1944).
12. Torgeson and Shomate, J. Amer. Chem. Soc. 69, 2103 (1947).
13. Taylor and Wells, J. Res. Natl. Bur. Std. 21, 133 (1938).
14. Wells and Taylor, J. Res. Natl. Bur. Std. 19, 215 (1937).
15. Backstrom, J. Amer. Chem. Soc. 51, 2678 (1929).
16. Thorvaldson, Brown, and Peaker, J. Amer. Chem. Soc. 51, 2678 (1929).
17. Guntz and Benoit, Ann. Chim. 20, 5 (1923).
18. Biltz and Wagner, Z. Anorg. Allgem. Chem. 134, 1 (1924).
19. Geiseler and Buchner, Z. Anorg. Allgem. Chem. 343, 286 (1966).
20. Kocherov, Gertman and Geld, Zh. Neorg. Khim. 4, 1106 (1959).
21. K. K. Kelley and G. E. Moore, J. Amer. Chem. Soc. 55, 1284 (1933).
22. R. M. Goodman and E. F. Westrum, Jr., J. Chem. Eng. Data 11, 294 (1966).
23. D. F. Smith, T. E. Gardner, B. B. Letson and A. R. Taylor, Jr., U. S. Bur. Mines RI 6316, 1963.
24. G. E. Moore, J. Amer. Chem. Soc. 65, 1700 (1943).
25. A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 67, 697 (1963).
26. M. V. Tokareva, Zh. Neorg. Khim. 2, 1591 (1957).
27. P. Chiotti, G. J. Gartner, E. R. Stevens and Y. Saito, J. Chem. Eng. Data 11, 571 (1966).

CaCl₂ (LIQUID) GFW = 110.986

$S_{298.15}^{\circ} = 29.608 \pm 1.2 \text{ gibbs/mol}$

$\Delta H_f^{\circ} = -185.013 \pm 0.5 \text{ kcal/mol}$

$\Delta H_m^{\circ} = 6.822 \pm 0.2 \text{ kcal/mol}$

$\Delta H_v^{\circ} = 56.2 \text{ kcal/mol}$

Heat of Formation

The heat of formation is calculated from that of the crystal by adding the heat of melting and the difference between H_{1045}° and H_{298}° for the crystal and the liquid.

Heat Capacity and Entropy

The constant heat capacity above the assumed glass transition at 700°K is derived from high temperature enthalpy data in a drop calorimeter from the melting point up to 1667°K by G. E. Moore, J. Amer. Chem. Soc. **65**, 1700 (1943). Below the glass transition point, the heat capacity is assumed to be the same as that of the crystal. A. S. Dworin and M. A. Bredig, J. Phys. Chem. **67**, 697 (1963), reported $C_p(\ell) = 23.6 \text{ gibbs/mol}$ from enthalpy measurements in a short temperature range by drop calorimetry.

The entropy $S_{298.15}^{\circ} = 29.608 \text{ gibbs/mol}$ is calculated in a manner analogous to that of the heat of formation.

Melting Data

See the crystal table for details.

Vaporization Data

The boiling point is calculated as the temperature at which $\Delta G = 0$ for $\text{CaCl}_2(\ell) + \text{CaCl}_2(g)$. The heat of vaporization is the difference in ΔH_f° between liquid and gas.

Calcium Chloride (CaCl₂)
(Liquid) GFW = 110.986

T, °K	Cp°	$S^{\circ} - (C^{\circ} - H^{\circ})_{298}/T$	$H^{\circ} - H_{298}^{\circ}$	ΔH_f°	ΔG_f°	Log Kp
0						
100						
200						
298	17.413	29.608	0.000	-185.013	-174.991	128.772
300	17.430	29.715	-0.132	-185.004	-174.929	127.936
400	18.040	34.629	10.301	-184.696	-171.617	93.767
500	18.440	38.905	31.628	-184.367	-168.343	73.600
600	18.690	42.269	53.131	-184.031	-165.214	60.141
700	18.840	44.643	74.817	-183.684	-162.222	48.053
800	18.900	46.000	96.578	-183.328	-159.362	37.004
900	18.900	46.463	118.417	-182.959	-156.632	26.996
1000	18.900	46.931	140.329	-182.578	-154.044	17.996
1100	18.900	47.400	162.317	-182.184	-151.596	9.996
1200	18.900	47.869	184.384	-181.778	-149.288	2.996
1300	18.900	48.338	206.531	-181.359	-147.011	-4.004
1400	18.900	48.807	228.758	-180.928	-144.764	-11.004
1500	18.900	49.276	251.065	-180.484	-142.547	-18.004
1600	18.900	49.745	273.452	-180.028	-140.360	-25.004
1700	18.900	50.214	295.919	-179.559	-138.203	-32.004
1800	18.900	50.683	318.466	-179.078	-136.076	-39.004
1900	18.900	51.152	341.093	-178.584	-133.979	-46.004
2000	18.900	51.621	363.700	-178.078	-131.912	-53.004
2100	18.900	52.090	386.287	-177.559	-129.875	-60.004
2200	18.900	52.559	408.854	-177.028	-127.868	-67.004
2300	18.900	53.028	431.401	-176.484	-125.891	-74.004
2400	18.900	53.497	453.928	-175.928	-123.944	-81.004
2500	18.900	53.966	476.435	-175.359	-122.027	-88.004
2600	18.900	54.435	498.922	-174.778	-120.140	-95.004
2700	18.900	54.904	521.389	-174.184	-118.283	-102.004
2800	18.900	55.373	543.836	-173.578	-116.456	-109.004
2900	18.900	55.842	566.263	-172.959	-114.659	-116.004
3000	18.900	56.311	588.670	-172.328	-112.892	-123.004

Point Group D_{2h} $\Delta H_f^\circ = -112.7 \pm 1 \text{ kcal/mol}$ $\Delta H_f^\circ = -112.7 \pm 1 \text{ kcal/mol}$

S_{298.15} = 69.3 ± 2 gibbs/mol $\Delta H_f^\circ = -112.7 \pm 1 \text{ kcal/mol}$

Ground State Quantum Weight = 1

CaCl₂

Calcium Chloride (CaCl₂) (Ideal Gas) GFW = 110.986

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log Kp
0	0.00	INFINITE	-	-	-112.748	INFINITE
100	11.00	55.007	6.443	2.444	-112.709	115.313
200	13.22	63.606	7.427	1.364	-112.697	124.490
298	14.179	69.347	8.000	1.000	-112.700	131.950
300	14.167	69.435	8.037	1.026	-112.701	131.441
400	14.476	73.561	8.906	1.461	-112.733	122.913
500	14.822	76.890	9.775	2.517	-112.776	105.152
600	14.705	79.482	10.536	4.363	-112.830	82.374
700	14.756	81.753	11.206	5.857	-112.887	61.502
800	14.790	83.726	11.800	7.334	-112.899	44.087
900	14.813	85.469	12.330	8.614	-112.951	30.644
1000	14.830	87.031	12.817	10.237	-113.067	20.684
1100	14.843	88.445	13.263	11.736	-113.239	13.618
1200	14.853	89.737	13.683	13.265	-113.463	8.219
1300	14.860	90.926	14.079	14.751	-113.742	4.441
1400	14.866	92.028	14.450	16.237	-114.070	1.962
1500	14.871	93.053	14.800	17.724	-114.459	0.847
1600	14.875	94.013	15.126	19.211	-114.900	0.362
1700	14.878	94.915	15.439	20.699	-115.411	0.141
1800	14.881	95.766	15.740	22.187	-116.000	0.056
1900	14.883	96.570	16.029	23.675	-116.667	0.021
2000	14.885	97.334	16.306	25.163	-117.418	0.008
2100	14.887	98.056	16.572	26.652	-118.256	0.001
2200	14.888	98.733	16.828	28.141	-119.180	0.000
2300	14.890	99.364	17.075	29.630	-120.192	0.000
2400	14.891	100.048	17.314	31.119	-121.294	0.000
2500	14.892	100.686	17.547	32.608	-122.498	0.000
2600	14.893	101.280	17.775	34.097	-123.804	0.000
2700	14.894	101.832	17.998	35.586	-125.214	0.000
2800	14.894	102.344	18.216	37.076	-126.730	0.000
2900	14.895	102.817	18.430	38.565	-128.354	0.000
3000	14.895	103.251	18.639	40.055	-130.088	0.000
3100	14.896	103.660	18.843	41.544	-131.934	0.000
3200	14.896	104.033	19.043	43.034	-133.894	0.000
3300	14.897	104.371	19.239	44.524	-135.970	0.000
3400	14.897	104.673	19.431	46.013	-138.164	0.000
3500	14.898	104.938	19.619	47.503	-140.478	0.000
3600	14.898	105.168	19.803	49.000	-142.918	0.000
3700	14.898	105.362	19.982	50.493	-145.484	0.000
3800	14.899	105.521	20.157	52.000	-148.178	0.000
3900	14.899	105.650	20.328	53.462	-150.999	0.000
4000	14.899	105.759	20.495	54.922	-153.948	0.000
4100	14.899	105.848	20.658	56.442	-157.026	0.000
4200	14.900	105.916	20.817	57.932	-160.234	0.000
4300	14.900	105.965	20.972	59.422	-163.572	0.000
4400	14.900	106.000	21.124	60.912	-167.042	0.000
4500	14.900	106.022	21.272	62.402	-170.646	0.000
4600	14.900	106.035	21.417	63.892	-174.386	0.000
4700	14.900	106.040	21.559	65.382	-178.264	0.000
4800	14.901	106.040	21.698	66.872	-182.282	0.000
4900	14.901	106.040	21.834	68.362	-186.442	0.000
5000	14.901	106.040	21.967	69.852	-190.756	0.000
5100	14.901	111.277	22.097	71.342	-195.226	0.000
5200	14.901	111.566	22.223	72.832	-200.856	0.000
5300	14.901	111.850	22.346	74.322	-206.646	0.000
5400	14.901	112.129	22.466	75.812	-212.596	0.000
5500	14.901	112.402	22.583	77.302	-218.716	0.000
5600	14.901	112.671	22.697	78.792	-224.996	0.000
5700	14.901	112.935	22.809	80.282	-231.436	0.000
5800	14.902	113.194	22.918	81.772	-238.036	0.000
5900	14.902	113.448	23.024	83.262	-244.796	0.000
6000	14.902	113.699	23.128	84.754	-251.716	0.000

Vibrational Frequencies and Degeneracies

W, cm ⁻¹	Number of Points	Temperature Range, °K	ΔH _{vib} (kcal/mol)	Drift
217 (1)	7	932-993	75.25	-1.746.9
64 (2)	12	1142-1226	64.99	71.24
402 (1)	17	1111-1281	68.71	71.24
	29	1111-1281	68.91	71.24
	4	1069-1225	59.37	71.03
	1	1819	---	>71.10
	5	1591-1701	72.25	72.30
	6	973-1023	78.0	69.01
	6	1073-1273	61.6	69.76
				+8.0

Heat Capacity and Entropy

The linear structure and vibrational frequencies were determined by D. White and co-workers (g) in the matrix-infrared-spectrometric studies. The linear structure is consistent within experimental error with the electric-quadrupole-deflection studies (2), and electron-diffraction data (g). Hayes (g) has qualitatively rationalized the linear structure through molecular orbital theory.

The bond length was measured by Akishin and Spiridonov (g). The moment of inertia is 74.174 × 10⁻³⁹ g cm².

Heat of Formation

Second and third law analyses of vapor pressure data are given below. The selected third law heat of vaporization is taken from Novikov's measurement (1) as ΔH_v²⁹⁸ = 72.30 kcal/mol which is combined with ΔH_f²⁹⁸ of the liquid to give ΔH_f²⁹⁸(CaCl₂, g) = -112.7 ± 1 kcal/mol.

Third law analyses indicate zero drift for Novikov's data, positive and negative drifts for Hildenbrand's (2) and Bautista's (3) data, respectively. Their heats are in agreement within ±1 kcal. Wartenberg (4) reported there was no boiling at 1819°K at 62 mm Hg pressure, and his value (ΔH_v²⁹⁸ = 71.1 ± 0.7 kcal/mol) serves as a guide for the minimum heat of vaporization.

Investigator	Method	Temperature Range, °K	Number of Points	ΔH _v ²⁹⁸ (kcal/mol)	Drift
Bautista and Hargrave (3)	Langmuir	932-993	7	75.25	-1.746.9
Hildenbrand and Potter (2)	Torsion Effusion	1142-1226	12	64.99	71.24
Hildenbrand and Potter (2)	Torsion Effusion	1111-1281	17	68.71	71.24
Hildenbrand and Potter (2)	Torsion Effusion	1111-1281	29	68.91	71.24
Dewing (5)	Knudsen Effusion	1069-1225	4	59.37	71.03
Wartenberg and Bosse (4)	Boiling Point	1819	1	---	>71.10
Novikov and Gavryuchenkov (1)	Boiling Point	1591-1701	5	72.25	72.30
Lukashenko and Reutova (10)	Langmuir	973-1023	6	78.0	69.01
	Knudsen Effusion	1073-1273	6	61.6	69.76
					+8.0

*Value in parentheses is the heat of sublimation.

Heat Capacity and Entropy

The linear structure and vibrational frequencies were determined by D. White and co-workers (g) in the matrix-infrared-spectrometric studies. The linear structure is consistent within experimental error with the electric-quadrupole-deflection studies (2), and electron-diffraction data (g). Hayes (g) has qualitatively rationalized the linear structure through molecular orbital theory.

The bond length was measured by Akishin and Spiridonov (g). The moment of inertia is 74.174 × 10⁻³⁹ g cm².

References

1. G. I. Novikov and F. G. Gavryuchenkov, Zh. Neorg. Khim. **9**, 260 (1964).
2. D. L. Hildenbrand and N. D. Potter, J. Phys. Chem. **67**, 2331 (1963).
3. R. G. Bautista and J. L. Margrave, J. Phys. Chem. **67**, 2411 (1963).
4. H. V. Wartenberg and O. Bosse, Z. Elektrochem. **28**, 384 (1922).
5. E. W. Dewing, Aluminum Laboratories, quoted in ref. (2).
6. Unpublished work cited by D. L. Hildenbrand, "Dissociation Energies and Chemical Bonding in the Alkaline-Earth Chlorides from Mass Spectrometric Studies," J. Chem. Phys., in press.
7. L. Wharton, R. A. Berg and W. Klemperer, J. Chem. Phys. **39**, 2023 (1963); **39**, 2299 (1963).
8. P. A. Akishin and V. P. Spiridonov, Kristallografiya **2**, 475 (1957).
9. E. F. Hayes, J. Phys. Chem. **70**, 3740 (1966).
10. E. E. Lukashenko and G. A. Reutova, Zhur. Fiz. Khim. **44**, 600 (1970).

Calcium Monofluoride (CaF)

GFW = 59.0784

CaF

$$\Delta H_f^\circ = -64.8 \pm 2 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -65.0 \pm 2 \text{ kcal/mol}$$

Ground State Configuration $2s^2$

$$S_{298.15}^\circ = 54.86 \pm 0.1 \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
$X^2\Sigma^+$	0
$A^2\Pi$	2
16482	2
16557	2
$B^2\Sigma$	2
18044	2
$C^2\Pi$	2
30256	2
30285	2
$D^2\Sigma$	2
30772	2
$E^2\Sigma$	2
34135	2
$F^2\Pi$	4
37548	4

$$\omega_e X_e = 2.74 \text{ cm}^{-1}$$

$$\sigma = 1$$

$$r_e = 2.01 \text{ \AA}$$

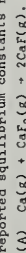
$$B_e = 0.3225 \text{ cm}^{-1}$$

$$a_e = [0.0020] \text{ cm}^{-1}$$

Heat of Formation

Hastie and Margrave (1) have recently reviewed the dissociation energy of CaF and conclude that it is 127.5 ± 2.5 kcal/mol. The analysis below considers basically the same data except that all values are JANAF.

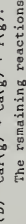
Hildenbrand and Murad (2) in a mass spectrometric determination of the equilibria among BF, BF₂, Ca, CaF and CaF₂ reported equilibrium constants for the reaction



Blue et al. (3) have also examined several equilibria mass-spectrometrically and report equilibrium constants for reaction



Ryabova and Gurvich (4) give a heat of dissociation from flame studies for the reaction



The remaining reactions considered by Hastie and Margrave (1) were not included since they involved subtracting reactions not performed simultaneously, or involve species such as SiF₂ whose heat of formation is dependent on that of CaF and CaF₂.

Reference	Range °K	Reaction	Points	ΔH_f° kcal/mol	Drift	ΔH_f° kcal/mol
Hildenbrand (2)	1593 - 1734	A	15	11.5 ± 6.8	2nd law	14.70 ± 1.27
Blue (3)	1271 - 1351	B	9	146.9 ± 8.0	3rd law	121.08 ± 1.65
Blue (3)	1271 - 1351	C	10*	34.6 ± 3.5		32.87 ± 0.47
Ryabova (4)		D		135 ± 7		-1.4 ± 2.7
Hildenbrand (5)	1423 - 1443	A	2			32.97

* 1 point rejected due to failure of a statistical test

** Calculated from third law value when available

The auxiliary heats of formation used were, in kcal/mol, AlF, g = -63.4, Al, g = 78, CaF₂, g = -187.5, CaF₂, c = -293.0 and Ca, g = 42.85.

We adopt a median value of $\Delta H_{298.15}^\circ(\text{CaF, g}) = -65 \pm 2$ kcal/mol which corresponds to a heat of dissociation of 126.7 ± 2 kcal/mol.

Heat Capacity and Entropy

Herzberg (6) gives the vibrational constants and electronic levels, Harvey (7) has reported a value for B₀ which corresponds to a bond length of 2.02 Å. The Morse potential function was used to calculate a_e .

References

1. J. W. Hastie and J. L. Margrave, J. Chem. Eng. Data **13**, 428 (1969).
2. D. L. Hildenbrand and E. Murad, J. Chem. Phys. **43**, 1400 (1965).
3. G. D. Blue, J. W. Green, R. G. Bautista, and J. L. Margrave, J. Phys. Chem. **67**, 877 (1963).
4. V. G. Ryabova and L. V. Gurvich, Teplofiz. Vys. Temp. **2**, 834 (1964).
5. D. L. Hildenbrand and E. Murad, J. Chem. Phys. **44**, 1524 (1966).
6. G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc. New York, 1950.
7. A. Harvey, Proc. Roy. Soc. (London), **133**, 336 (1931).

Dec. 31, 1968

Calcium Difluoride (CaF₂)
(Crystal) GFW = 78.0768

$\Delta H_f^\circ = -292.3 \pm 1.5$ kcal/mol
 $\Delta H_{298.15}^\circ = -293.0 \pm 1.5$ kcal/mol
 $\Delta H_f^\circ = 1.14 \pm 0.1$ kcal/mol
 $\Delta H_m^\circ = 7.10 \pm 0.1$ kcal/mol
 $\Delta H_{298.15}^\circ = 105.5 \pm 0.8$ kcal/mol

CaF₂S_{298.15} = 16.39 ± 0.08 gibbs/mol

Tt = 1424 ± 20°K (α-β)

Tm = 1691 ± 5°K

Heat of Formation

Torgeson and Sahama (1) measured the heat of solution of CaO in aqueous 20.1% HF as -54.96 ± 0.02 kcal/mol. Using ΔH_{298}° (CaO, c) = -151.79 kcal/mol (2), ΔH_{298}° (H₂O, l) = -68.317 kcal/mol (3) and ΔH_{298}° (HF, 4.4% H₂O) = -76.60 kcal/mol (4), we obtain ΔH_{298}° (CaF₂, c) = -293.6 ± 0.6 kcal/mol.

Smyslyayev and Edeleva (5) report the solubility product of CaF₂ as $2.7 \pm 0.27 \times 10^{-11}$ in dilute HCl, which yields $\Delta G_{298}^\circ = 14.42$ kcal/mol for the reaction $\text{CaF}_2(\text{c}) + \text{Ca}^{2+}(\infty, \text{aq.}) + 2\text{F}^{-}(\infty, \text{aq.})$. Using ΔG_{298}° (Ca²⁺, ∞ aq.) = -132.30 kcal/mol (2) and ΔG_{298}° (F⁻, ∞ aq.) = -66.95 kcal/mol (4) we obtain ΔG_{298}° (CaF₂, c) = -280.84 ± 0.6 kcal/mol, which using the adopted functions yields ΔH_{298}° (CaF₂, c) = -293.1 ± 0.6 kcal/mol.

Vecher and Vecher (11) have measured the ent of a high temperature solid state cell and report $\Delta G_{1700}^\circ = -17.6 \pm 0.2$ kcal/mol for the reaction $\text{CaO}(\text{c}) + \text{HgF}_2(\text{c}) + \text{CaF}_2(\text{c}) + \text{MgO}(\text{c})$. This reduces to $\Delta H_{298}^\circ = -17.6$ kcal/mol which, using JANAF values for HgO and HgF₂ and CaO from reference 2, yields ΔH_{298}° (CaF₂, c) = -294.4 ± 1.3 kcal/mol.

Kohlrausch (13) reported the solubility of CaF₂ and fluorapatite, which yield solubility products of 3.6×10^{-11} and 2.8×10^{-11} . From these we obtain, as above, ΔH_{298}° (CaF₂, c) = -292.9 and -293.1 kcal/mol.

Guntz (13) made measurements on the neutralization of $\text{Ca}(\text{OH})_2(\text{aq})$ and HF(aq) which yield ΔH_{298}° (CaF₂, c) = -293.1 kcal/mol, according to Parker (2).

A median value of ΔH_{298}° (CaF₂, c) = -293 ± 1.5 kcal/mol is adopted.

Heat Capacity and Entropy

Huffman and Norwood (6) have measured the low temperature heat capacity in the range 3.6° to 30°K. Eucken and Schwes (7) in the range 17° to 85°K and Todd (8) from 54° to 296.5°K. We have fitted a smooth polynomial curve through the data of references 6 and 8 and the yields $S_{298}^\circ = 16.39 \pm 0.08$ eu based on $S_{13.6}^\circ = 0.0002$ eu. The values of reference 7 deviate considerably at the lowest temperatures but are in reasonable agreement at higher temperatures.

The high temperature enthalpy of calcium fluoride has been reported by Naylor (9) to 1789°K, Krestnikov and Karetnikov (10) to 1273°K, and Lyashenko (11) to 1490°K. All the data are in approximate agreement and the more extensive results of Naylor on a very pure sample are adopted. The heat capacities, below 1424°K were derived from a polynomial fit of the enthalpy data of the form $H = at^3 + bt^2 + c + d/T + e/T^2$.

Transition Data

The temperature of transition is that reported by Naylor (9), the large uncertainty has been assigned since at 1424°K the enthalpies indicate complete conversion to β-CaF₂, and the next lower point is at 1407°K. Evidence in support of a transition in this region comes from Lyashenko (11) whose plot indicates a break between 1273° and 1413°K. In addition, SrCl₂ which has the fluorite structure has a transition near the melting point. The enthalpy of transition is that reported by Naylor (9).

Melting Data

McCreary (12) reports the melting point of a 99.1% pure sample as $1687 \pm 5^\circ\text{K}$. Porter and Brown (13) report $1675 \pm 5^\circ\text{K}$ as the melting point of 99.81 pure CaF₂ and Rogers et al. (14) obtained 1694°K as the melting point. The adopted melting point is $1691 \pm 5^\circ\text{K}$, for a sample of natural fluorite of high purity, was reported by Naylor (9). The heat of melting, 7100 cal, is that measured by Naylor (9). Three determinations from high temperature phase diagrams give 7750 ± 350 cal (15), 5500 cal (16) and 9800 cal (14).

Sublimation Data

See the CaF₂(g) table for details.

References:

1. D. R. Torgeson and T. G. Sahama, J. Am. Chem. Soc. 70, 2156 (1948).
2. V. B. Parker, Natl. Bur. Std., private communication Jan. 1969.
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. Consistent with the ΔH_f° value.
5. S. Smyslyayev and M. P. Edeleva, Vysokiykh Uchebn. Zavedeni, Khim. i Khim. Tekhnol. 5, 871 (1962).
6. D. E. Huffman and M. H. Norwood, Phys. Rev. 117, 709 (1960).
7. A. Eucken and F. Schwes, Ber. Deut. Physik. Ges. 15, 578 (1913).
8. S. S. Todd, J. Am. Chem. Soc. 71, 4115 (1949).
9. B. F. Naylor, J. Am. Chem. Soc. 62, 150 (1945).
10. B. F. Krestnikov and G. A. Karetnikov, Legkie Metal. 3, 29 (1934) and 16 (1935).
11. V. S. Lyashenko, J. Am. Chem. Soc. 71, 2113 (1955).
12. W. J. McCreary, J. Am. Chem. Soc. 77, 2113 (1955).
13. B. Porter and E. A. Brown, J. Am. Ceram. Soc. 45, 49 (1962).
14. P. S. Rogers, J. W. Tomlinson and F. D. Richardson, Met. Soc. Conf. 8, 909 (1961).
15. F. Debove, Compt. Rend. 252, 2192 (1961).
16. D. Vechev and A. Kremnau, Compt. Rend. 273, 360 (1966).
17. D. Kohlrausch, Z. Physik. Chem. 141, 2103 (1967).
18. F. Kohlrausch, Z. Physik. Chem. 64, 129 (1900).
19. A. Guntz, Ann. Chim. Phys. 3, 5 (1884).

(LIQUID)

CALCIUM DIFLUORIDE (CaF₂)

GFW = 78.0768

 $S_{298}^{\circ} = 22.125$ gibbs/mol $\Delta H_{298}^{\circ} = -283.477 \pm 1.5$ kcal/mol $\Delta H_m^{\circ} = 7.10 \pm 0.1$ kcal/mol $T_m = 1691 \pm 5^{\circ}\text{K}$ $\Delta H_v^{\circ} = 73.78 \pm 0.8$ kcal/mol $T_b = 2806.5 \pm 30^{\circ}\text{K}$

Heat of Formation

The heat of formation is obtained from that of the crystal by adding the heat of melting and the difference between $H_{1691} - H_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is derived from the heat content measurements of B. F. Naylor, J. Am. Chem. Soc. **57**, 150 (1943). The heat capacity is constant in the real liquid range but at 1000°K a glass transition is assumed below which it follows that of the crystal. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the crystal table for details.

Vaporization Data

The boiling point is calculated as the temperature at which $\Delta G = 0$ for the vaporization process. The heat of vaporization is the difference in $\Delta H_{T_b}^{\circ}$ between liquid and gas.

Calcium Difluoride (CaF₂)

GFW = 78.0768

(Liquid)

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log Kp
0							
100							
200							
298	16.393	22.125	22.125	.000	-283.477	-272.668	199.871
300	16.437	22.227	22.126	.030	-283.472	-272.601	199.590
400	16.511	22.456	22.130	.075	-283.465	-272.556	199.290
500	16.617	22.707	22.136	.134	-283.458	-272.526	198.980
600	16.766	23.029	22.545	.5391	-282.455	-262.100	95.470
700	16.861	37.468	27.043	7.287	-282.052	-256.739	60.782
800	20.057	40.099	28.513	9.269	-281.940	-255.411	69.775
900	22.253	42.254	30.264	11.421	-281.828	-254.083	78.768
1000	23.680	44.732	31.305	13.426	-281.300	-256.411	54.386
1100	23.680	47.008	32.431	15.614	-280.762	-245.632	46.803
1200	23.680	49.086	33.417	18.202	-282.043	-242.308	44.130
1300	23.680	50.997	34.156	20.590	-281.298	-239.026	40.184
1400	23.680	52.763	34.763	22.763	-280.530	-235.786	35.845
1500	23.680	54.414	35.203	25.366	-279.780	-232.633	33.095
1600	23.680	55.955	35.602	27.475	-279.027	-229.516	31.350
1700	23.680	57.403	35.972	30.142	-278.277	-226.443	29.111
1800	23.680	58.768	36.320	32.530	-277.530	-223.425	27.044
1900	23.680	60.034	36.651	34.681	-276.786	-220.468	25.037
2000	23.680	61.284	36.961	36.730	-276.049	-217.561	23.037
2100	23.680	62.449	37.247	38.684	-275.314	-214.694	21.044
2200	23.680	63.560	37.512	40.542	-274.582	-211.862	19.061
2300	23.680	64.622	37.760	42.307	-273.853	-209.067	17.083
2400	23.680	65.636	37.994	43.984	-273.128	-206.306	15.116
2500	23.680	66.611	38.214	45.576	-272.406	-203.576	13.166
2600	23.680	67.549	38.420	47.090	-271.687	-200.882	11.233
2700	23.680	68.451	38.612	48.542	-270.970	-198.222	9.316
2800	23.680	69.319	38.772	49.940	-270.256	-195.592	7.416
2900	23.680	70.157	38.918	51.292	-269.544	-193.000	5.533
3000	23.680	70.967	39.057	52.607	-268.834	-190.446	3.666
3100	23.680	71.750	39.192	53.884	-268.126	-187.928	1.816
3200	23.680	72.508	39.314	55.122	-267.420	-185.444	0.981
3300	23.680	73.243	39.432	56.322	-266.716	-182.994	0.161
3400	23.680	73.957	39.546	57.484	-266.014	-180.576	-0.644
3500	23.680	74.648	39.656	58.608	-265.314	-178.188	-1.466
3600	23.680	75.320	39.764	59.694	-264.616	-175.830	-2.306
3700	23.680	75.975	39.869	60.742	-263.920	-173.502	-3.166
3800	23.680	76.612	39.972	61.752	-263.226	-171.204	-4.046
3900	23.680	77.232	40.072	62.724	-262.534	-168.936	-4.946
4000	23.680	77.838	40.170	63.658	-261.844	-166.700	-5.866

Dec. 31, 1968

CALCIUM DIFLUORIDE (CaF₂)

(IDEAL GAS)

GFW = 78.0766

$$\Delta H_f^\circ = -187 \pm 2 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -187.5 \pm 2 \text{ kcal/mol}$$

Point Group = C_{2v}

$$S_{298.15}^\circ = 65.41 \pm 0.5 \text{ gibbs/mol}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$$\omega, \text{ cm}^{-1}$$

484 (1)
163 (1)
554 (1)

$$\sigma = 2$$

Bond Distance: Ca-F = 2.1 Å

Bond Angle: F-Ca-F = 135 ± 7°

$$\text{Product of the Moments of Inertia: } I_{AB} I_C = 1.2836 \times 10^{-114} \text{ g}^3 \text{ cm}^6$$

Heat of Formation

The heat of formation is obtained from that of the crystal by adding $\Delta H_{298.15}^\circ$. The vapor pressure data of five authors was analysed by 2nd and 3rd law methods to give $\Delta H_{298.15}^\circ$ as listed below. Note that the drifts are small and both positive and negative confirming the correctness of the functions used.

Reference	Range °K	Points	2nd law	3rd law	Drift
Freeman (1)	1463 - 1668	9	106.2 ± 3.7	105.66 ± 0.9	-0.2 ± 2.3
Blue et al. (2)	1246 - 1498	6	99.6 ± 2.5	106.00 ± 1.0	4.1 ± 2.0
Schulz and Searcy (3)	1421 - 1683	34	102.4 ± 0.3	104.00 ± 0.2	1.0 ± 0.2
Pottier (4)	1823	1		106.4	
Ruff and LeBoucher (5)	2086 - 2208	7	106.7 ± 4.8	105.22 ± 0.5	-0.7 ± 2.2
Blue et al. (2) *	1242 - 1669	19	104.7 ± 0.5		

* This set was not analysed by the third law since the absolute pressures were adjusted by the authors to match their weight loss values.

A median value of 105.5 ± 0.5 kcal/mol is adopted for the heat of sublimation which yields $\Delta H_{298.15}^\circ$ (CaF₂, g) = -187.5 ± 2 kcal/mol.

Heat Capacity and Entropy

The bond length was measured by Akishin and Spiridonov (6), but the diffraction patterns were interpreted as indicating a linear molecule. The vibrational frequencies and bond angle are those reported by Calder (7) using matrix isolation spectroscopy and isotopically enriched materials.

The individual moments are $I_A = 2.092 \times 10^{-39}$, $I_B = 2.3749 \times 10^{-38}$, and $I_C = 2.5840 \times 10^{-38} \text{ g cm}^2$.

References

1. R. D. Freeman, Tech. Doc. Rept. ASD TDR 63-754, Part II, Oklahoma State University, 1965.
2. G. D. Blue, J. W. Green, R. G. Bautista and J. L. Margrave, J. Phys. Chem. **67**, 877 (1963).
3. D. A. Schulz and A. W. Searcy, J. Phys. Chem. **67**, 103 (1963).
4. R. W. Pottier, quoted in Reference 1.
5. O. Ruff and L. LeBoucher, Z. Anorg. Chem. **219**, 376 (1934).
6. P. A. Akishin and V. P. Spiridonov, Kristallografiya, **2**, 475 (1957).
7. G. V. Calder, Natl. Bur. Std. Rept. 3389, July 1966.

Calcium Difluoride (CaF₂)

(Ideal Gas)

GFW = 78.0766

T, °K	C _p ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log Kp
0	0.000	0.000	INFINITE	3.025	-187.044	-187.044	INFINITE
100	9.365	53.684	75.485	1.179	-187.127	-188.046	410.974
200	11.121	60.738	66.501	1.153	-187.343	-188.876	206.396
298	12.253	65.412	65.412	0.000	-187.500	-189.597	138.131
300	12.266	65.468	65.412	0.023	-187.503	-189.611	138.131
400	12.675	69.110	65.902	1.283	-187.650	-190.290	103.970
500	13.209	72.022	66.684	2.589	-187.797	-190.933	83.457
600	13.688	74.849	67.915	3.920	-187.940	-191.546	69.770
700	13.954	76.526	69.001	5.268	-188.105	-192.133	59.987
800	13.619	78.339	70.037	6.626	-188.406	-192.668	52.635
900	13.678	79.947	71.068	7.991	-188.969	-193.155	46.904
1000	13.721	81.381	72.030	9.361	-189.389	-193.598	42.311
1100	13.753	82.700	72.941	10.735	-189.665	-193.907	38.544
1200	13.778	83.915	73.805	12.109	-189.897	-194.197	35.246
1300	13.797	85.031	74.624	13.490	-190.082	-194.455	32.474
1400	13.812	86.024	75.402	14.872	-190.229	-194.695	30.162
1500	13.825	86.978	76.143	16.252	-190.341	-194.918	28.356
1600	13.835	87.890	76.846	17.635	-190.422	-195.122	26.968
1700	13.842	88.765	77.511	19.014	-190.475	-195.305	25.905
1800	13.847	89.591	78.145	20.404	-190.505	-195.463	25.183
1900	13.851	90.250	78.742	21.789	-190.513	-195.600	24.660
2000	13.852	90.961	79.373	23.175	-190.554	-195.718	24.280
2100	13.856	91.637	79.941	24.562	-190.609	-195.814	23.959
2200	13.860	92.286	80.454	25.950	-190.685	-195.895	23.687
2300	13.864	92.906	80.924	27.336	-190.780	-195.955	23.461
2400	13.867	93.489	81.351	28.723	-190.869	-196.002	23.280
2500	13.869	94.056	81.741	30.111	-190.940	-196.036	23.146
2600	13.871	94.600	82.085	31.499	-191.021	-196.067	23.059
2700	13.873	95.124	82.488	32.886	-191.111	-196.085	22.999
2800	13.875	95.628	82.858	34.276	-191.216	-196.097	22.959
2900	13.877	96.116	83.198	35.666	-191.335	-196.105	22.936
3000	13.879	96.587	83.506	37.053	-191.471	-196.110	22.928
3100	13.880	97.043	83.782	38.442	-191.624	-196.117	22.924
3200	13.882	97.481	84.020	39.830	-191.793	-196.123	22.924
3300	13.883	97.891	84.220	41.216	-191.975	-196.128	22.924
3400	13.884	98.276	84.390	42.600	-192.170	-196.132	22.924
3500	13.884	98.636	84.536	43.999	-192.374	-196.136	22.924
3600	13.885	98.970	84.651	45.398	-192.588	-196.139	22.924
3700	13.886	99.282	84.736	46.796	-192.811	-196.142	22.924
3800	13.887	99.571	84.796	48.192	-193.042	-196.144	22.924
3900	13.887	99.837	84.833	49.587	-193.281	-196.146	22.924
4000	13.888	100.084	84.847	50.987	-193.528	-196.148	22.924
4100	13.889	100.317	84.837	52.387	-193.783	-196.150	22.924
4200	13.890	100.536	84.804	53.787	-194.046	-196.152	22.924
4300	13.890	100.741	84.749	55.187	-194.317	-196.154	22.924
4400	13.891	100.932	84.676	56.587	-194.595	-196.156	22.924
4500	13.891	101.109	84.586	57.987	-194.880	-196.158	22.924
4600	13.891	101.272	84.481	59.387	-195.171	-196.160	22.924
4700	13.891	101.422	84.361	60.787	-195.468	-196.162	22.924
4800	13.891	101.558	84.228	62.187	-195.771	-196.164	22.924
4900	13.891	101.681	84.084	63.587	-196.080	-196.166	22.924
5000	13.891	101.791	83.931	64.987	-196.394	-196.168	22.924
5100	13.891	101.888	83.768	66.387	-196.713	-196.170	22.924
5200	13.891	101.972	83.595	67.787	-197.037	-196.172	22.924
5300	13.891	102.043	83.412	69.187	-197.366	-196.174	22.924
5400	13.891	102.101	83.219	70.587	-197.699	-196.176	22.924
5500	13.891	102.146	83.016	71.987	-198.036	-196.178	22.924
5600	13.891	102.178	82.804	73.387	-198.377	-196.180	22.924
5700	13.891	102.198	82.582	74.787	-198.721	-196.182	22.924
5800	13.891	102.206	82.351	76.187	-199.067	-196.184	22.924
5900	13.891	102.202	82.111	77.587	-199.415	-196.186	22.924
6000	13.891	102.187	81.856	78.987	-199.765	-196.188	22.924

Dec. 31, 1968

Point Group [C_{∞v}]

$$\Delta H_f^\circ = 88.5 \pm 15 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = 55.4 \pm 21 \text{ gibbs/mol}$$

$$S_{298.15}^\circ = 55.4 \pm 21 \text{ gibbs/mol}$$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	
[733] (1)	
[320] (2)	
[3600] (1)	

Bond Distance: Ca-O = [1.82] Å O-H = [0.96] Å

Bond Angle: Ca-O-H = [180°]

Rotational Constant: B₀ = [0.3926] cm⁻¹

Heat of Formation

D. E. Jensen (1) determined the heat of reaction $\Delta H_r^\circ = 35 \pm 10 \text{ kcal/mol}$ for $\text{Ca(g)} + \text{OH(g)} \rightarrow \text{CaOH}^+(\text{g}) + e^-$ in atmospheric pressure hydrogen-nitrogen-oxygen flames using the microwave cavity resonance method. This value was calculated assuming a bent model for CaOH; the value is not significantly changed, within the uncertainty, by the change in configuration. Combining ΔH_r° with JANAF heats of formation of Ca(g) and OH(g) and electron, we obtain $\Delta H_f^\circ(\text{CaOH}^+, \text{g}) = 87.7 \text{ kcal/mol}$, which is adopted in the table. This corresponds to an ionization potential of 6.11 eV.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that gaseous NaOH, KOH, CaOH, RbOH are linear (2, 3, 4). This evidence also confirms the prediction of A. D. Walsh (5) that "HAB" molecules with 10 or less valence electrons (CaOH⁺ has 8 valence electrons) will be linear in their ground state. The molecules of CaOH⁺ has an isoelectronic structure of KOH.

The bond distances O-H and Ca-O are assumed to be the same as those in H₂O(g) and CaO(g), respectively (6, 7). The moment of inertia is $7.1294 \times 10^{-39} \text{ g cm}^2$.

The Ca-O stretching frequency 733 cm^{-1} is estimated from those of CaO(g) (2, 8) and CaF(g) (9). The O-H stretching frequency, 3600 cm^{-1} , is estimated from those of H₂O(g) (6) and Ca(OH)₂(g) (10). The bending vibrational frequency, 370 cm^{-1} , is estimated by comparison with those of NaOH, CaOH, RbOH (2, 4).

The enthalpy change between 0° and 298°K is 2.630 kcal/mol.

References

1. D. E. Jensen, Combustion and Flame **12**, 261 (1968).
2. N. Acquista, S. Abramowitz and D. R. Lide, J. Chem. Phys. **43**, 780 (1965).
3. R. L. Kuczkowski and D. R. Lide, J. Chem. Phys. **44**, 3131 (1966).
4. N. Acquista and S. Abramowitz, Natl. Bur. Stds. Report 9905, July 1968.
5. A. D. Walsh, J. Chem. Soc. **1953**, 2288 (1953).
6. JANAF H₂O(g) table, dated Mar. 31, 1961.
7. M. Hultin and A. Lagerqvist, Arkiv. Fysik, **2**, 471 (1950).
8. JANAF CaF(g) table, dated Dec. 31, 1968.
9. L. Brewer and R. Hauge, J. Mol. Spectry. **25**, 330 (1968).
10. O. Oehler and H. H. Günthard, J. Chem. Phys. **51**, 4714 (1969).

Calcium Monohydroxide Uniprotonated Ion (CaOH⁺)

GFW = 57.08682

(Ideal Gas)

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈)/T	H ^o - H ₂₉₈	ΔH _f ^o	ΔG _f ^o	Log K _p
0						
100						
200						
298	10.993	55.380	0.000	87.700	84.620	- 62.028
300						
350	11.009	55.484	-0.020	87.708	84.600	- 61.431
400	11.027	55.614	0.000	87.716	84.592	- 60.835
500	12.056	61.162	2.345	88.322	82.367	- 56.003
600	12.312	63.864	3.564	88.660	81.145	- 52.557
700	12.506	65.497	4.633	89.004	79.864	- 49.004
800	12.653	66.980	5.573	89.268	78.548	- 45.353
900	12.767	68.340	6.390	89.456	77.298	- 41.602
1000	12.856	69.600	7.080	89.592	76.012	- 37.752
1100	13.118	71.283	9.935	89.344	74.517	- 34.017
1200	13.253	72.630	11.293	87.576	73.167	- 30.366
1300	13.367	73.782	12.400	85.808	70.972	- 26.799
1400	13.467	74.782	13.290	84.195	69.071	- 23.306
1500	13.605	75.627	15.284	88.509	69.711	- 19.860
1600	13.705	76.308	16.669	88.464	68.464	- 16.459
1700	13.776	77.142	18.078	88.142	67.167	- 13.102
1800	13.826	77.980	19.460	87.548	65.831	- 9.780
1900	13.858	78.683	20.800	86.731	64.464	- 6.498
2000	14.023	79.403	22.199	85.642	63.065	- 3.258
2100	14.085	80.088	23.604	84.174	61.772	- 0.064
2200	14.181	80.745	25.016	82.719	60.485	3.200
2300	14.301	81.382	26.432	81.280	59.200	6.433
2400	14.444	82.000	27.850	79.858	57.929	9.664
2500	14.582	82.562	29.260	78.452	56.669	12.894
2600	14.722	83.123	30.711	76.978	55.420	16.124
2700	14.857	83.664	32.144	75.532	54.177	19.354
2800	14.980	84.182	33.570	74.110	52.949	22.584
2900	15.100	84.682	35.000	72.710	51.730	25.814
3000	15.217	85.162	36.444	71.330	50.520	29.044
3100	15.473	85.654	37.912	69.980	49.320	32.274
3200	15.497	86.116	39.360	68.664	48.130	35.504
3300	15.538	86.596	40.800	67.380	46.960	38.734
3400	15.587	87.017	42.244	66.140	45.810	41.964
3500	15.644	87.379	43.719	64.940	44.680	45.194
3600	15.714	87.698	45.175	63.780	43.570	48.424
3700	15.790	88.000	46.624	62.660	42.480	51.654
3800	15.872	88.296	48.064	61.580	41.410	54.884
3900	15.960	88.580	49.500	60.540	40.360	58.114
4000	16.052	88.856	50.944	59.540	39.330	61.344
4100	16.148	89.124	52.400	58.580	38.320	64.574
4200	16.248	89.384	53.864	57.660	37.330	67.804
4300	16.352	89.636	55.344	56.780	36.360	71.034
4400	16.460	89.880	56.840	55.940	35.410	74.264
4500	16.572	90.116	58.360	55.140	34.480	77.494
4600	16.688	90.344	59.900	54.380	33.570	80.724
4700	16.808	90.564	61.464	53.660	32.680	83.954
4800	16.932	90.776	63.064	52.980	31.810	87.184
4900	17.060	90.980	64.700	52.340	30.960	90.414
5000	17.192	91.176	66.360	51.740	30.130	93.644
5100	17.328	91.364	68.064	51.180	29.320	96.874
5200	17.468	91.544	69.800	50.660	28.530	100.104
5300	17.612	91.716	71.560	50.180	27.760	103.334
5400	17.760	91.880	73.360	49.740	27.010	106.564
5500	17.912	92.036	75.200	49.340	26.280	109.794
5600	18.068	92.184	77.080	48.980	25.570	113.024
5700	18.228	92.324	79.000	48.660	24.880	116.254
5800	18.392	92.456	80.960	48.380	24.210	119.484
5900	18.560	92.580	82.960	48.140	23.560	122.714
6000	18.732	92.696	85.000	47.940	22.930	125.944
6100	18.908	92.804	87.080	47.780	22.320	129.174
6200	19.088	92.904	89.200	47.660	21.730	132.404
6300	19.272	93.000	91.360	47.580	21.160	135.634
6400	19.460	93.092	93.560	47.540	20.610	138.864
6500	19.652	93.180	95.800	47.540	20.080	142.094
6600	19.848	93.264	98.080	47.580	19.570	145.324
6700	20.048	93.344	100.400	47.660	19.080	148.554
6800	20.252	93.420	102.760	47.780	18.610	151.784
6900	20.460	93.492	105.160	47.940	18.160	155.014
7000	20.672	93.560	107.600	48.140	17.730	158.244

June 30, 1970

Calcium Monohydroxide (CaOH)

(Ideal Gas) $\Delta H_f^\circ = 57.08737$

CALCIUM MONOHYDROXIDE (CaOH)

(IDEAL GAS)

GFV = 57.08737

Point Group $[C_{\infty v}]$ $\Delta H_f^\circ = -52.5 \pm 5 \text{ kcal/mol}$ $S_{298.15}^\circ = (56.8 \pm 2) \text{ gibbs/mol}$ $\Delta H_f^\circ_{298.15} = -53.3 \pm 5 \text{ kcal/mol}$

T, °K	C_p°	gibbs/mol $S^\circ - (C_p^\circ - H^\circ_{298})/T$	— $H^\circ - H^\circ_{298}$ — ΔH°	kcal/mol ΔG°	Log Kp
0	7.821	INFINITE	- 2.431	- 52.512	INFINITE
100	9.695	66.095	- 1.919	- 52.759	117.405
200	9.883	52.591	- 1.028	- 51.059	59.664
298	10.993	56.757	0.000	- 51.300	40.538
300	11.009	56.825	0.020	- 51.305	40.298
400	12.055	57.517	0.702	- 51.507	30.713
500	12.056	62.740	2.385	- 51.681	24.716
600	12.312	64.942	3.564	- 53.840	20.400
700	12.506	66.875	4.805	- 51.992	17.995
800	12.673	68.556	6.064	- 58.474	15.877
900	12.826	70.037	7.340	- 58.322	14.216
1000	12.976	71.417	8.630	- 58.205	12.803
1100	13.118	72.680	9.935	- 55.640	11.782
1200	13.253	73.808	11.253	- 57.005	10.629
1300	13.379	74.873	12.585	- 57.959	10.017
1400	13.500	75.886	13.840	- 58.277	9.216
1500	13.606	76.804	15.064	- 58.469	8.216
1600	13.705	77.686	16.260	- 58.644	8.177
1700	13.797	78.519	17.425	- 58.823	7.705
1800	13.880	79.310	18.409	- 58.896	7.209
1900	13.956	80.067	19.265	- 59.316	6.699
2000	14.028	80.781	20.000	- 59.812	6.038
2100	14.093	81.467	20.606	- 95.773	5.540
2200	14.153	82.124	21.018	- 95.736	5.087
2300	14.210	82.754	21.436	- 95.704	4.673
2400	14.264	83.366	21.794	- 95.677	4.294
2500	14.315	83.983	22.228	- 95.654	3.946
2600	14.365	84.506	22.689	- 95.646	3.624
2700	14.413	85.049	23.127	- 41.094	3.327
2800	14.461	85.574	23.606	- 95.654	3.050
2900	14.506	86.092	24.054	- 95.675	2.792
3000	14.554	86.595	24.405	- 95.713	2.552
3100	14.601	87.053	24.806	- 95.765	2.327
3200	14.648	87.517	25.194	- 95.837	2.114
3300	14.695	87.976	25.576	- 95.929	1.914
3400	14.741	88.430	25.967	- 96.042	1.731
3500	14.791	88.868	26.308	- 96.174	1.540
3600	14.840	89.253	26.643	- 96.341	1.387
3700	14.889	89.661	27.009	- 96.530	1.229
3800	14.939	90.068	27.347	- 96.746	1.079
3900	14.987	90.477	27.678	- 96.993	0.936
4000	15.039	90.827	28.002	- 97.269	0.800
4100	15.089	91.199	28.319	- 97.574	0.670
4200	15.139	91.563	28.630	- 97.912	0.544
4300	15.180	91.920	28.935	- 98.289	0.427
4400	15.220	92.264	29.237	- 98.669	0.314
4500	15.269	92.613	29.596	- 99.117	0.205
4600	15.319	92.950	29.909	- 99.590	0.100
4700	15.368	93.280	30.099	- 100.076	0.030
4800	15.416	93.604	30.377	- 100.602	0.000
4900	15.463	93.923	40.650	- 101.157	- 0.099
5000	15.509	94.236	60.919	- 101.740	- 0.199
5100	15.575	94.544	81.183	- 102.352	- 0.283
5200	15.620	94.847	81.443	- 102.989	- 0.370
5300	15.663	95.145	81.698	- 103.651	- 0.455
5400	15.705	95.436	81.950	- 104.338	- 0.537
5500	15.746	95.727	82.196	- 105.045	- 0.616
5600	15.786	96.011	82.442	- 105.774	- 0.693
5700	15.825	96.291	82.683	- 106.520	- 0.768
5800	15.862	96.566	82.920	- 107.285	- 0.841
5900	15.898	96.837	83.153	- 108.066	- 0.911
6000	15.932	97.105	83.384	- 108.861	- 0.980
			82.330	- 108.661	- 1.047

June 30, 1970

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	(2)
(16000)	(2)
(16100)	(2)

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	g_i
[733] (1)	[320] (2)
[3600] (1)	[3600] (1)

Bond Distance: Ca-O = [1.82] Å

Bond Angle: Ca-O-H = [180°]

Rotational Constant: $B_0 = [0.3926] \text{ cm}^{-1}$ $\sigma = 1$

Heat of Formation

Cotton and Jenkins (1) determined the equilibrium constants in the temperature range 1570°K-2030°K for the reaction $\text{Ca}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CaOH}(g) + \text{H}(g)$ by atomic absorption spectroscopy in a fuel-rich hydrogen-nitrogen-oxygen flame. Using all JANAF functions, third law analyses of the data give $\Delta H_f^\circ_{298} = 13.8 \text{ kcal/mol}$ and the drift $1.9 \pm 2.9 \text{ eu}$. This leads to the heat of formation, $\Delta H_f^\circ(\text{CaOH}, g) = -53.3 \text{ kcal/mol}$ which is adopted in the tabulation. The bond dissociation energy, $D_0(\text{Ca-OH})$, is 104.6 kcal/mol .

Rybava and Gurvich (2) reported the bond dissociation energy $D_0(\text{Ca-OH})$ as 100 kcal/mol . Schofield and Sugden (3) found $D_0(\text{Ca-OH})_2$ as $217 \pm 12 \text{ kcal/mol}$. Using the relation $D_0(\text{H-X})/D_0(\text{H-M-X}) = 0.47$ suggested by Kent, McDonald and Margrave (4), we obtain $D_0(\text{Ca-OH}) = 102 \text{ kcal/mol}$.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that gaseous NaOH, KOH, CaOH and RbOH are linear (5, 6, 7). This evidence also confirms the prediction of A. D. Walsh (8) that "HAB" molecules with 10 or less valence electrons (CaOH has 9 valence electrons) will be linear in their ground state.

The ground state is assumed to be Σ by analogy with isoelectronic CaF (9). The electronic levels are estimated from band spectra of CaOH reported by Gaydon (10).

The bond distances O-H and Ca-O are assumed to be the same as those in $\text{H}_2\text{O}(g)$ and $\text{CaO}(g)$, respectively (10, 11).

The moment of inertia is $7.1295 \times 10^{-39} \text{ g cm}^2$.

The O-H stretching frequency, 3600 cm^{-1} , is estimated from those of $\text{H}_2\text{O}(g)$ (10) and $\text{CaOH}(g)$ (12). The bending frequency, 320 cm^{-1} , is estimated by comparison with those of NaOH, CaOH and RbOH (5, 7). The Ca-O stretching frequency, 733 cm^{-1} , is estimated to be the same as that of $\text{CaO}(g)$ observed by Hultin and Lagerqvist (11) and Brewer and Hauge (13).

References

1. D. H. Cotton and D. R. Jenkins, *Trans. Faraday Soc.*, **54**, 2388 (1958).
2. V. G. Rybava and L. V. Gurvich, *Teplotfizika Vysokikh Temperatur*, **3**, 318, (1965).
3. K. Schofield and T. M. Sugden, *Trans. Faraday Soc.*, **62**, 566 (1966).
4. R. A. Kent, J. D. McDonald and J. L. Margrave, *J. Phys. Chem.*, **70**, 874 (1966).
5. N. Acquista, S. Abramowitz and D. R. Lide, *J. Chem. Phys.*, **49**, 780 (1968).
6. R. L. Kuczkowski and D. R. Lide, *J. Chem. Phys.*, **44**, 3131 (1966).
7. N. Acquista and S. Abramowitz, *Natl. Bur. Stds. Report* 9905, July, 1968.
8. A. D. Walsh, *J. Chem. Soc.*, **1933**, 2288 (1933).
9. JANAF CaF₂ table dated Dec. 31, 1968.
10. JANAF $\text{H}_2\text{O}(g)$ table dated Mar. 31, 1961.
11. M. Hultin and Lagerqvist, *Arkiv Fysik*, **2**, 471 (1950).
12. O. Oehler and H. H. Günthard, *J. Chem. Phys.*, **51**, 4714 (1969).
13. L. Brewer and R. Hauge, *J. Mol. Spectry*, **25**, 330 (1968).
14. A. G. Gaydon, *Proc. Roy. Soc. (London)*, **A233**, 437 (1955).

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	Log K _p
100	4.000	INFINITE	1.459	28,520	INFINITE	INFINITE
200	5.038	37,412	1.503	26,316	28,780	28,780
298	5.219	36,456	.000	26,805	25,102	18,400
300	5.223	36,468	.010	26,824	25,079	18,269
400	5.410	36,461	1.081	26,154	22,451	7,613
500	5.538	42,220	40,058	1,625	29,284	21,100
600	5.445	43,212	40,503	1,625	29,284	21,100
700	5.424	44,050	40,952	2,169	29,368	19,731
800	5.386	44,772	41,385	2,710	29,466	18,367
900	5.351	45,405	41,817	3,256	29,558	16,987
1000	5.314	45,767	42,187	3,760	29,644	15,587
1100	5.280	46,472	42,554	4,310	29,725	14,133
1200	5.249	46,930	42,900	4,836	29,801	12,713
1300	5.221	47,349	43,226	5,359	29,873	11,286
1400	5.197	47,735	43,534	5,880	29,941	9,853
1500	5.175	48,092	43,827	6,399	30,006	8,416
1600	5.156	48,426	44,104	6,915	30,068	6,975
1700	5.140	48,738	44,367	7,430	30,128	5,530
1800	5.125	49,031	44,618	7,943	30,184	4,080
1900	5.112	49,308	44,858	8,455	30,239	2,629
2000	5.101	49,570	45,087	8,966	30,292	1,174
2100	5.091	49,819	45,306	9,476	30,343	.029
2200	5.081	50,055	45,517	9,984	30,393	-1,782
2300	5.073	50,281	45,719	10,492	30,440	-3,204
2400	5.066	50,498	45,914	10,999	30,486	-4,625
2500	5.059	50,703	46,101	11,505	30,532	-6,046
2600	5.053	50,902	46,282	12,011	30,575	-7,461
2700	5.048	51,092	46,457	12,516	30,617	-8,873
2800	5.043	51,276	46,626	13,020	30,658	-10,283
2900	5.038	51,453	46,789	13,524	30,698	-11,693
3000	5.034	51,623	46,947	14,028	30,737	-13,103
3100	5.031	51,788	47,101	14,531	30,775	-14,513
3200	5.027	51,948	47,250	15,034	30,812	-15,923
3300	5.024	52,103	47,395	15,537	30,848	-17,333
3400	5.021	52,253	47,535	16,039	30,883	-18,743
3500	5.018	52,398	47,672	16,541	30,917	-20,153
3600	5.016	52,539	47,805	17,043	30,950	-21,563
3700	5.013	52,677	47,935	17,544	30,982	-22,973
3800	5.011	52,810	48,062	18,045	31,013	-24,383
3900	5.009	52,941	48,185	18,546	31,044	-25,793
4000	5.007	53,067	48,308	19,047	31,073	-27,203
4100	5.006	53,191	48,423	19,548	31,102	-28,613
4200	5.004	53,312	48,538	20,048	31,130	-30,023
4300	5.002	53,429	48,651	20,548	31,157	-31,433
4400	5.001	53,544	48,761	21,048	31,184	-32,843
4500	5.000	53,657	48,868	21,549	31,209	-34,253
4600	4.998	53,767	48,973	22,049	31,234	-35,663
4700	4.997	53,874	49,077	22,548	31,258	-37,073
4800	4.996	53,979	49,176	23,048	31,281	-38,483
4900	4.995	54,082	49,277	23,549	31,305	-39,893
5000	4.994	54,183	49,374	24,049	31,328	-41,303
5100	4.993	54,282	49,469	24,546	31,347	-42,713
5200	4.992	54,379	49,563	25,046	31,366	-44,123
5300	4.991	54,474	49,654	25,545	31,386	-45,533
5400	4.990	54,568	49,743	26,044	31,407	-46,943
5500	4.990	54,659	49,833	26,543	31,425	-48,353
5600	4.989	54,749	49,920	27,042	31,443	-49,763
5700	4.988	54,837	50,005	27,541	31,460	-51,173
5800	4.988	54,924	50,090	28,039	31,476	-52,583
5900	4.987	55,009	50,172	28,538	31,492	-53,993
6000	4.986	55,093	50,254	29,037	31,507	-55,403

Chlorine Unipositive Ion (Cl⁺)
(Ideal Gas) Mol. Wt. = 35.45245

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	keal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100	5.487	40.021	40.021	0.000	330.600	325.125	- 238.311
200	5.497	40.021	40.021	0.010	330.612	325.090	- 236.817
300	5.491	40.035	40.035	0.018	331.282	323.154	- 176.534
400	5.486	40.050	40.050	0.024	331.689	321.055	- 140.526
500	5.486	40.054	40.054	0.028	332.516	318.829	- 116.128
600	5.622	43.954	41.121	1.700	333.132	316.499	- 98.811
700	5.555	44.815	41.589	2.258	333.738	314.082	- 85.799
800	5.486	45.552	42.039	2.810	334.335	311.589	- 75.660
900	5.486	46.289	42.466	3.362	334.925	309.029	- 67.535
1000	5.355	46.753	42.868	3.915	335.507	306.412	- 60.876
1100	5.317	47.272	43.246	4.429	336.084	303.742	- 55.316
1200	5.276	47.733	43.601	4.959	336.655	301.022	- 50.604
1300	5.231	48.134	43.935	5.485	337.222	298.252	- 45.838
1400	5.182	48.474	44.249	6.027	337.786	295.458	- 41.026
1500	5.188	48.800	44.549	6.577	338.347	292.617	- 36.968
1600	5.168	49.234	44.831	7.045	338.905	289.743	- 32.247
1700	5.151	49.547	45.099	7.561	339.460	286.834	- 27.825
1800	5.139	49.851	45.355	8.075	340.015	283.896	- 22.654
1900	5.112	50.149	45.598	8.589	340.567	280.930	- 17.097
2000	5.118	50.631	46.054	9.101	341.118	277.932	- 12.923
2100	5.117	50.869	46.267	9.612	341.668	274.911	- 9.309
2200	5.118	51.097	46.472	10.125	342.216	271.863	- 5.832
2300	5.121	51.315	46.669	10.637	342.765	268.793	- 2.476
2400	5.120	51.524	46.859	11.149	343.312	265.700	- 0.226
2500	5.133	51.725	47.043	12.174	343.859	262.585	- 22.071
2600	5.133	51.919	47.220	12.688	344.406	259.449	- 21.000
2700	5.151	52.106	47.391	13.202	344.952	256.293	- 20.004
2800	5.152	52.287	47.557	13.718	345.497	253.117	- 19.074
2900	5.164	52.462	47.717	14.233	346.043	249.920	- 18.206
3000	5.186	52.632	47.873	14.753	346.589	246.707	- 17.392
3100	5.199	52.797	48.024	15.272	347.134	243.478	- 16.628
3200	5.213	52.957	48.171	15.793	347.679	240.231	- 15.909
3300	5.221	53.113	48.314	16.315	348.224	236.967	- 15.231
3400	5.221	53.265	48.454	16.838	348.769	233.685	- 14.591
3500	5.256	53.412	48.589	17.363	349.314	230.393	- 13.986
3600	5.270	53.557	48.722	17.889	349.859	227.077	- 13.412
3700	5.285	53.697	48.851	18.417	350.405	223.755	- 12.868
3800	5.293	53.835	48.977	18.946	350.951	220.414	- 12.351
3900	5.313	53.969	49.100	19.477	351.495	217.059	- 11.859
4000	5.326	54.101	49.220	20.009	352.042	213.687	- 11.390
4100	5.339	54.229	49.338	20.542	352.588	210.311	- 10.943
4200	5.352	54.355	49.453	21.077	353.135	206.916	- 10.516
4300	5.366	54.476	49.566	21.612	353.682	203.513	- 10.108
4400	5.377	54.598	49.677	22.149	354.229	200.088	- 9.717
4500	5.388	54.717	49.785	22.688	354.778	196.660	- 9.343
4600	5.400	54.833	49.891	23.227	355.327	193.217	- 8.984
4700	5.410	54.947	49.995	23.768	355.876	189.758	- 8.639
4800	5.420	55.059	50.097	24.309	356.426	186.293	- 8.309
4900	5.430	55.168	50.196	24.852	356.976	182.819	- 7.991
5000	5.439	55.276	50.295	25.395	357.528	179.326	- 7.684
5100	5.448	55.381	50.393	25.930	358.080	175.833	- 7.390
5200	5.456	55.485	50.488	26.465	358.633	172.320	- 7.105
5300	5.464	55.587	50.582	27.001	359.187	168.799	- 6.831
5400	5.470	55.688	50.674	27.537	359.741	165.266	- 6.567
5500	5.477	55.786	50.764	28.073	360.295	161.724	- 6.311
5600	5.483	55.883	50.853	28.613	360.850	158.178	- 6.065
5700	5.489	55.979	50.941	29.154	361.406	154.613	- 5.826
5800	5.495	56.073	51.027	29.700	361.962	151.040	- 5.595
5900	5.499	56.165	51.112	30.250	362.519	147.467	- 5.371

Cl⁺

MOL. WT. = 35.45245

(IDEAL GAS)

CHLORINE UNIPOSITIVE ION (Cl⁺)

Ground State Configuration ³P₂
ΔH_f^o 0 = 328.7 ± .5 kcal./mole⁻¹
ΔH_f^o 298.15 = 330.8 ± .5 kcal./mole⁻¹
S_{298.15}^o = 40.021 cal. deg.⁻¹ mole⁻¹

Electronic Levels and Quantum Weight				
E _i , cm. ⁻¹	g _i	E _i , cm. ⁻¹	g _i	
0.0	5	27900.0	1	
		93366.6	5	
		93998.7	3	
		94332.8	1	

Heat of Formation.

The heat of formation was calculated from the equation: Cl(g) - e⁻ → Cl⁺(g) with the JANAP auxiliary value for Cl(g) using an I.P. = 1.04991 X 10⁵ cm.⁻¹ (300.206 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, loc. cit. The electronic levels above 1 X 10⁵ cm.⁻¹ were omitted because their contribution is negligible below 6000°K. The H^o-H₂₉₈^o value at 0°K. is -1.526 kcal./mole.

Cl⁺

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0						
100	4.968	36.628	0.000	- 55.900	- 57.389	42.066
200	4.968	36.628	0.009	- 55.907	- 57.398	41.813
300	4.968	36.628	0.066	- 56.322	- 57.834	31.597
400	4.968	36.628	0.203	- 56.749	- 58.262	25.421
500	4.968	36.628	0.321	- 57.176	- 58.690	21.272
600	4.968	36.628	0.430	- 57.599	- 59.117	18.286
700	4.968	36.628	0.530	- 58.017	- 59.544	15.678
800	4.968	36.628	0.621	- 58.430	- 59.967	13.426
900	4.968	36.628	0.704	- 58.839	- 60.386	11.516
1000	4.968	36.628	0.780	- 59.244	- 60.801	9.926
1100	4.968	36.628	0.849	- 59.645	- 61.212	8.646
1200	4.968	36.628	0.912	- 60.042	- 61.619	7.632
1300	4.968	36.628	0.970	- 60.435	- 62.022	6.857
1400	4.968	36.628	1.023	- 60.824	- 62.421	6.282
1500	4.968	36.628	1.071	- 61.209	- 62.816	5.872
1600	4.968	36.628	1.115	- 61.590	- 63.207	5.512
1700	4.968	36.628	1.155	- 61.967	- 63.594	5.192
1800	4.968	36.628	1.191	- 62.340	- 63.977	4.912
1900	4.968	36.628	1.223	- 62.709	- 64.356	4.672
2000	4.968	36.628	1.251	- 63.074	- 64.731	4.472
2100	4.968	36.628	1.275	- 63.435	- 65.102	4.312
2200	4.968	36.628	1.296	- 63.792	- 65.469	4.182
2300	4.968	36.628	1.313	- 64.145	- 65.832	4.082
2400	4.968	36.628	1.327	- 64.494	- 66.191	3.992
2500	4.968	36.628	1.339	- 64.839	- 66.546	3.912
2600	4.968	36.628	1.348	- 65.180	- 66.897	3.842
2700	4.968	36.628	1.355	- 65.517	- 67.244	3.782
2800	4.968	36.628	1.360	- 65.850	- 67.587	3.732
2900	4.968	36.628	1.363	- 66.179	- 67.926	3.692
3000	4.968	36.628	1.365	- 66.504	- 68.261	3.662
3100	4.968	36.628	1.366	- 66.825	- 68.592	3.642
3200	4.968	36.628	1.366	- 67.142	- 68.919	3.632
3300	4.968	36.628	1.365	- 67.455	- 69.242	3.632
3400	4.968	36.628	1.363	- 67.764	- 69.561	3.642
3500	4.968	36.628	1.360	- 68.069	- 69.876	3.662
3600	4.968	36.628	1.356	- 68.370	- 70.187	3.692
3700	4.968	36.628	1.351	- 68.667	- 70.494	3.732
3800	4.968	36.628	1.345	- 68.960	- 70.797	3.782
3900	4.968	36.628	1.338	- 69.249	- 71.096	3.842
4000	4.968	36.628	1.330	- 69.534	- 71.391	3.912
4100	4.968	36.628	1.321	- 69.815	- 71.682	3.992
4200	4.968	36.628	1.311	- 70.092	- 71.969	4.082
4300	4.968	36.628	1.300	- 70.365	- 72.252	4.182
4400	4.968	36.628	1.288	- 70.634	- 72.531	4.292
4500	4.968	36.628	1.275	- 70.899	- 72.806	4.412
4600	4.968	36.628	1.261	- 71.160	- 73.077	4.542
4700	4.968	36.628	1.246	- 71.417	- 73.344	4.682
4800	4.968	36.628	1.230	- 71.670	- 73.607	4.832
4900	4.968	36.628	1.213	- 71.919	- 73.866	4.992
5000	4.968	36.628	1.195	- 72.164	- 74.121	5.162
5100	4.968	36.628	1.176	- 72.405	- 74.372	5.342
5200	4.968	36.628	1.156	- 72.642	- 74.619	5.532
5300	4.968	36.628	1.135	- 72.875	- 74.862	5.732
5400	4.968	36.628	1.113	- 73.104	- 75.101	5.942
5500	4.968	36.628	1.090	- 73.329	- 75.336	6.162
5600	4.968	36.628	1.066	- 73.550	- 75.567	6.392
5700	4.968	36.628	1.041	- 73.767	- 75.794	6.632
5800	4.968	36.628	1.015	- 73.980	- 76.017	6.882
5900	4.968	36.628	0.988	- 74.189	- 76.236	7.142
6000	4.968	36.628	0.960	- 74.394	- 76.451	7.412

June 30, 1965

CHLORINE UNINEGATIVE ION (Cl⁻) (IDEAL GAS) MOL. WT. = 35.45355

Ground State Configuration 1s₀
S°_{298.15} = 36.628 cal. deg.⁻¹ mole⁻¹
ΔH°_f 0 = -54.8 ± .5 kcal. mole⁻¹
ΔH°_f 298.15 = -55.9 ± .5 kcal. mole⁻¹

Electronic Levels and Quantum Weight

E, cm. ⁻¹	g _i
0.0	1
93143.8	5
93750.639	3
94553.707	1
95399.870	3

Heat of Formation.

The heat of formation was calculated from the equation: Cl(g) + e⁻ → Cl⁻(g) with the JANAF auxiliary values for Cl(g); using the measured electron affinity = 3.613 e.v. (83.316 kcal/mole) obtained from R. S. Berry and C. W. Reimann, J. Chem. Phys. 39, 1540 (1963). Other calculated values for the electron affinity are: 3.70 e.v. reported by B. Edlen, J. Chem. Phys. 33, 98 (1960) and 3.56 e.v. reported by E. Clementi, A. D. McLean, D. L. Reimondi and M. Yoshimine, Phys. Rev. 133, A1274 (1964).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Argon. The electronic levels above 1 X 10⁵ cm.⁻¹ were omitted because their contribution is negligible below 6000°K. The H°-H°₂₉₈ value at 0°K. is -1.481 kcal/mole.

Cl⁻

Cesium Chloride (CsCl)

(Crystal)

GFW = 168.358

T, °K	Cp	$S^{\circ} - (G^{\circ} - H_{298}^{\circ})/T$	gibbs/mol	$H^{\circ} - H_{298}^{\circ}$	kcal/mol	ΔH_f°	ΔG_f°	Log Kp
0	10.530	11.924	34.996	2.317	-105.875	-105.875	11.91715	
100	11.521	15.294	25.314	-1.204	-105.968	-103.679	226.599	
200	12.534	24.183	16.183	.000	-105.840	-101.300	110.596	
298	12.541	24.193	16.183	.000	-105.840	-99.038	77.597	
300	12.541	24.261	16.183	.000	-105.838	-98.894	72.119	
400	13.500	35.915	25.640	2.637	-106.077	-94.157	41.160	
500	14.125	33.441	26.735	4.024	-105.867	-91.803	33.439	
600	14.550	35.458	27.854	5.462	-105.607	-89.479	27.537	
700	15.720	38.071	29.943	7.863	-104.390	-87.266	23.240	
800	16.220	40.521	31.952	10.230	-102.774	-85.234	19.574	
900	16.460	42.693	33.424	12.482	-100.167	-82.520	15.600	
1000	15.580	43.772	33.427	14.046	-118.550	-74.852	13.632	
1200	15.700	45.133	33.427	14.046	-118.550	-74.852	13.632	
1300	15.720	45.994	33.377	15.622	-117.962	-71.236	11.976	
1400	15.840	47.271	33.278	16.210	-117.289	-64.167	9.346	
1500	15.960	48.075	33.135	16.810	-116.634	-60.467	8.287	
1600	16.180	49.715	36.951	20.422	-115.975	-60.467	8.287	
1700	16.310	50.700	37.731	22.047	-115.305	-57.233	7.358	
1800	16.530	51.636	38.476	23.684	-114.658	-53.826	6.537	
1900	16.750	52.524	39.178	25.324	-114.024	-50.376	5.815	
2000	16.970	53.376	39.882	26.964	-113.291	-47.156	5.153	

CESIUM CHLORIDE (CsCl)

(CRYSTAL)

GFW = 168.358

S_{298,15}[°] = 24.183 ± 0.005 gibbs/mol $\Delta H_f^{\circ} = -105.84 \pm 0.2$ kcal/mol

Tf(α-β) = 743°K

 $\Delta H_f^{\circ} = -105.84 \pm 0.2$ kcal/mol

Tm = 918°K

 $\Delta H_m^{\circ} = 3.8$ kcal/mol $\Delta H_f^{\circ} = 0.90$ kcal/mol $\Delta H_m^{\circ} = 3.8$ kcal/mol $\Delta H_f^{\circ} = 48.74$ kcal/mol

Heat of Formation

The heat of solution (ΔHsoln) of CsCl(c) in water has been measured by Forcand (1, 2), Haigh (3), Samoilov (4, 5), and Rodnikova (6). Based on their results, Parker (7) derived the corresponding ΔHsoln_{298,15}(∞ H₂O) values as 4.30, 4.32, 4.08, 4.25, 4.18 and 4.18 kcal/mol. Borob'ev (8) determined the same quantity and reported ΔHsoln₂₉₈(CsCl, ∞ H₂O) = 4.20 ± 0.04 kcal/mol. Using this value, 4.20 kcal/mol, and ΔH_f[°] = -61.69 (9) and -39.952 kcal/mol (10) for Cs⁺(∞ H₂O) and Cl⁻(∞ H₂O), respectively, we evaluate ΔH_f[°](CsCl, c) = -105.84 ± 0.2 kcal/mol, which is adopted.

Heat Capacity and Entropy

Taylor (11) measured the low temperature heat capacities, 7.19 - 299.38°K, with an adiabatic calorimeter; the sample purity was >99.95 per cent. Employing these data we derive the value S₂₉₈[°] = 24.183 eu based on S₁₉[°] = 0.031 eu.

The high temperature enthalpies, 385.2 - 904.9°K, were measured by Kaylor (21, 22, 23), using a Bunsen ice calorimeter and a CsCl sample of 99.8 per cent purity. The heat capacities derived from the reported enthalpy data at temperatures 385.2 - 740.5°K appear too low (less than the adopted Cp's systematically) by 0.9 gibbs/mol to join smoothly with the low temperature data at 298°K. The Cp values derived from the measured enthalpy data in the temperature range 760 - 920°K increase rapidly from 14.46 to 16.3 gibbs/mol. In order to rationalize this situation, we adopt the high temperature heat capacities, 298 - 743°K, for CsCl(α) obtained by linear extrapolation of the low temperature data. The Cp values for CsCl(β) are adjusted such that the rate of increase in heat capacities is linear and less rapid than the original one, and the total enthalpy remains essentially unchanged. The discrepancy between the high and low temperature Cp for CsCl(α) may be caused by the incomplete β → α phase conversion involved. In order to resolve this discrepancy, independent enthalpy measurements using a high purity sample with composition well characterized before and after each drop experiment seem necessary.

Transition Data

The temperature of transition (in °K) has been reported by many investigators as 718 (14), 752 (15), 745 (16), 742 (21), 742.5 (12), 743 (20), and 733 (17), using different methods and samples of different purity. The value adopted is 743°K.

The heat of transition (in kcal/mol) was reported to be 1.8 (14), 1.55 (18), 1.4 (19), 0.80 (21), 0.58 (12), 0.90 (13), and 1.1 (17). A median value 0.90 kcal/mol is tentatively adopted.

Melting Data

See CsCl(β) table for details.

Heat of Sublimation

ΔH_s[°]₂₉₈ is calculated as the difference between ΔH_f[°] for CsCl(g) and CsCl(c).

References

1. R. de Forcand, *Compt. Rend.* **143**, 98 (1906); 1 point, concentration m = 0.25 (19°K) where m is molality.
2. R. de Forcand, *Ann. Chim. Phys.* **81**, 24, 256 (1911); *Compt. Rend.* **132**, 27 (1911); 1 point, m = 0.50 (15°K).
3. E. J. Haigh, *Ann. Chem. Soc.* **25**, 358, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000.
4. O. Y. Rodnikova, *Zh. Neorg. Khim.* **3**, 2417 (1958); 6 points, m = 0.05 (15, 35°K).
5. O. Y. Samoilov and M. N. Buslaeva, *Stroenie Veshchestva i Spektroskopiya*, Akad. Nauk SSSR, 102 (1960); 3 points, m = 0.06 (15, 35°K).
6. V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-NBS 2, 1965.
7. A. R. Borob'ev, M. A. Abram, and S. G. Kuratov, *Russ. J. Inorg. Chem. (English Transl.)* **11**, 13 (1966).
8. A. R. Borob'ev, *Chem. Abstr.* **57**, 1386 (1957).
9. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
10. A. R. Taylor, Jr., T. E. Gardner, and D. F. Smith, U. S. Bur. Mines RI 6157 (1963).
11. D. F. Smith, C. E. Kaylor, G. E. Walden, and D. F. Smith, *J. Phys. Chem.* **64**, 276 (1960).
12. D. F. Smith, C. E. Kaylor, G. E. Walden, and D. F. Smith, *J. Phys. Chem.* **64**, 276 (1960).
13. W. M. Wagner and L. R. Applegate, *J. Phys. Chem.* **64**, 276 (1960).
14. J. W. Wood, N. Seconda, and C. H. McBride, *J. Am. Chem. Soc.* **80**, 307 (1958).
15. J. W. Wood, N. Seconda, and C. H. McBride, *J. Am. Chem. Soc.* **80**, 307 (1958).
16. J. W. Wood, N. Seconda, and C. H. McBride, *J. Am. Chem. Soc.* **80**, 307 (1958).
17. A. J. Hajundar and R. Roy, *J. Inorg. Nucl. Chem.* **27**, 1961 (1965).
18. J. Krogh-Moe, *J. Am. Chem. Soc.* **82**, 2399 (1960).
19. J. Krogh-Moe, *J. Am. Chem. Soc.* **82**, 6196 (1960).
20. C. E. Johnson, J. A. McGon, and H. A. Bredig, *J. Am. Chem. Soc.* **77**, 2734 (1955).
21. C. E. Kaylor, Ph. D. Thesis, University of Alabama, 1958.

(Liquid)

GFW = 168.358

CESIUM CHLORIDE (CsCl)

(LIQUID)

GFW = 168.358

$$S_{298.15}^{\circ} = 24.309 \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} = -103.84 \pm 2.0 \text{ kcal/mol}$$

$$T_m = 918^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 3.8 \pm 1 \text{ kcal/mol}$$

$$T_b = 1597.3^{\circ}\text{K}$$

$$\Delta H_v^{\circ} = 27.52 \text{ kcal/mol of liquid (to equilibrium mixture)}$$

Heat of Formation

 $\Delta H_f^{\circ}(s) \text{ is obtained from } \Delta H_f^{\circ}(c) \text{ by adding } \Delta H_m^{\circ} \text{ and the difference between } H_{918}^{\circ} - H_{298}^{\circ} \text{ for crystal and liquid.}$

Heat Capacity and Entropy

The enthalpies of CsCl(*l*) at temperatures 923.6 - 1164.0°K were measured with a Bunsen ice calorimeter by Kaylor (1, 2). Dworkin (3) derived the heat capacity of CsCl(*l*) as 18.5 gibbs/mol from enthalpy data at temperatures 918 - 980°K. This value is adopted since it is in agreement with the enthalpy values reported by Kaylor et al. The heat capacity at temperatures above 1168 and below 923.6°K is assumed to be 18.5 gibbs/mol. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting temperature (in °K) of CsCl(*c*) has been determined by many investigators as 904 ± 3 (4), 918 (5), 912 (6), 911 (7), 918 (8), 916 (9), and 919 (13). The cause of the discrepancies is probably due to the difference in purity of the samples. The melting temperature adopted is 918°K.

The heat of melting (in kcal/mol) was reported to be 4.84 (10), 4.97 (15), 4.58 (10), 4.96 (11), and 4.78 (2), which were obtained calorimetrically. Using a modification of Kelley's method of obtaining heat of melting from freezing point data on binary systems involving CsCl (18), we derive the value of ΔH_m° as 3.6 - 4.0 kcal/mol, based on the following systems:

CsCl-NaCl (5), CsCl-CuCl (9), CsCl-AgCl (9), CsCl-LiCl (9), and CsCl-Cs₃(PO₃)₃ (12). The heat of melting for CsCl(*c*) is tentatively adopted as 3.8 kcal/mol. The ΔH_m° values obtained calorimetrically are not used due to the uncertainties of the state of the sample before and after the enthalpy measurements.

Vaporization Data

T_b is the temperature at which the calculated total pressures of CsCl(*g*) and Cs₂Cl₂(*g*) equal one atmosphere. The vapor composition at *T_b* is derived as CsCl 80.4 per cent and Cs₂Cl₂ 19.6 per cent. The boiling point of CsCl(*l*) has been determined by several investigators as 1562 (12), 1572 (18), and 1576 (19). The heat required to vaporize one mole of liquid to the above vapor mixture at *T_b* is ΔH_v° .

References

1. C. E. Kaylor, G. E. Walden, and D. F. Smith, *J. Phys. Chem.* **64**, 276 (1960).
2. D. F. Smith, C. E. Kaylor, G. E. Walden, A. R. Teylor, Jr., and J. B. Gayle, U. S. Bur. Mines RI 5832, 1961.
3. A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tennessee, December 1, 1964.
4. T. Carnalley and Carleton-Williams, *J. Chem. Soc.* **37**, 125 (1960).
5. S. Zenzuzny and F. Rembach, *Z. Anorg. Chem.* **65**, 415 (1910).
6. C. Sandomini, *Atti Acc. Linc. Ser. 5*, **21** II, 77 (1912).
7. E. Korng, *Z. Anorg. Chem.* **91**, 194 (1915).
8. T. W. Richards and W. B. Meldrum, *J. Am. Chem. Soc.* **39**, 1816 (1917).
9. B. F. Markov and I. D. Panchenko, *Russ. J. Gen. Chem. (English Transl.)* **25**, 1987 (1955).
10. C. E. Kaylor, Ph. D. Thesis, University of Alabama, 1958.
11. C. E. Kaylor, G. E. Walden, and D. F. Smith, *J. Phys. Chem.* **64**, 276 (1960).
12. G. A. Bukhalova and I. V. Hardirosova, *Russ. J. Inorg. Chem. (English Transl.)* **12**, 1158 (1967).
13. G. A. Bukhalova and D. V. Semetsova, *Russ. J. Inorg. Chem. (English Transl.)* **10**, 1027 (1965).
14. A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.* **64**, 269 (1960).
15. Determined by D. F. Smith, University of Alabama; quoted by Dworkin (14).
16. K. K. Kelley, U. S. Bur. Mines Bull. **393**, 1936.
17. O. Ruff and S. Magdan, *Z. Anorg. Allgem. Chem.* **117**, 147 (1921).
18. I. G. Murgulescu and L. Topor, *Rev. Roum. Chim.* **12**, 1077 (1967).
19. H. von Wartenberg and H. Schulz, *Z. Elektrochem.* **27**, 568 (1921).

June 30, 1968

CICs

CESIUM CHLORIDE (CsCl)

(IDEAL GAS)

GFW = 168.358

Ground State Configuration $1s^2$ $\Delta H_f^\circ = -56.9 \pm 1 \text{ kcal/mol}$ $S_{298.15}^\circ = 61.175 \pm 0.005 \text{ gibbs/mol}$ $\Delta H_f^\circ = -57.4 \pm 1 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	1
$\omega_e = 213.08 \pm 0.05 \text{ cm}^{-1}$	$\omega_e x_e = 0.733 \pm 0.008 \text{ cm}^{-1}$
$B_e = 0.07134 \text{ cm}^{-1}$	$\alpha_e = 0.000332 \text{ cm}^{-1}$
	$\sigma = 1$
	$r_e = 2.906 \text{ \AA}$

Heat of Formation

The total pressures of CsCl(g) and $\text{Cs}_2\text{Cl}_2(\text{g})$ over CsCl(c) and CsCl(l) in the temperature range 605 - 1577°K have been determined by manometric, transpiration and Knudsen effusion methods by many investigators. Based on the reported results, the partial pressures of CsCl(g) and $\text{Cs}_2\text{Cl}_2(\text{g})$ are calculated using the derived free energy functions for CsCl(c), CsCl(l), CsCl(g) and $\text{Cs}_2\text{Cl}_2(\text{g})$, and the heats of sublimation and vaporization which are adjusted so that the sum of the calculated partial pressures of CsCl(g) and $\text{Cs}_2\text{Cl}_2(\text{g})$ approaches the measured total pressures, and the evaluated second and third law ΔH_{298}° values are in reasonable agreement. The results obtained are presented in the table below. The value of $\Delta H_{298}^\circ(\text{CsCl}, \text{g})$ adopted is $-57.4 \pm 1 \text{ kcal/mol}$.

Gaydon (10) reported $D_0(\text{Cs-Cl}) = 4.6 \pm 0.2 \text{ eV}$ or $106.08 \pm 4.61 \text{ kcal/mol}$. Using this D_0 value and $\Delta H_f^\circ = 18.683$ and 28.52 kcal/mol for Cs(g) and Cl(g), we evaluate $\Delta H_{298}^\circ = -59.4 \pm 4.6 \text{ kcal/mol}$ for CsCl(g), which is in fair agreement with the adopted value.

Investigator	Reaction*	Method	Temperature, °K	No. of Points	Second Law $\Delta H_{298}^\circ, \text{kcal/mol}$	Third Law $\Delta H_{298}^\circ, \text{kcal/mol}$	Drift eu $\Delta H_{298}^\circ, \text{kcal/mol}$
1. Miwa (1938)	1	A	793-893	11	46.81±0.35	49.32	3.7±0.4
2. Coggin (1948)	1	A	690-891	28	47.80±0.31	47.88	0.1±0.4
3. Treadwell (1953)	1	B	784-905	10	47.08±0.26	49.17	2.5±0.3
4. Mesnyanov (1960)	1	A	505-851	16	45.26±0.38	48.74	4.7±0.5
5. Martenben (1921)	2	C	1335-1577	9	49.36±0.50	46.27	-2.1±0.3
6. Ruff (1921)	2	C	1259-1568	7	51.61±1.08	46.17	-3.8±0.8
7. Flock (1926)	2	C	1098-1293	9	47.57±0.08	46.52	-0.9±0.1
8. Kangro (1938)	2	B	1133-1263	3	48.73±2.09	47.00	-1.4±1.7
9. Schrier (1961)	2	C	1165-1387	10	47.46±0.08	46.36	-0.9±0.1
16. Murgulescu (1967)	1	A	1174-1353	10	47.97±0.15	46.54	-1.1±0.1
*1. CsCl(c) = CsCl(g); 2. CsCl(l) = CsCl(g); A = Knudsen effusion; B = transpiration; and C = manometric.							
**Calculation based on the third law ΔH_{298}° value.							

Heat Capacity and Entropy

Clausen (11) studied the pure rotational spectra of CsCl(g) in the 0.36 - 3 mm range of the microwave region with the molecular-beam spectrometer, and derived the values of B_e , α_e , ω_e , $\omega_e x_e$ and r_e , which are adopted and corrected to the average isotopic species.

The Cs-Cl bond distance was measured as $3.06 \pm 0.03 \text{ \AA}$ by the electron diffraction method by Maxwell (12), which is not used. Similar values of B_e and α_e were reported by Honig (13) and Rice (14), determined from microwave and infrared spectra, respectively. Barrow (15) gave $\omega_e = 240 \text{ cm}^{-1}$ (CsCl₃₅) which is significantly different from the adopted value 214.22 cm^{-1} for CsCl₃₅ and the value $209 \pm 6 \text{ cm}^{-1}$ reported by Rice (14). The moment of inertia is $3.924 \times 10^{-38} \text{ g cm}^2$.

References

1. K. Niwa, J. Fac. Sci., Hokkaido Univ., Ser. III, 2, 201 (1938).
2. E. F. Coker, G. K. Kell, J. Chem. Phys., 15, 1035 (1948).
3. W. D. Treadwell and W. Werner, Helv. Chim. Acta, 36, 1436 (1953).
4. A. N. Mesnyanov and L. A. Sazonov, Russ. J. Inorg. Chem. (English Transl.), 5, 248 (1960).
5. H. von Martenben and H. Schulz, Z. Elektrochem., 57, 568 (1953).
6. O. Ruff and S. Hugdun, Z. Anorg. Allgem. Chem., 117, 147 (1921).
7. F. Flock and W. H. Riedel, Ann. Chem., 522, 221 (1936).
8. W. Kangro, J. Chem. Phys., 6, 522 (1938).
9. E. Schrier, Ph. D. Thesis, Rensselaer Polytechnic Institute, 1961.
10. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.
11. P. L. Clausen and W. Gordy, Phys. Rev., 134, A863 (1964).
12. L. R. Maxwell, S. B. Hendricks and V. H. Noyes, Phys. Rev., 52, 968 (1937).
13. L. Honig, H. Mandel, H. L. Sticht and H. H. Townes, Phys. Rev., 137, 137 (1956).
14. R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London), A219, 120 (1953).
15. I. G. Murgulescu and L. Topor, Rev. Roum. Chim., 12, 1077 (1967).

T, °K	C _p	cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0							
100							
200							
298	11.400	20.800	20.800	0.000	-33.000	-28.898	21.183
300	11.656	20.872	20.800	0.022	-32.997	-28.873	21.034
400	13.600	24.540	21.287	1.301	-32.720	-27.535	19.044
500	14.300	27.656	22.758	2.669	-32.374	-26.275	11.465
600	14.700	30.300	23.384	4.149	-31.991	-25.002	9.140
700	15.000	32.589	24.039	5.635	-31.589	-23.072	7.484
800	15.220	34.607	25.671	7.146	-31.178	-22.014	6.260
900	15.389	36.410	26.768	8.677	-30.759	-21.005	5.319
1000	15.540	38.039	27.615	10.224	-30.338	-20.044	4.577
1100	15.662	39.326	28.413	11.784	-29.912	-20.025	3.979
1200	15.777	40.494	29.764	13.356	-29.486	-19.146	3.497
1300	15.884	42.161	30.669	14.939	-29.058	-18.301	3.077
1400	15.983	43.542	31.533	16.532	-31.815	-17.368	2.714
1500	16.075	44.447	32.357	18.135	-31.415	-16.371	2.385

$S_{298}^{0,15} = 20.8 \pm 1.0$ cal. deg.⁻¹ mole⁻¹
 $T_m = 703^\circ\text{K}.$

$\Delta H_f^0 = \text{Unknown}$
 $\Delta H_f^0 298.15 = -33.0 \pm 0.4$ kcal. mole⁻¹
 $\Delta H_m^0 = 2.445$ kcal. mole⁻¹
 $\Delta H_g^0 298.15 = 54.77 \pm 0.5$ kcal. mole⁻¹ of monomer
 $\Delta H_g^0 298.15 = 37.2 \pm 0.2$ kcal. mole⁻¹ of trimer

Heat of Formation.

There have been three calorimetric determinations of the heat of formation. Thomsen, "Thermochemische Untersuchungen", Barth, Leipzig (1882-1886) reported -32.675 kcal. mole⁻¹. Barthelot, Ann. Chim. Phys. 20, 504 (1880) reported -35.6 kcal. mole⁻¹ and H. V. Wartenberg and H. Werth, Z. physik. Chem. A 151, 109 (1930) reported -32.1 ± 0.4 kcal. mole⁻¹. In addition, values of the heat of formation have been derived from several sets of equilibrium data. A. A. Noyes and M. Chow, J. Am. Chem. Soc. 40, 739 (1918) from a study of cell potentials derived $\Delta H_f^0 = 7.19$ kcal. for the reaction $\text{Cu(c)} + \text{HCl(aq)} \rightarrow \text{CuCl(c)} + 1/2 \text{H}_2(\text{g})$ which yields $\Delta H_f^0 298(\text{CuCl}) = -32.76$ kcal. mole⁻¹. Several investigators have studied the reaction $2\text{CuCl(c)} + \text{H}_2(\text{g}) \rightarrow 2\text{Cu(c)} + 2\text{HCl(g)}$ and its reverse reaction. These include A. B. Eggesarian, Trans. Am. Electrochem. Soc. 51, 449 (1927) who reported equilibrium constants which result in 2nd and 3rd law heats of reaction of 24.3 and 23.2 kcal. mole⁻¹; A. F. Kapustinsky, J. Am. Chem. Soc. 59, 460 (1936) who obtained similarly 20.1 and 21.8 kcal. mole⁻¹; S. A. Shchukarev and M. A. Orenskaia, Z. Obshchei. Khim. 24, 1928 (1954) obtained 25.4 and 21.5 kcal. mole⁻¹ for the 2nd and 3rd law heat of reaction. These yield values for $\Delta H_f^0 298(\text{CuCl})$ ranging from -32.1 to -34.8 . M. Watanabe, Bull. Inst. Phys. Chem. Res. 9, 94 (1929) from cell studies reports $\Delta H_f^0 298(\text{CuCl}) = -34.6$ kcal. mole⁻¹. A value of $\Delta H_f^0 298$ can also be obtained from $\Delta H_f^0(\text{CuCl}_2(\text{g}))$, which is fixed independently and known with good precision. Using the 3rd law heat of sublimation of CuCl(c) to trimer determined by D. W. Magee, Doctoral Thesis, Ohio State University (1955) [See trimer table], we obtain $\Delta H_f^0 298 \text{ CuCl(c)} = -33.01 \pm 0.3$ kcal. mole⁻¹. A weighted average of -33.0 ± 0.4 kcal. mole⁻¹ was adopted.

Heat Capacity and Entropy.

The entropy of CuCl was obtained from the several pieces of equilibrium data reported above and the adopted $\Delta H_f^0 298$. A weighted average of 20.8 ± 1 cal/(mole-deg) was adopted for $S_{298}^0 \text{ CuCl(c)}$. The enthalpy and heat capacity above $298^\circ\text{K}.$ have been reported by A. N. Kretzovnikov and O. A. Kretzovnikov, Jour. Oen. Chem. (USSR) 5, 955 (1936). However these values were not adopted since they do not give reasonable heat capacities and other data by these workers is not in agreement with established values. Heat capacities equal to those of AgCl, as given by K. K. Kelley, U. S. Bureau of Mines Bulletin 584, Washington 1960, were adopted here above $298^\circ\text{K}.$

Melting Data.

The temperature end heat of melting were those selected by K. K. Kelley, U. S. Bur. Mines Bulletin 393 (1936), from phase studies. The heat of melting was reported by Kretzovnikov and Kretzovnikov loc. cit. as 2.54 kcal. mole⁻¹.

Sublimation Data.

The heat of sublimation was calculated from the adopted heats of formation at 298° for the reaction $x \text{ CuCl(c)} \rightarrow (\text{CuCl})_x(\text{g})$ where $x = 1$ or 3 . See the respective gas tables for details.

Copper Monochloride (CuCl)

Mol. Wt. = 98.993

(Liquid)

COPPER MONOCHLORIDE (CuCl)

(LIQUID)

ClCu

MOL. WT. = 98.993

T, °K.	C _p (cal. mole ⁻¹ deg ⁻¹)	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ (kcal. mole ⁻¹)	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100						
200						
298	16.000	22.407	22.407	0.000	- 31.350	- 27.727
300	16.000	22.506	22.407	0.030	- 31.339	- 27.705
400	16.000	27.109	23.035	1.630	- 30.751	- 26.584
500	16.000	30.679	24.220	3.230	- 30.193	- 25.606
600	16.000	33.596	25.457	4.830	- 29.661	- 24.730
700	16.000	36.093	26.578	6.430	- 29.145	- 23.960
800	16.000	38.199	28.182	8.030	- 28.645	- 23.254
900	16.000	40.084	29.384	9.630	- 28.157	- 22.609
1000	16.000	41.770	30.540	11.230	- 27.682	- 22.019
1100	16.000	43.294	31.631	12.830	- 27.216	- 21.474
1200	16.000	44.667	32.632	14.430	- 26.762	- 20.974
1300	16.000	45.967	33.637	16.030	- 26.317	- 20.508
1400	16.000	47.153	34.561	17.630	- 25.881	- 20.077
1500	16.000	48.257	35.437	18.230	- 25.470	- 19.672
1600	16.000	49.290	36.271	20.830	- 25.074	- 19.284
1700	16.000	50.264	37.066	22.430	- 24.692	- 18.914
1800	16.000	51.174	37.824	24.030	- 24.324	- 18.566
1900	16.000	52.039	38.550	25.630	- 23.969	- 18.235
2000	16.000	52.860	39.245	27.230	- 23.628	- 17.917
2100	16.000	53.641	39.912	28.830	- 23.305	- 17.611
2200	16.000	54.385	40.553	30.430	- 22.994	- 17.315
2300	16.000	55.096	41.170	32.030	- 22.694	- 17.035
2400	16.000	55.777	41.765	33.630	- 22.404	- 16.765
2500	16.000	56.430	42.338	35.230	- 22.124	- 16.505
2600	16.000	57.058	42.892	36.830	- 21.854	- 16.255
2700	16.000	57.662	43.426	38.430	- 21.594	- 16.015
2800	16.000	58.243	43.947	40.030	- 21.344	- 15.785
2900	16.000	58.805	44.450	41.630	- 21.104	- 15.565
3000	16.000	59.347	44.937	43.230	- 20.874	- 15.355

 $S_{298.15}^{\circ} = 22.4 \pm 1$ cal. deg⁻¹ mole⁻¹ $\Delta H_f^{\circ} 298.15 = -31.35 \pm 0.4$ kcal. mole⁻¹ $T_m = 703^{\circ}\text{K.}$ $\Delta H_m^{\circ} = 2.445$ kcal. mole⁻¹ $T_b = [1485]^{\circ}\text{K.}$ (to equilibrium mixture) $\Delta H_v^{\circ} = [5.18]$ kcal. mole⁻¹ (to equilibrium mixture)

Heat of Formation.

Calculated from $\Delta H_f^{\circ} 298$ of the crystal plus ΔH_m° and the difference between $H_m - H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated to be constant at 8 cal. deg⁻¹ gm. atom⁻¹. The entropy was calculated in a manner analogous to that of the heat of formation.

Boiling Data.

The boiling point and heat of vaporization were calculated from the respective liquid, monomer and trimer gas tables. The boiling point was taken as the point where the total pressure reached 1 atm. At this point the partial pressures are 0.021 atm. of monomer and 0.979 atm. of trimer.

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(H°-H° ₂₉₈)/T	cal. mole ⁻¹	H°-H° ₂₉₈	ΔH _f ⁰	Log K _p
0	7.000	0.000	INFINITE	-	2.244	21.298	21.298	INFINITE
100	7.000	48.130	1.564	21.298	21.298	21.298	21.298	16.995
200	7.972	53.387	57.425	-	21.003	17.374	17.374	11.126
298	8.428	56.667	56.667	0.000	21.770	15.178	15.178	11.126
300	8.433	56.710	56.667	0.016	21.767	15.137	15.137	11.027
400	8.678	59.119	57.001	1.771	21.611	12.950	12.950	7.076
500	8.812	61.112	57.658	1.744	21.441	10.603	10.603	4.723
600	8.854	62.733	58.357	2.625	21.255	8.695	8.695	3.167
700	8.905	64.101	59.082	3.514	21.059	6.618	6.618	2.066
800	8.942	65.293	59.786	4.406	20.851	4.567	4.567	1.248
900	8.972	66.358	60.457	5.302	20.635	2.545	2.545	0.618
1000	8.996	67.293	61.094	6.200	20.409	0.546	0.546	0.119
1100	9.017	68.153	61.698	7.101	20.175	-1.428	-1.428	0.284
1200	9.036	68.938	62.269	8.004	19.932	-3.381	-3.381	0.616
1300	9.052	69.592	62.810	8.908	19.681	-5.313	-5.313	1.093
1400	9.066	70.163	63.261	9.812	19.422	-7.233	-7.233	1.693
1500	9.078	70.660	63.612	10.722	19.154	-9.142	-9.142	2.426
1600	9.088	71.147	64.278	11.631	18.877	-11.042	-11.042	3.294
1700	9.112	72.009	64.722	12.541	18.593	-12.943	-12.943	4.294
1800	9.126	72.620	65.146	13.453	18.303	-14.843	-14.843	5.426
1900	9.139	73.114	65.552	14.367	18.007	-16.743	-16.743	6.686
2000	9.151	73.593	65.942	15.281	17.715	-18.643	-18.643	8.076
2100	9.164	74.070	66.317	16.197	17.423	-20.543	-20.543	9.596
2200	9.176	74.456	66.677	17.114	17.131	-22.443	-22.443	11.246
2300	9.188	74.864	67.024	18.032	16.839	-24.343	-24.343	13.026
2400	9.199	75.241	67.359	18.951	16.547	-26.243	-26.243	14.936
2500	9.212	75.632	67.685	19.872	16.255	-28.143	-28.143	16.976
2600	9.224	75.993	67.995	20.794	15.963	-30.043	-30.043	19.146
2700	9.236	76.341	68.288	21.717	15.671	-31.943	-31.943	21.446
2800	9.248	76.678	68.561	22.641	15.379	-33.843	-33.843	23.876
2900	9.259	77.000	68.812	23.565	15.087	-35.743	-35.743	26.436
3000	9.271	77.316	69.042	24.493	14.795	-37.643	-37.643	29.126
3100	9.283	77.621	69.420	25.421	14.503	-39.543	-39.543	31.946
3200	9.294	77.916	69.681	26.350	14.211	-41.443	-41.443	34.896
3300	9.306	78.202	69.935	27.280	13.919	-43.343	-43.343	37.976
3400	9.317	78.479	70.184	28.211	13.627	-45.243	-45.243	41.186
3500	9.329	78.750	70.425	29.143	13.335	-47.143	-47.143	44.526
3600	9.340	79.013	70.658	30.077	13.043	-49.043	-49.043	47.996
3700	9.352	79.269	70.888	31.011	12.751	-50.943	-50.943	51.596
3800	9.363	79.519	71.111	31.947	12.459	-52.843	-52.843	55.326
3900	9.374	79.762	71.330	32.882	12.167	-54.743	-54.743	59.186
4000	9.386	79.999	71.544	33.822	11.875	-56.643	-56.643	63.176
4100	9.397	80.231	71.753	34.761	11.583	-58.543	-58.543	67.296
4200	9.409	80.458	71.958	35.701	11.291	-60.443	-60.443	71.546
4300	9.420	80.679	72.158	36.643	11.000	-62.343	-62.343	75.926
4400	9.431	80.894	72.354	37.582	10.708	-64.243	-64.243	80.436
4500	9.443	81.108	72.546	38.529	10.416	-66.143	-66.143	85.076
4600	9.454	81.316	72.735	39.474	10.124	-68.043	-68.043	89.846
4700	9.465	81.519	72.919	40.420	9.832	-69.943	-69.943	94.746
4800	9.477	81.719	73.101	41.367	9.540	-71.843	-71.843	99.776
4900	9.488	81.916	73.280	42.312	9.248	-73.743	-73.743	104.936
5000	9.499	82.106	73.453	43.265	8.956	-75.643	-75.643	110.226
5100	9.510	82.294	73.625	44.215	8.664	-77.543	-77.543	115.646
5200	9.522	82.479	73.793	45.167	8.372	-79.443	-79.443	121.196
5300	9.533	82.660	73.959	46.120	8.080	-81.343	-81.343	126.876
5400	9.544	82.838	74.121	47.072	7.788	-83.243	-83.243	132.686
5500	9.556	83.014	74.282	48.028	7.496	-85.143	-85.143	138.626
5600	9.567	83.186	74.439	48.984	7.204	-87.043	-87.043	144.696
5700	9.578	83.356	74.594	49.942	6.912	-88.943	-88.943	150.896
5800	9.589	83.522	74.746	50.900	6.620	-90.843	-90.843	157.226
5900	9.600	83.686	74.896	51.858	6.328	-92.743	-92.743	163.686
6000	9.612	83.848	75.044	52.820	6.036	-94.643	-94.643	170.276

Mar. 31, 1966

COPPER MONOCHLORIDE (CuCl)

(IDEAL GAS)

MOL. WT. = 98.993

Ground State Configuration $1\sum^+$
 $S_{298.15}^0 = 56.667 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = 21.80 \pm 0.4 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0_{298.15} = 21.77 \pm 0.4 \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$$\frac{\epsilon_i, \text{ cm.}^{-1}}{0} \frac{g_i}{1}$$

$\omega_e = 414.9 \text{ cm.}^{-1}$
 $B_e = 0.1761 \text{ cm.}^{-1}$
 $\alpha_e = 0.0001 \text{ cm.}^{-1}$
 $\omega_e x_e = 1.577 \text{ cm.}^{-1}$
 $\sigma = 1$
 $r_e = 2.050 \text{ \AA}$

Heat of Formation.

The heat of formation was obtained from the equilibrium data of L. Brewer and N. L. Lofgren, J. Am. Chem. Soc. 72, 3038 (1950). They studied the reaction $\text{Cu(c)} + \text{x HCl(g)} \rightarrow \text{CuCl}_x(\text{g}) + \text{x/2 H}_2(\text{g})$ by measuring the amount of CuCl formed when various ratios of HCl:H₂ were passed over heated copper. Brewer and Lofgren analyzed the data by a least squares fitting technique and deduced partial pressures of monomer and trimer. The monomer pressure were subjected to second and third law analysis and gave $\Delta H_f^0_{298} = 46.85 \pm 3.2$ and $43.83 \pm 0.4 \text{ kcal. mole}^{-1}$ respectively. The 3rd law value yields $\Delta H_f^0_{298} \text{ CuCl(g)} = 21.77 \pm 0.4 \text{ kcal. mole}^{-1}$, which was adopted.

Heat Capacity and Entropy.

The molecular constants were corrected for normal isotopic abundance of both copper and chlorine and were calculated from the values for $^{65}\text{Cu}^{35}\text{Cl}$ given by R. K. Aeundi, P. R. Rao and J. K. Brody, Nature 192, 444 (1961). The rotational constants were in good agreement with those reported by A. Lagerqvist and V. Leszerove-Giremov for $\text{Cu}^{63}\text{Cl}^{35}$, Naturwissenschaften 49, 68 (1961).

ClCu

Chlorine Monofluoride (ClF)

Mol. Wt. = 54.4514

ClF

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	6.961	44.228	58.559	- 2.129	- 12.117	- 12.117	- 12.117	INFINITE
200	7.421	52.750	67.768	- 1.834	- 12.120	- 12.120	- 12.120	1.454
298	7.608	54.451	70.864	- 1.600	- 12.126	- 12.126	- 12.126	1.454
300	7.677	52.111	72.064	- 1.604	- 12.140	- 12.140	- 12.140	1.454
400	8.067	56.376	78.370	- 1.403	- 12.152	- 12.152	- 12.152	1.403
500	8.334	58.207	82.960	- 1.263	- 12.161	- 12.161	- 12.161	1.263
600	8.513	59.763	86.633	- 1.146	- 12.169	- 12.169	- 12.169	1.046
700	8.639	60.965	89.416	- 1.048	- 12.175	- 12.175	- 12.175	0.848
800	8.729	61.825	91.364	- 0.964	- 12.180	- 12.180	- 12.180	0.764
900	8.798	62.458	92.565	- 0.892	- 12.184	- 12.184	- 12.184	0.692
1000	8.851	62.917	93.943	- 0.835	- 12.186	- 12.186	- 12.186	0.635
1100	8.894	63.333	95.481	- 0.789	- 12.203	- 12.203	- 12.203	0.589
1200	8.930	63.698	97.166	- 0.750	- 12.211	- 12.211	- 12.211	0.550
1300	8.960	64.024	98.890	- 0.718	- 12.219	- 12.219	- 12.219	0.518
1400	8.986	64.318	100.654	- 0.692	- 12.227	- 12.227	- 12.227	0.492
1500	9.010	64.581	102.462	- 0.670	- 12.235	- 12.235	- 12.235	0.470
1600	9.031	64.815	104.312	- 0.651	- 12.245	- 12.245	- 12.245	0.451
1700	9.051	65.024	106.207	- 0.634	- 12.254	- 12.254	- 12.254	0.434
1800	9.069	65.207	108.146	- 0.619	- 12.265	- 12.265	- 12.265	0.419
1900	9.086	65.369	110.128	- 0.605	- 12.275	- 12.275	- 12.275	0.405
2000	9.102	65.511	112.152	- 0.592	- 12.287	- 12.287	- 12.287	0.392
2100	9.117	65.636	114.218	- 0.580	- 12.298	- 12.298	- 12.298	0.380
2200	9.132	65.746	116.324	- 0.569	- 12.311	- 12.311	- 12.311	0.369
2300	9.146	65.841	118.470	- 0.559	- 12.324	- 12.324	- 12.324	0.359
2400	9.160	65.921	120.654	- 0.550	- 12.338	- 12.338	- 12.338	0.350
2500	9.173	66.000	122.876	- 0.542	- 12.354	- 12.354	- 12.354	0.342
2600	9.186	66.074	125.136	- 0.535	- 12.370	- 12.370	- 12.370	0.335
2700	9.199	66.146	127.434	- 0.529	- 12.388	- 12.388	- 12.388	0.329
2800	9.211	66.214	129.770	- 0.524	- 12.406	- 12.406	- 12.406	0.324
2900	9.224	66.278	132.144	- 0.519	- 12.426	- 12.426	- 12.426	0.319
3000	9.236	66.339	134.556	- 0.515	- 12.447	- 12.447	- 12.447	0.315
3100	9.248	66.396	137.004	- 0.511	- 12.470	- 12.470	- 12.470	0.311
3200	9.260	66.450	139.488	- 0.507	- 12.494	- 12.494	- 12.494	0.307
3300	9.271	66.501	142.006	- 0.504	- 12.519	- 12.519	- 12.519	0.304
3400	9.283	66.549	144.558	- 0.501	- 12.546	- 12.546	- 12.546	0.301
3500	9.295	66.594	147.144	- 0.498	- 12.574	- 12.574	- 12.574	0.298
3600	9.306	66.636	149.764	- 0.495	- 12.603	- 12.603	- 12.603	0.295
3700	9.318	66.676	152.416	- 0.492	- 12.634	- 12.634	- 12.634	0.292
3800	9.329	66.714	155.098	- 0.489	- 12.666	- 12.666	- 12.666	0.289
3900	9.340	66.750	157.810	- 0.487	- 12.699	- 12.699	- 12.699	0.287
4000	9.351	66.784	160.552	- 0.485	- 12.734	- 12.734	- 12.734	0.285
4100	9.363	66.816	163.324	- 0.483	- 12.769	- 12.769	- 12.769	0.283
4200	9.374	66.846	166.126	- 0.481	- 12.806	- 12.806	- 12.806	0.281
4300	9.385	66.874	168.958	- 0.479	- 12.844	- 12.844	- 12.844	0.279
4400	9.396	66.901	171.820	- 0.477	- 12.881	- 12.881	- 12.881	0.277
4500	9.407	66.926	174.712	- 0.475	- 12.919	- 12.919	- 12.919	0.275
4600	9.418	66.950	177.634	- 0.473	- 12.958	- 12.958	- 12.958	0.273
4700	9.429	66.972	180.586	- 0.471	- 12.998	- 12.998	- 12.998	0.271
4800	9.440	67.000	183.568	- 0.469	- 13.038	- 13.038	- 13.038	0.269
4900	9.451	67.024	186.580	- 0.467	- 13.079	- 13.079	- 13.079	0.267
5000	9.462	67.046	189.622	- 0.465	- 13.120	- 13.120	- 13.120	0.265
5100	9.473	67.068	192.694	- 0.463	- 13.161	- 13.161	- 13.161	0.263
5200	9.483	67.089	195.796	- 0.461	- 13.202	- 13.202	- 13.202	0.261
5300	9.494	67.109	198.928	- 0.459	- 13.244	- 13.244	- 13.244	0.259
5400	9.505	67.129	202.090	- 0.457	- 13.286	- 13.286	- 13.286	0.257
5500	9.516	67.149	205.282	- 0.455	- 13.327	- 13.327	- 13.327	0.255
5600	9.527	67.169	208.504	- 0.453	- 13.369	- 13.369	- 13.369	0.253
5700	9.537	67.189	211.756	- 0.451	- 13.412	- 13.412	- 13.412	0.251
5800	9.548	67.209	215.038	- 0.449	- 13.453	- 13.453	- 13.453	0.249
5900	9.559	67.229	218.350	- 0.447	- 13.495	- 13.495	- 13.495	0.247
6000	9.570	67.249	221.692	- 0.445	- 13.537	- 13.537	- 13.537	0.245

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CHLORINE MONOFLUORIDE (ClF)

(IDEAL GAS)

MOL. WT. = 54.4514

Ground State Configuration $1\Sigma^+$
 $S_{298.15}^{\circ} = 52.064 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{\circ} 0 = -12.12 \pm 0.6 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = -12.14 \pm 0.6 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

State	ϵ , cm ⁻¹	g _i
$1\Sigma^+$	0	1
$3\Sigma^+$	19,592	1
$3\Pi_0$	19,592	2
$3\Pi_2$	19,592	2

$\lambda = 784.39 \text{ cm.}^{-1}$
 $\omega_e = 6.20 \text{ cm.}^{-1}$
 $\omega_e x_e = 0.004329 \text{ cm.}^{-1}$
 $r_e = 1.62913 \text{ \AA}$

Heat of Formation

The $\Delta H_f^{\circ} 298.15 = -12.14 \text{ kcal. mole}^{-1}$ was calculated from the dissociation energy ($D_0^{\circ} = 58.99$) obtained from the visible band spectra measured by H. Schmitz and H. J. Schumacher, Z. Naturforsch. 2a, 359 (1947) and A. L. Wahneftig, J. Chem. Phys. 10, 248 (1941). The convergence limit of $21,512 \pm 20 \text{ cm.}^{-1}$ for the A state leads to the selected D_0° assuming that the products are $\text{Cl}(^2P_{3/2})$ and $\text{F}(^2P_{3/2})$ or to $D_0^{\circ} = 60.36$ assuming $\text{Cl}(^2P_{3/2})$ and $\text{F}(^2P_{1/2})$. Calorimetric values bracket the two possibilities but more weight was given to the results of Wicke.

Method	Reaction	Observation
1 Spectroscopic	$\text{ClF} = \text{Cl}(^2P_{3/2}) + \text{F}(^2P_{3/2})$	$D_0^{\circ} = 58.99$
2 Spectroscopic	$\text{ClF} = \text{Cl}(^2P_{3/2}) + \text{F}(^2P_{1/2})$	$D_0^{\circ} = 60.36$
3 Calorimetric	$1/2 \text{ Cl}_2 + 1/2 \text{ F}_2 = \text{ClF}$	$\Delta H_{295}^{\circ} = -11.6 \pm 0.1$
4 Explosion method	$1/2 \text{ Cl}_2 + 1/2 \text{ F}_2 = \text{ClF}$	$\Delta H_0^{\circ} = -11.7 \pm 0.5$
5a Calorimetric	$\text{NaCl} + \text{ClF} = \text{NaF} + \text{Cl}_2$	$\Delta H_{290}^{\circ} = -24.5 \pm 0.5$
5b Calorimetric	$\text{NaCl} + 0.5 \text{ F}_2 = \text{NaF} + 0.5 \text{ Cl}_2$	$\Delta H_{290}^{\circ} = -39.5 \pm 0.5$

Sources
 1, 2 H. Schmitz and H. J. Schumacher, Z. Naturforsch. 2a, 359 (1947).
 3 E. Wicke, Nachr. Acad. Wiss. Gottigen Math-Physik Klasse p. 89 (1946).
 4 E. Wicke and H. Friz, Z. Elektrochem. 57, 9 (1953).
 5a, 5b H. Schmitz and H. J. Schumacher, Z. Naturforsch. 2a, 362 (1947).

*Based on $\Delta H_f^{\circ} 298(\text{NaCl}(c)) = -98.26$ and $\Delta H_f^{\circ} 298(\text{NaF}(c)) = -137.1 \text{ kcal. mole}^{-1}$
 **Based on the difference between the two calorimetric reactions of reference 5a, 5b.

Heat Capacity and Entropy

The rotational constants were obtained from the microwave spectrum by D. A. Gilbert, A. Roberts and P. A. Ortolano, Phys. Rev. 76, 1723 (1949) and by D. A. Gilbert and A. Roberts Phys. Rev. 77, 742 (1950). The vibrational constants were obtained from the analysis vibration-rotation fine structure in the infrared by A. H. Nielsen and E. A. Jones, J. Chem. Phys. 19, 1117 (1951).

The rotational and vibrational constants were adjusted to $\text{Cl}^{35} = 75.4\%$ and $\text{Cl}^{37} = 24.6\%$.

ClF

T, °K.	C _p ^o	S ^o	-(F°-H ₂₉₈ °)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	2.208	-179.046	-179.046	-179.046	INFINITE
100	6.538	51.590	73.435	-179.170	-179.170	-179.170	362.651
200	12.369	56.597	64.327	-179.711	-179.711	-179.711	196.645
298	15.019	64.037	5.000	-180.200	-179.980	-179.980	131.922
300	15.054	64.130	45.037	-180.209	-179.979	-179.979	131.106
400	15.635	68.492	64.449	-180.681	-179.632	-179.632	94.253
500	17.591	72.519	64.851	-182.611	-179.422	-179.422	76.421
600	18.195	73.762	67.241	-183.096	-178.736	-178.736	65.101
700	18.595	76.620	64.668	-183.580	-177.937	-177.937	55.564
800	18.869	81.121	70.071	-183.705	-177.135	-177.135	48.205
900	19.063	85.173	77.721	-184.659	-175.587	-175.587	38.329
1000	19.212	87.209	73.956	-184.973	-174.486	-174.486	34.658
1200	19.404	88.894	73.132	-185.311	-173.475	-173.475	31.593
1300	19.475	90.450	70.251	-185.439	-172.460	-172.460	28.774
1400	19.528	91.824	67.335	-186.289	-170.402	-170.402	26.826
1500	19.570	93.244	62.801	-186.604	-169.331	-169.331	24.126
1600	19.606	94.508	79.306	-24.322	-165.586	-165.586	21.287
1700	19.632	95.697	80.264	-237.010	-155.586	-155.586	18.791
1800	19.653	96.864	81.366	-237.010	-145.586	-145.586	16.409
1900	19.670	98.001	82.517	-256.634	-135.634	-135.634	14.332
2000	19.701	98.694	82.801	-256.634	-122.644	-122.644	10.721
2100	19.714	99.856	83.591	-256.601	-144.098	-144.098	14.996
2200	19.731	100.773	84.331	-256.759	-136.730	-136.730	13.791
2300	19.753	102.691	84.792	-256.469	-128.004	-128.004	12.452
2400	19.761	103.297	85.476	-256.634	-122.644	-122.644	10.721
2500	19.770	104.073	87.138	-256.603	-117.288	-117.288	9.858
2600	19.776	104.619	87.779	-256.579	-111.930	-111.930	9.060
2700	19.785	105.338	88.601	-256.560	-106.572	-106.572	8.315
2800	19.789	105.984	89.589	-256.550	-101.216	-101.216	7.623
2900	19.784	106.603	89.589	-256.550	-95.859	-95.859	6.963
3000	19.800	107.553	90.158	-256.540	-90.500	-90.500	6.360
3100	19.805	108.181	90.712	-256.579	-85.144	-85.144	5.815
3200	19.809	108.781	91.250	-256.611	-79.786	-79.786	5.284
3300	19.815	109.556	92.286	-256.708	-74.428	-74.428	4.763
3400	19.816	110.515	92.785	-256.776	-69.067	-69.067	4.313
3500	19.821	111.058	93.271	-256.661	-63.705	-63.705	3.867
3600	19.827	112.101	93.216	-256.599	-58.344	-58.344	3.446
3700	19.827	112.403	94.664	-257.024	-52.982	-52.982	3.046
4000	19.829	112.403	94.664	-257.206	-42.231	-42.231	2.307
4100	19.831	113.093	95.108	-257.355	-36.882	-36.882	1.964
4200	19.832	113.571	95.542	-257.523	-31.474	-31.474	1.638
4300	19.834	114.063	95.969	-257.710	-26.060	-26.060	1.326
4400	19.836	114.539	96.790	-258.145	-20.646	-20.646	1.026
4500	19.836	114.939	96.790	-258.145	-15.231	-15.231	0.763
4600	19.840	115.375	97.169	-258.396	-9.907	-9.907	0.471
4700	19.842	115.802	97.580	-258.670	-4.506	-4.506	0.210
4800	19.843	116.220	97.964	-258.967	0.904	0.904	0.041
4900	19.845	116.629	98.311	-259.289	6.194	6.194	0.210
5000	19.845	117.030	98.711	-259.650	11.751	11.751	0.514
5100	19.846	117.423	99.074	-260.035	17.182	17.182	0.736
5200	19.847	117.808	99.430	-260.451	22.624	22.624	0.951
5300	19.849	118.185	99.759	-260.909	28.068	28.068	1.157
5400	19.849	118.557	100.123	-261.399	33.512	33.512	1.357
5500	19.849	118.921	100.464	-261.907	38.955	38.955	1.549
5600	19.850	119.279	100.796	-262.466	44.402	44.402	1.735
5700	19.850	119.630	101.124	-263.070	49.854	49.854	1.915
5800	19.851	120.015	101.444	-263.724	55.307	55.307	2.088
5900	19.851	120.315	101.763	-264.469	60.761	60.761	2.258
6000	19.852	120.649	102.075	-265.150	66.461	66.461	2.421

December 31, 1960.

DILITHIUM CHLORIDE FLUORIDE (Li₂ClF)

Mol. Wt. = 68.34

ΔH_f^o 298.15 = [-180.2] kcal. mole⁻¹

S_{298.15}^o = [64.037] cal. deg.⁻¹ mole⁻¹

ΔH_f^o 298.15 from National Bureau of Standards Report No. 6297, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine (Revised)", January, 1959. Cp from R. R. Koppang, C. M. Sherwood, and G. S. Bahn, Marquardt Corp., Van Nuys, Calif., "Some Provisional Tables of Species Thermodynamic Properties", October, 1959.

Magnesium Chloride Fluoride (MgClF)

(Ideal Gas) Mol. wt. = 78.7634

CIFMg

MAGNESIUM CHLORIDE FLUORIDE (MgClF) (IDEAL GAS) MOL. WT. = 78.7634

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	INFINITE	2.947	-135.599	-135.599	INFINITE
100	9.089	51.367	72.543	2.118	-135.622	-136.237	297.745
200	10.916	58.126	82.814	1.180	-135.606	-136.863	149.557
298	11.959	62.756	87.150	0.000	-135.600	-137.415	100.591
300	11.945	62.830	87.156	0.022	-136.003	-137.222	99.966
400	12.619	66.367	83.234	1.253	-136.186	-137.602	75.182
500	13.015	69.229	84.156	2.537	-136.375	-137.933	60.290
600	13.259	71.625	85.207	3.851	-136.580	-138.226	50.349
700	13.418	73.682	86.274	5.186	-136.803	-138.482	43.236
800	13.526	75.481	87.315	6.533	-137.036	-138.707	37.893
900	13.603	77.079	88.313	7.890	-137.284	-138.896	33.728
1000	13.659	78.515	89.262	9.253	-137.549	-139.050	30.350
1100	13.701	79.819	90.164	10.621	-137.826	-139.177	27.570
1200	13.733	81.013	91.019	11.993	-138.117	-139.266	25.247
1300	13.759	82.113	91.830	13.368	-138.426	-139.327	23.277
1400	13.779	83.134	92.602	14.745	-138.752	-139.378	21.508
1500	13.796	84.085	93.336	16.123	-139.105	-139.425	19.722
1600	13.809	84.976	94.036	17.504	-139.488	-139.460	18.159
1700	13.821	85.813	94.704	18.885	-139.895	-139.481	16.779
1800	13.830	86.604	95.344	20.268	-140.338	-139.488	15.553
1900	13.838	87.352	95.956	21.651	-140.818	-139.481	14.455
2000	13.845	88.062	96.544	23.035	-141.338	-139.460	13.473
2100	13.851	88.737	97.108	24.420	-141.898	-139.411	12.573
2200	13.856	89.382	97.652	25.806	-142.500	-139.338	11.760
2300	13.861	89.998	98.175	27.192	-143.154	-139.246	11.017
2400	13.865	90.588	98.680	28.578	-143.864	-139.134	10.337
2500	13.869	91.154	99.168	29.965	-144.634	-139.007	9.710
2600	13.872	91.698	99.639	31.352	-145.468	-138.863	9.132
2700	13.874	92.221	100.096	32.739	-146.370	-138.698	8.596
2800	13.877	92.726	100.538	34.126	-147.344	-138.518	8.099
2900	13.879	93.213	100.967	35.514	-148.394	-138.314	7.635
3000	13.881	93.684	101.383	36.902	-149.526	-138.087	7.203
3100	13.883	94.139	101.787	38.291	-150.744	-137.838	6.798
3200	13.885	94.580	102.180	39.679	-152.054	-137.564	6.418
3300	13.886	95.007	102.562	41.067	-153.461	-137.266	6.051
3400	13.888	95.421	102.934	42.456	-154.968	-136.944	5.725
3500	13.889	95.824	103.297	43.845	-156.580	-136.601	5.408
3600	13.890	96.215	103.650	45.234	-158.302	-136.238	5.109
3700	13.891	96.596	103.995	46.623	-160.140	-135.858	4.825
3800	13.892	96.966	104.332	48.011	-162.098	-135.464	4.557
3900	13.893	97.327	104.660	49.401	-164.182	-135.058	4.302
4000	13.894	97.679	104.981	50.791	-166.398	-134.641	4.059
4100	13.895	98.022	105.295	52.180	-168.744	-134.212	3.820
4200	13.895	98.357	105.598	53.570	-171.222	-133.770	3.593
4300	13.896	98.684	105.898	54.959	-173.834	-133.318	3.399
4400	13.897	99.003	106.197	56.349	-176.488	-132.856	3.198
4500	13.897	99.316	106.485	57.739	-179.288	-132.384	3.007
4600	13.898	99.621	106.767	59.128	-182.232	-131.902	2.823
4700	13.898	99.920	107.044	60.518	-185.326	-131.410	2.647
4800	13.899	100.213	107.315	61.908	-188.574	-130.908	2.478
4900	13.899	100.499	107.581	63.298	-191.988	-130.398	2.316
5000	13.900	100.780	107.846	64.688	-195.572	-129.878	2.160
5100	13.900	101.055	108.099	66.078	-199.338	-129.348	2.010
5200	13.900	101.325	108.351	67.468	-203.288	-128.808	1.866
5300	13.901	101.590	108.598	68.858	-207.428	-128.258	1.727
5400	13.901	101.850	108.841	70.248	-211.762	-127.698	1.593
5500	13.902	102.105	109.080	71.638	-216.302	-127.128	1.463
5600	13.902	102.355	109.315	73.028	-221.052	-126.548	1.338
5700	13.902	102.601	109.545	74.418	-226.022	-125.958	1.217
5800	13.902	102.843	109.773	75.809	-231.228	-125.358	1.100
5900	13.903	103.081	109.996	77.199	-236.678	-124.748	0.987
6000	13.903	103.314	110.216	78.589	-242.378	-124.128	0.877

Dec. 31, 1960; Mar. 31, 1966

Point Group C_{2v} ΔH_f^o 0 = [-135.6 ± 5] kcal. mole⁻¹
ΔH_f^o 298.15 = [-136.0 ± 5] kcal. mole⁻¹

S_{298.15}^o = [62.76] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e, cm.⁻¹

[719](1)

[205](1)

[453](1)

Bond Distances: Mg-Cl = [2.18] Å Mg-F = [1.77] Å

Bond Angle: Cl-Mg-F = [170]°

Product of the Moments of Inertia: I_AI_BI_C = [1.5643 × 10⁻¹¹⁵] g.³ cm.⁶

σ = 2

Heat of Formation.

The heat of formation is based on an estimated ΔH_f^o 298 = 0 for the reaction MgCl₂(g) + MgF₂(g) → 2MgClF(g), using ΔH_f^o 298.15 = -95.85 and -176.2 kcal. mole⁻¹ for MgCl₂(g) and MgF₂(g), respectively.

Heat Capacity and Entropy.

The bond angle is taken to be the value we have adopted for MgCl₂(g). The Mg-Cl and Mg-F bond distances are assumed to be the same as those in MgCl₂(g) and MgF₂(g). The vibration frequencies are the averages of those for MgCl₂(g) and MgF₂(g). The three principal moments of inertia are: I_A = 0.0977 × 10⁻³⁹, I_B = 39.958 × 10⁻³⁹ and I_C = 40.054 × 10⁻³⁹ g. cm.²

CIFMg

(Ideal Gas) Mol. Wt. = 102.457

PERCHLORYL FLUORIDE (ClO₃F)

(IDEAL GAS)

MOL. WT. = 102.457

T. °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	Log K _p
0	4.000	INFINITE	INFINITE	3.178	-	3.034	INFINITE
100	12.073	51.000	67.926	1.362	4.715	6.401	2.7095
200	15.517	66.653	66.653	1.000	5.120	12.000	0.861
300	15.573	66.749	66.653	1.029	5.125	12.196	0.864
400	18.152	71.602	67.297	1.722	5.266	16.002	0.935
500	20.000	75.853	68.593	3.635	5.312	23.631	10.416
600	21.319	79.633	70.125	5.704	5.226	29.633	10.401
700	22.271	82.994	71.728	7.866	5.076	35.455	11.069
800	22.947	86.016	73.328	10.150	4.894	41.231	11.263
900	23.487	88.753	74.874	12.474	4.685	46.863	11.408
1000	23.883	91.249	76.405	14.843	4.462	52.710	11.519
1100	24.159	93.540	77.860	17.248	4.175	58.410	11.604
1200	24.430	95.655	79.256	19.679	3.914	64.090	11.672
1300	24.624	97.619	80.594	22.132	3.649	69.746	11.725
1400	24.760	99.449	81.876	24.602	3.382	75.380	11.767
1500	24.849	101.164	83.106	27.087	3.112	80.990	11.801
1600	25.016	102.775	84.285	29.584	2.843	86.596	11.828
1700	25.105	104.294	85.418	32.000	2.574	92.179	11.850
1800	25.181	105.731	86.507	34.404	2.311	97.744	11.867
1900	25.246	107.094	87.555	36.795	2.051	103.297	11.881
2000	25.301	108.391	88.564	39.163	1.795	108.833	11.892
2100	25.349	109.626	89.538	41.185	1.544	114.359	11.901
2200	25.391	110.807	90.478	43.723	1.300	119.871	11.908
2300	25.428	111.936	91.387	46.264	1.060	125.374	11.913
2400	25.461	113.019	92.266	48.808	0.828	130.866	11.917
2500	25.489	114.059	93.117	51.357	0.605	136.347	11.919
2600	25.515	115.059	93.942	54.006	0.386	141.823	11.921
2700	25.538	116.023	94.742	56.748	0.176	147.289	11.922
2800	25.558	116.952	95.518	59.518	0.027	152.747	11.922
2900	25.577	117.849	96.273	62.320	0.223	158.199	11.922
3000	25.593	118.716	97.007	65.129	0.411	163.641	11.921
3100	25.608	119.556	97.721	67.689	0.593	169.082	11.920
3200	25.622	120.369	98.416	70.250	0.767	174.513	11.918
3300	25.635	121.158	99.093	72.813	0.935	179.937	11.916
3400	25.647	121.927	100.757	75.377	1.095	185.360	11.914
3500	25.657	122.667	100.398	77.942	1.249	190.776	11.912
3600	25.666	123.390	101.026	80.508	1.396	196.192	11.910
3700	25.675	124.093	101.640	83.075	1.537	201.600	11.907
3800	25.683	124.778	102.240	85.643	1.673	207.009	11.905
3900	25.691	125.445	102.827	88.212	1.803	212.404	11.902
4000	25.698	126.098	103.400	90.782	1.926	217.803	11.900
4100	25.704	126.730	103.961	93.352	2.043	223.200	11.897
4200	25.711	127.350	104.511	95.922	2.156	228.592	11.894
4300	25.716	127.955	105.049	98.494	2.264	233.986	11.892
4400	25.721	128.546	105.577	101.066	2.366	239.370	11.889
4500	25.726	129.124	106.093	103.630	2.464	244.755	11.886
4600	25.731	129.690	106.600	106.211	2.558	250.143	11.884
4700	25.735	130.243	107.097	108.784	2.646	255.525	11.881
4800	25.739	130.785	107.585	111.358	2.731	260.904	11.879
4900	25.743	131.316	108.064	113.922	2.812	266.277	11.876
5000	25.747	131.838	108.534	116.507	2.889	271.652	11.873
5100	25.750	132.346	108.996	119.082	2.961	277.029	11.871
5200	25.753	132.846	109.450	121.657	3.030	282.399	11.868
5300	25.756	133.336	109.896	124.232	3.097	287.779	11.866
5400	25.759	133.819	110.335	126.808	3.158	293.140	11.863
5500	25.762	134.290	110.766	129.384	3.220	298.516	11.861
5600	25.765	134.755	111.190	131.960	3.274	303.861	11.859
5700	25.767	135.211	111.608	134.537	3.327	309.248	11.857
5800	25.769	135.659	112.019	137.114	3.378	314.621	11.855
5900	25.771	136.093	112.423	139.691	3.425	319.982	11.852
6000	25.773	136.533	112.821	142.268	3.470	325.349	11.850

March 31, 1961

Phosphoryl Difluoride Chloride (POClF₂)

(Ideal Gas) Mol. Wt. = 120.432

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
100	9.119	58.627	24.368	3.393	-226.287	-226.287	-226.287	INFINITE
200	13.155	66.184	73.466	2.574	-226.961	-226.961	-226.961	490.116
298	16.453	72.081	81.460	1.460	-227.565	-227.565	-227.565	241.647
300	16.453	72.081	81.460	1.460	-228.000	-228.000	-228.000	159.917
300	16.453	72.081	81.460	1.460	-228.007	-228.007	-228.007	158.886
400	18.960	77.287	82.080	1.491	-228.300	-228.300	-228.300	117.766
500	20.484	81.715	84.119	3.798	-228.482	-228.482	-228.482	92.380
600	21.889	85.599	75.715	5.930	-228.595	-228.595	-228.595	75.732
700	22.743	89.041	77.378	8.164	-228.673	-228.673	-228.673	63.635
800	23.360	92.120	79.071	10.471	-249.157	-249.157	-249.157	56.361
900	23.807	94.811	80.784	12.811	-248.600	-248.600	-248.600	50.404
1000	24.161	97.427	82.197	15.231	-248.746	-248.746	-248.746	42.759
1100	24.427	99.743	83.688	17.661	-248.517	-248.517	-248.517	37.819
1200	24.636	101.878	85.116	20.114	-248.278	-248.278	-248.278	33.706
1300	24.807	103.777	86.483	22.586	-248.032	-248.032	-248.032	30.230
1400	24.952	105.471	87.804	25.074	-247.781	-247.781	-247.781	27.355
1500	25.047	107.424	89.042	27.573	-247.527	-247.527	-247.527	24.676
1600	25.138	109.044	90.242	30.082	-247.272	-247.272	-247.272	22.423
1700	25.215	110.570	91.393	32.600	-247.016	-247.016	-247.016	20.437
1800	25.283	112.013	92.499	35.125	-246.761	-246.761	-246.761	18.674
1900	25.335	113.375	93.566	37.662	-246.506	-246.506	-246.506	17.120
2000	25.382	114.682	94.586	40.192	-246.253	-246.253	-246.253	15.681
2100	25.423	115.922	95.573	42.732	-246.005	-246.005	-246.005	14.400
2200	25.459	117.105	96.525	45.276	-245.760	-245.760	-245.760	13.237
2300	25.490	118.237	97.445	47.823	-245.516	-245.516	-245.516	12.176
2400	25.516	119.317	98.328	50.374	-245.272	-245.272	-245.272	11.209
2500	25.542	120.365	99.194	52.927	-245.042	-245.042	-245.042	10.312
2600	25.564	121.367	100.028	55.482	-244.811	-244.811	-244.811	9.488
2700	25.583	122.332	100.836	58.039	-244.585	-244.585	-244.585	8.726
2800	25.600	123.263	101.621	60.599	-244.363	-244.363	-244.363	8.020
2900	25.615	124.163	102.387	63.162	-244.146	-244.146	-244.146	7.362
3000	25.630	125.030	103.123	65.722	-243.933	-243.933	-243.933	6.749
3100	25.643	125.871	103.844	68.285	-243.727	-243.727	-243.727	6.176
3200	25.655	126.685	104.545	70.846	-243.526	-243.526	-243.526	5.640
3300	25.665	127.475	105.228	73.416	-243.329	-243.329	-243.329	5.136
3400	25.674	128.241	105.893	75.983	-243.138	-243.138	-243.138	4.662
3500	25.684	128.986	106.542	78.551	-242.951	-242.951	-242.951	4.216
3600	25.692	129.709	107.176	81.120	-242.769	-242.769	-242.769	3.795
3700	25.700	130.413	107.795	83.690	-242.592	-242.592	-242.592	3.396
3800	25.707	131.099	108.399	86.260	-242.419	-242.419	-242.419	3.019
3900	25.714	131.767	108.989	88.831	-242.250	-242.250	-242.250	2.662
4000	25.719	132.418	109.567	91.401	-242.090	-242.090	-242.090	2.323
4100	25.724	133.053	110.132	93.975	-241.932	-241.932	-241.932	2.000
4200	25.730	133.673	110.685	96.547	-241.779	-241.779	-241.779	1.693
4300	25.734	134.278	111.227	99.121	-241.628	-241.628	-241.628	1.401
4400	25.738	134.870	111.758	101.694	-241.484	-241.484	-241.484	1.122
4500	25.743	135.448	112.278	104.268	-241.343	-241.343	-241.343	.856
4600	25.747	136.014	112.788	106.843	-241.203	-241.203	-241.203	.601
4700	25.751	136.568	113.288	109.418	-241.070	-241.070	-241.070	.357
4800	25.754	137.110	113.778	111.993	-240.939	-240.939	-240.939	.123
4900	25.757	137.643	114.259	114.569	-240.811	-240.811	-240.811	.000
5000	25.760	138.162	114.755	117.144	-240.688	-240.688	-240.688	.315
5100	25.763	138.672	115.197	119.721	-240.567	-240.567	-240.567	.521
5200	25.766	139.172	115.653	122.297	-240.449	-240.449	-240.449	.719
5300	25.768	139.663	116.102	124.874	-240.334	-240.334	-240.334	.910
5400	25.771	140.145	116.559	127.451	-240.221	-240.221	-240.221	1.095
5500	25.773	140.618	116.976	130.028	-240.113	-240.113	-240.113	1.270
5600	25.775	141.082	117.402	132.605	-240.008	-240.008	-240.008	1.441
5700	25.777	141.538	117.822	135.183	-239.905	-239.905	-239.905	1.605
5800	25.779	141.997	118.235	137.761	-239.804	-239.804	-239.804	1.764
5900	25.781	142.457	118.641	140.340	-239.706	-239.706	-239.706	1.916
6000	25.783	142.861	119.041	142.917	-239.611	-239.611	-239.611	2.064

March 31, 1963

CIF₂OP

MOL. WT. = 120.432

PHOSPHORYL DIFLUORIDE CHLORIDE (POClF₂)

(IDEAL GAS)

Point Group C_s

ΔH_f⁰ = [-226] kcal. mole⁻¹

S_{298.15} = 72.081 cal. deg.⁻¹ mole⁻¹

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
274 (1)	424 (2)	948 (2)
410 (1)	618 (1)	1358 (1)
	895 (1)	

Bond Distance: P-Cl = 2.01 ± 0.04 Å P-P = 1.51 ± 0.03 Å P-O = 1.55 ± 0.03 Å

Bond Angle: P-P-P = P-P-Cl = 103° σ = 1

Product of the Moments of Inertia: I_AI_BI_C = 4.2790825 X 10⁻¹¹³ g.³ cm.⁶

Heat of Formation.

The ΔH_f⁰ 298.15 of POClF₂ was estimated to be -228 kcal. mole⁻¹ from the ΔH_f⁰ 298.15 of POCl₃ by assuming bond energies of 120 kcal. for D(P-F) and 80 kcal. for D(P-Cl). The D(P-P) and D(P-Cl) values were taken from E. Neale and L. T. D. Williams, J. Chem. Soc., 2465 (1955) Part I and E. Neale, L. T. D. Williams and V. T. Moores, J. Chem. Soc., 422 (1955) Part II.

Essentially the same ΔH_f⁰ 298.15 may be obtained by assuming a ΔH_f⁰ = 0 for the following reaction:



Heat Capacity and Entropy.

The molecular constants were determined by L. O. Brockway and J. Y. Beech, J. Am. Chem. Soc., 50, 1836 (1928) and by Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys., 20, 164 (1952). Brockway and Beach used electron diffraction. Q. Williams et al. measured microwave spectra. Brockway and Beach assumed that the P-P-F and P-P-Cl angles were equal in POCl₂Cl, POClF₂, POCl₃, and POF₃. An analysis of Brockway and Beach's data by Q. Williams et al., indicates that the angles in POCl₂Cl, POClF₂, POCl₃, and POF₃ should be 103° rather than the reported 108° ± 3°. The principal moments of inertia calculated from these parameters were I_A = 3.24319 X 10⁻³⁶ g. cm.², I_B = 1.87015 X 10⁻³⁶ g. cm.², and I_C = 3.13456 g. cm.² X 10⁻³⁶.

The Raman spectra and vibrational frequencies for POCl₂Cl were reported by M. L. Delwaule and P. Francoia, Compt. Rend. 222, 550 (1946). The frequencies were reassigned by M. L. Delwaule and P. Francoia in J. Chim. Phys. 46, 87 (1949).

CIF₂OP

CHLORINE TRIFLUORIDE (ClF₃)

(IDEAL GAS)

MOL. WT. = 92.4482

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞	INFINITE	- 3.262	- 36.970	- 36.970	INFINITE
100	8.872	54.430	- 2.450	- 34.630	- 34.630	75.680
200	12.582	68.588	- 1.577	- 31.552	- 31.552	34.477
298	15.260	77.279	+0.000	- 31.970	- 28.416	20.830
300	15.298	67.374	+0.028	- 37.970	- 28.360	20.659
400	16.875	72.012	1.644	- 37.924	- 25.160	13.746
500	17.798	75.885	3.382	- 37.824	- 21.980	9.607
600	18.366	79.184	5.102	- 37.696	- 18.823	6.854
700	18.734	82.045	7.008	- 37.555	- 15.688	4.898
800	18.984	84.564	9.395	- 37.410	- 12.576	3.435
900	19.162	86.811	12.463	- 37.262	- 9.480	2.302
1000	19.291	88.837	16.071	- 37.113	- 6.402	1.399
1100	19.380	90.680	20.316	- 36.965	- 3.328	+0.63
1200	19.434	92.330	25.150	- 36.818	- 0.280	+0.63
1300	19.453	93.831	30.547	- 36.674	2.752	+0.63
1400	19.450	95.379	36.547	- 36.532	5.780	+0.02
1500	19.438	96.871	43.177	- 36.392	8.798	- 1.282
1600	19.410	97.997	50.468	- 36.257	11.806	- 1.613
1700	19.366	99.189	58.421	- 36.127	14.795	- 2.161
1800	19.308	100.314	66.935	- 35.993	17.767	- 2.850
1900	19.237	101.379	75.934	- 35.866	20.782	- 3.696
2000	19.157	102.393	85.418	- 35.742	23.762	- 4.632
2100	19.077	103.353	95.316	- 35.622	26.730	- 5.662
2200	18.990	104.260	105.612	- 35.506	29.686	- 6.782
2300	18.900	105.116	116.316	- 35.393	32.631	- 7.991
2400	18.808	105.923	127.434	- 35.284	35.567	- 9.288
2500	18.716	106.687	138.970	- 35.180	38.500	- 10.672
2600	18.624	107.410	150.930	- 35.079	41.427	- 12.137
2700	18.530	108.094	163.316	- 34.982	44.347	- 13.682
2800	18.436	108.739	176.130	- 34.888	47.261	- 15.307
2900	18.342	109.344	189.476	- 34.794	50.170	- 16.999
3000	18.248	109.910	203.354	- 34.717	53.070	- 18.750
3100	18.154	110.436	217.766	- 34.646	55.960	- 20.550
3200	18.060	110.922	232.710	- 34.579	58.840	- 22.390
3300	17.966	111.368	248.194	- 34.516	61.710	- 24.270
3400	17.872	111.774	264.216	- 34.452	64.580	- 26.190
3500	17.778	112.140	280.776	- 34.384	67.450	- 28.150
3600	17.684	112.466	297.874	- 34.320	70.320	- 30.150
3700	17.590	112.752	315.510	- 34.260	73.190	- 32.190
3800	17.496	113.000	333.684	- 34.204	76.060	- 34.270
3900	17.402	113.218	352.394	- 34.151	78.930	- 36.390
4000	17.308	113.406	371.640	- 34.100	81.800	- 38.540
4100	17.214	113.564	391.420	- 34.055	84.670	- 40.720
4200	17.120	113.692	411.734	- 34.014	87.540	- 42.930
4300	17.026	113.790	432.574	- 33.976	90.410	- 45.170
4400	16.932	113.858	453.940	- 33.942	93.280	- 47.440
4500	16.838	113.896	475.834	- 33.911	96.150	- 49.730
4600	16.744	113.904	498.254	- 33.882	99.020	- 52.040
4700	16.650	113.882	521.200	- 33.856	101.890	- 54.370
4800	16.556	113.830	544.674	- 33.832	104.760	- 56.720
4900	16.462	113.748	568.684	- 33.809	107.630	- 59.090
5000	16.368	113.636	593.230	- 33.787	110.500	- 61.480
5100	16.274	113.494	618.320	- 33.765	113.370	- 63.890
5200	16.180	113.322	643.954	- 33.743	116.240	- 66.320
5300	16.086	113.120	670.134	- 33.720	119.110	- 68.770
5400	15.992	112.888	696.860	- 33.697	121.980	- 71.240
5500	15.898	112.626	724.134	- 33.674	124.850	- 73.720
5600	15.804	112.334	751.954	- 33.650	127.720	- 76.210
5700	15.710	112.012	780.320	- 33.626	130.590	- 78.710
5800	15.616	111.660	809.240	- 33.602	133.460	- 81.220
5900	15.522	111.278	838.714	- 33.577	136.330	- 83.740
6000	15.428	110.866	868.740	- 33.552	139.200	- 86.270

Dec. 31, 1960; June 30, 1961; Sept. 30, 1965

Point Group C_{2v}
S°_{298.15} = 67.279 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 1

ΔH°_f 0 = -36.97 ± 0.7 kcal. mole⁻¹
ΔH°_f 298.15 = -37.97 ± 0.7 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹ g, cm.⁻¹

752 (1) 703 (1)
528 (1) 434 (1)
328 (1) 364 (1)

Bond Distances: Cl-F₁ = Cl-F₂ = 1.698 Å Cl-F₃ = 1.598 Å

Bond Angle: F₁-Cl-F₂ = F₂-Cl-F₃ = 87° 29' F₃-Cl-F₁ = 185° 02'

Product of Moments of Inertia: I_AI_BI_C = 2.6923061 X 10⁻¹¹⁴ g.³ cm.⁶

σ° = 2

Heat of Formation.

The ΔH°_f 298.15 = -37.97 kcal. mole⁻¹ was calculated from ΔH°_f 298 = 25.63 kcal. mole⁻¹ obtained by third law analysis of the equilibrium data of H. Schmitz and H. T. Schumacher, Z. Naturforsch. **28**, 362 (1947) for the reaction ClF₃(g) = ClF(g) + F₂(g). Similar values are obtained from the equilibrium data of K. Schifer and E. Wicke, Z. Elektrochemie **52**, 205-209 (1948). Calorimetric values scatter widely, as summarized below; these were given little weight.

Source	Method	Reaction	Observation ₂₉₈ (kcal. mole ⁻¹)	3rd Law Drift (e.u.)	ΔH° _f 298 (kcal. mole ⁻¹)
1e	K _p (523-623°K)	ClF ₃ (g) → ClF(g) + F ₂ (g)	ΔH° _f 298 = 25.63	0.8 ± 0.3	-37.97
2e	K _p (733°K)	ClF ₃ (g) → ClF(g) + F ₂ (g)	ΔH° _f 298 = 25.77	---	-37.91
2b	K _p (570-680°K)	ClF ₃ (g) → ClF(g) + F ₂ (g)	ΔH° _f 298 = 26.12	6 ± 3	-38.26
1b	Calorimetric	3NaCl + ClF ₃ → 3NaF + 2Cl ₂	ΔH° _f 291 = -76.5	---	-40.02
1c	Calorimetric	NaCl + 0.5 F ₂ → NaF + 0.5 Cl ₂	ΔH° _f 291 = -39.5	---	-42.0*
3	Calorimetric	3NaCl + ClF ₃ → 3NaF + 2Cl ₂	ΔH° _f 291 = -86.8	---	-29.7
4	Calorimetric	0.5 F ₂ + NaCl → NaF + 0.5 Cl ₂	ΔH° _f 293 = -39.3	---	-31.1**
5	Flow reaction	0.5 Cl ₂ (g) + 1.5 F ₂ (g) = ClF ₃ (g)	ΔH° _f 473 = -26.4	---	-26.4

*From combination of 1b and 1c. **From combination of 3 and 4.

Sources

- 1 H. Schmitz and H. T. Schumacher Z. Naturforsch. **28**, 362 (1947).
- 2e (Hot wire) K. Schefer and E. Wicke, Z. Elektrochem. **52**, 205 (1948).
- 2b (From the Graph) K. Schefer and E. Wicke, Z. Elektrochem. **52**, 205 (1948).
- 3 H. v. Wertenberg Z. anorg. allgem. Chem. **258**, 356 (1949).
- 4 H. v. Wertenberg and O. Pitzner, A. anorg. allgem. Chem. **151**, 313 (1928).
- 5 C. F. Swinehart, private communication from the Hercules Chemical Co., March, 1963.

Heat Capacity and Entropy.

The structural constants were obtained from the microwave study of D. P. Smith, J. Chem. Phys. **21**, 609 (1953). The plunger distorted "m" structure is similar to that derived from X-ray studies of the solid by R. D. Burbank and P. N. Benaev, J. Chem. Phys. **21**, 802 (1953). Fundamental frequencies are taken from the infrared and Raman spectra of H. H. Claessen, B. Weinstein and J. G. Malm, J. Chem. Phys. **28**, 285 (1958). These data confirm the "m" structure as opposed to the pyramidal structure used in earlier spectral analyses.

Claessen, et al., loc. cit., calculate thermodynamic functions virtually identical with the JANAF values. These authors also correct the third law entropy reported by J. W. Gaiser, H. A. Bernhardt and G. D. Oliver, J. Am. Chem. Soc. **73**, 5725 (1951) from measurements of heat capacity (14-285°K.) and vapor pressure (226-303°K.). The entropy at the normal boiling point becomes S°_{284.91} = 67.04 cal. deg.⁻¹ mole⁻¹ when a non-ideality correction consistent with the dimer-monomer vapor equilibrium is applied. The corresponding statistical entropy, S°_{284.91} = 66.59 cal. deg.⁻¹ mole⁻¹, is consistent with the third law value within the probable error in the entropy of the liquid and the entropy of vaporization. The three principal moments of inertia are: I_A = 6.1114 X 10⁻³⁹, I_B = 1.81545 X 10⁻³⁸ and I_C = 2.42859 X 10⁻³⁸ g. cm.²



Chlorotrifluorosilane (ClSiF₃)
(Ideal Gas) Mol. Wt. = 120.547

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H ₂₉₈)/T	H°-H ₂₉₈ ΔH _f ⁰	ΔF ⁰	Log K _P
0	0.00	INFINITE	3.971	-313.953	INFINITE
100	11.114	57.326	3.064	-311.820	36.415
200	15.557	66.799	1.719	-308.664	337.615
298	18.671	73.751	0.000	-315.000	-224.335
300	19.018	73.868	0.035	-315.002	222.912
400	22.095	79.466	2.038	-315.046	131.110
500	22.431	84.507	4.203	-315.073	131.110
600	23.305	88.660	6.519	-315.039	106.159
700	23.694	92.319	8.681	-314.993	91.766
800	24.001	95.482	10.715	-314.945	69.919
900	24.403	98.819	13.736	-314.883	287.945
1000	24.821	101.023	16.210	-314.771	62.275
1100	24.967	103.397	18.704	-314.699	291.984
1200	25.117	105.577	21.206	-314.627	50.613
1300	25.253	107.543	23.696	-314.556	45.495
1400	25.301	109.843	26.181	-314.491	276.049
1500	25.366	111.211	28.703	-314.427	270.132
1600	25.423	112.650	31.322	-314.365	267.180
1700	25.469	114.393	34.071	-314.307	33.954
1800	25.507	115.850	36.816	-314.254	31.023
1900	25.539	117.069	39.561	-314.206	23.333
2000	25.568	118.530	41.524	-314.123	27.682
2100	25.593	119.766	44.082	-314.032	25.966
2200	25.614	120.980	46.642	-313.943	25.424
2300	25.632	122.110	49.225	-313.856	23.016
2400	25.648	123.169	51.841	-313.771	20.540
2500	25.663	124.257	54.334	-313.693	20.540
2600	25.676	125.264	56.901	-313.616	231.342
2700	25.687	126.233	59.469	-313.541	10.431
2800	25.697	127.166	62.009	-313.469	17.491
2900	25.707	128.081	64.581	-313.401	15.768
3000	25.715	128.941	67.180	-313.336	216.663
3100	25.723	129.764	69.752	-313.274	15.033
3200	25.729	130.601	72.325	-313.216	209.631
3300	25.736	131.393	74.896	-313.161	14.316
3400	25.740	132.156	77.469	-313.109	206.020
3500	25.747	132.898	80.046	-313.061	13.010
3600	25.751	133.633	82.621	-313.017	12.413
3700	25.756	134.339	85.196	-312.979	194.721
3800	25.760	135.026	87.772	-312.946	8.713
3900	25.763	135.689	90.352	-312.917	13.132
4000	25.767	136.347	92.925	-312.892	10.479
4100	25.770	136.983	95.502	-312.871	7.673
4200	25.773	137.604	98.079	-312.852	148.466
4300	25.776	138.211	100.656	-312.836	11.132
4400	25.779	138.804	103.232	-312.822	182.211
4500	25.781	139.363	105.812	-312.810	10.479
4600	25.783	139.949	108.390	-312.800	7.167
4700	25.786	140.504	110.969	-312.792	9.272
4800	25.789	141.076	113.547	-312.786	163.471
4900	25.791	141.626	116.126	-312.781	11.132
5000	25.791	142.100	118.705	-312.778	10.479
5100	25.793	142.610	121.284	-312.776	7.673
5200	25.795	143.111	123.864	-312.775	148.466
5300	25.797	143.683	126.444	-312.774	11.132
5400	25.799	144.236	129.025	-312.773	182.211
5500	25.799	144.556	131.603	-312.773	10.479
5600	25.800	145.023	134.183	-312.773	7.167
5700	25.801	145.480	136.763	-312.773	9.272
5800	25.802	145.929	139.343	-312.773	163.471
5900	25.804	146.403	141.925	-312.773	11.132
6000	25.804	146.403	144.508	-312.773	10.479

December 31, 1960.

Chlorotrifluorosilane (ClSiF₃) (Ideal Gas)

Mol. Wt. = 120.547
 ΔH_f^0 298.15 = [-315 ± 15] kcal. mole⁻¹
 S^0 298.15 = [73.8 ± 4] cal. deg⁻¹ mole⁻¹
 Point Group C_{3v}
 Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ω cm ⁻¹	
[870] (1)	
[550] (1)	
[275] (1)	
[900] (2)	
[400] (2)	
[200] (2)	

Moments of Inertia: $I_A = [19.9 \times 10^{-39}]$ g. cm.²
 $I_B = [33.9 \times 10^{-39}]$ g. cm.²
 $I_C = [33.9 \times 10^{-39}]$ g. cm.²
 $\sigma = 3$

Heat of Formation. ΔH_f^0 298.15 was estimated in Henderson and Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. The molecular constants were estimated by C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.



CHLORINE PENTAFLUORIDE (ClF₅)
(IDEAL GAS) GFW = 130.445

T, °K	Cp°	$\frac{gibbs/mole}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°	Log Kp
0	.000	.000	INFINITE	INFINITE	INFINITE	INFINITE
100	10.087	56.580	91.062	- 4.285	- 54.913	10.087
200	17.526	55.999	76.216	- 2.043	- 56.162	10.793
298	23.223	54.251	74.251	.000	- 57.870	12.000
300	23.266	74.385	74.242	.043	- 36.999	25.457
400	26.295	81.539	75.157	2.537	- 56.845	15.085
500	28.013	87.608	77.088	5.760	- 56.567	8.887
600	29.058	92.815	79.286	8.117	- 56.224	4.777
700	29.732	97.348	81.250	11.059	- 55.668	3.061
800	30.188	101.350	83.779	14.057	- 55.459	1.138
900	30.510	104.926	85.934	17.092	- 55.058	1.089
1000	30.746	108.153	87.997	20.156	- 54.654	1.3321
1100	30.922	111.092	89.965	23.240	- 54.240	1.4683
1200	31.056	113.789	91.840	26.330	- 53.842	1.5708
1300	31.165	116.279	93.625	29.450	- 53.439	1.6584
1400	31.250	118.592	95.337	32.571	- 53.038	1.7347
1500	31.319	120.750	96.950	35.700	- 52.640	1.7999
1600	31.376	122.773	98.492	38.835	- 52.244	1.8571
1700	31.423	124.677	99.966	41.975	- 51.850	1.9069
1800	31.463	126.474	101.408	45.119	- 51.472	1.9503
1900	31.496	128.176	102.773	48.267	- 51.090	1.9881
2000	31.525	129.792	104.084	51.410	- 50.714	2.0214
2100	31.550	131.331	105.345	54.572	- 50.343	2.0507
2200	31.571	132.799	106.560	57.728	- 49.978	2.0758
2300	31.590	134.203	107.731	60.886	- 49.617	2.0970
2400	31.607	135.548	108.862	64.046	- 49.263	2.1150
2500	31.622	136.839	109.956	67.207	- 48.916	2.1315
2600	31.635	138.079	111.014	70.370	- 48.573	2.1461
2700	31.646	139.273	112.038	73.534	- 48.235	2.1597
2800	31.656	140.424	113.032	76.699	- 47.903	2.1726
2900	31.666	141.535	113.996	79.865	- 47.579	2.1846
3000	31.674	142.609	114.932	83.032	- 47.262	2.1957
3100	31.682	143.648	115.841	86.200	- 46.940	2.2059
3200	31.689	144.654	116.726	89.369	- 46.644	2.2153
3300	31.695	145.629	117.587	92.538	- 46.345	2.2239
3400	31.701	146.575	118.426	95.708	- 46.051	2.2318
3500	31.706	147.494	119.243	98.878	- 45.766	2.2390
3600	31.711	148.387	120.041	102.049	- 45.484	2.2456
3700	31.715	149.256	120.818	105.220	- 45.211	2.2517
3800	31.719	150.102	121.578	108.392	- 44.943	2.2573
3900	31.723	150.926	122.320	111.564	- 44.684	2.2625
4000	31.727	151.729	123.065	114.737	- 44.428	2.2673
4100	31.730	152.513	123.784	117.909	- 44.181	2.2718
4200	31.733	153.278	124.468	121.083	- 43.930	2.2760
4300	31.736	154.024	125.127	124.256	- 43.700	2.2799
4400	31.739	154.754	125.783	127.430	- 43.472	2.2835
4500	31.741	155.467	126.444	130.604	- 43.247	2.2868
4600	31.743	156.165	127.093	133.778	- 43.027	2.2898
4700	31.745	156.848	127.730	136.952	- 42.815	2.2925
4800	31.747	157.516	128.353	140.127	- 42.606	2.2950
4900	31.749	158.171	128.955	143.302	- 42.404	2.2973
5000	31.751	158.812	129.517	146.477	- 42.208	2.2994
5100	31.753	159.441	130.097	149.652	- 42.016	2.3013
5200	31.754	160.057	130.667	152.827	- 41.830	2.3030
5300	31.756	160.662	131.228	156.003	- 41.649	2.3045
5400	31.757	161.256	131.778	159.179	- 41.475	2.3059
5500	31.759	161.839	132.320	162.354	- 41.304	2.3071
5600	31.760	162.411	132.852	165.530	- 41.140	2.3081
5700	31.761	162.973	133.375	168.706	- 40.980	2.3089
5800	31.762	163.525	133.890	171.883	- 40.824	2.3095
5900	31.763	164.068	134.397	175.050	- 40.676	2.3100
6000	31.764	164.602	134.896	178.235	- 40.532	2.3104

June 30, 1966

Point Group C_{4v}
S_{298.15} = 74.241 gibbs/mol
Round State Quantum Weight = [1]

$$\Delta H^\circ_0 = [-54.9 \pm 15] \text{ kcal/mol}$$

$$\Delta H^\circ_{298.15} = [-57 \pm 15] \text{ kcal/mol}$$

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}	ω_e, cm^{-1}
712 (1)	488 (1)	732 (2)
541 (1)	346 (1)	[440](2)
486 (1)	375 (1)	302 (2)

$$\text{Bond Distances: (Cl-P)}_{\text{basal}} = 1.72 \text{ \AA}$$

$$\text{Bond Angle: P-I-P} = 90^\circ$$

$$\text{Product of Moments of Inertia: } I_{A,B,C} = 2.47289 \times 10^{-113} \text{ g}^3 \text{ cm}^6$$

The heat of formation was estimated by assuming that the ratio $[A.B.E.(ClF_3)]/[A.B.E.(ClF_5)] - A.B.E.(ClF_3)$ was equal to $[A.B.E.(BrF_3)]/[A.B.E.(BrF_5)] - A.B.E.(BrF_3)$, where A.B.E. represents average bond energy. All values were taken from these tables. A.B.E.(ClF₅) was thus calculated to be 36 kcal/mol which leads to $\Delta H^\circ = -57 \pm 15$ kcal/mol.

Heat Capacity and Entropy.

O. M. Begun, W. H. Fletcher and D. P. Smith, J. Chem. Phys. **42**, 2236 (1965), have reported the infrared spectra of the gas and the Raman spectra of the liquid. Their assignments have been adopted here, including one frequency ν_6 obtained from a valence force-field treatment. The values are consistent with those for IF₅(g) and BrF₅(g). D. P. Smith, Science **141**, 1039 (1963), had previously reported three infrared bands. The structure of the molecule has not been determined but the spectra can only be interpreted assuming C_{4v} symmetry; this is in accord with IF₅ and BrF₅(g). Begun et al. assumed a square pyramidal structure with the chlorine in the base of the pyramid. There is some evidence that the chlorine may not lie in the basal plane but this would not appreciably affect the calculations. The structure adopted was that given by Begun et al. The individual moments of inertia are $I_A = I_B = 25.7380 \times 10^{-39} \text{ g cm}^2$ and $I_C = 37.3298 \times 10^{-39} \text{ g cm}^2$.

Iron Monochloride (FeCl)

(Ideal Gas) Mol. Wt. = 91.300

T, °K.	C _p ^o	-cal. mole ⁻¹ deg ⁻¹	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈	ΔH _f ^o	Log K _p
0	0.000	INFINITE	-	2.480	59.462	INFINITE
100	8.232	52.018	69.431	-1.791	59.977	-12.004
200	8.621	57.954	62.363	-0.892	60.054	-59.377
298	9.136	61.537	61.537	0.000	60.000	51.543
300	9.141	61.593	61.437	0.17	59.998	51.491
400	9.478	64.347	61.484	0.864	59.975	48.671
500	9.678	66.361	61.568	1.886	59.975	45.680
600	9.816	68.093	63.365	2.836	59.511	43.137
700	9.920	69.560	64.148	3.788	59.235	40.429
800	9.915	70.831	64.906	4.740	58.876	37.765
900	9.898	71.922	65.626	5.691	58.451	35.116
1000	9.814	72.954	66.311	6.643	57.953	32.602
1100	9.622	73.861	67.057	7.595	56.882	30.134
1200	9.532	74.690	67.667	8.547	56.221	27.725
1300	9.545	75.453	68.145	9.501	55.901	25.365
1400	9.571	76.161	68.643	10.456	55.565	23.079
1500	9.572	76.821	69.213	11.413	55.216	20.716
1600	9.584	77.439	69.708	12.371	54.851	18.428
1700	9.595	78.021	70.180	13.330	54.180	16.168
1800	9.605	78.569	70.631	14.290	53.694	13.948
1900	9.614	79.087	71.062	15.251	49.522	11.693
2000	9.619	79.582	71.473	16.212	48.970	9.953
2100	9.623	80.052	71.873	17.174	48.414	8.036
2200	9.627	80.499	72.255	18.137	47.854	6.129
2300	9.630	80.927	72.623	19.100	47.289	4.283
2400	9.632	81.336	72.978	20.063	46.715	2.588
2500	9.632	81.730	73.320	21.028	46.140	1.000
2600	9.633	82.108	73.651	21.989	45.566	-1.264
2700	9.633	82.472	73.971	22.952	44.981	-2.47
2800	9.632	82.822	74.281	23.916	44.391	-3.65
2900	9.632	83.160	74.581	24.879	43.795	-4.82
3000	9.631	83.487	74.873	25.842	43.194	-5.95
3100	9.631	83.802	75.156	26.805	42.588	-7.05
3200	9.630	84.108	75.431	27.768	41.949	-8.14
3300	9.629	84.405	75.698	28.731	41.603	-9.27
3400	9.629	84.692	75.958	29.694	41.767	-10.38
3500	9.628	84.971	76.212	30.657	41.940	-11.45
3600	9.628	85.242	76.459	31.620	42.122	-12.50
3700	9.628	85.506	76.700	32.582	42.314	-13.53
3800	9.628	85.763	76.935	33.545	42.515	-14.54
3900	9.628	86.013	77.165	34.508	42.725	-15.53
4000	9.629	86.257	77.389	35.471	42.947	-16.50
4100	9.630	86.495	77.608	36.434	43.176	-17.45
4200	9.631	86.727	77.823	37.397	43.417	-18.39
4300	9.632	86.953	78.032	38.360	43.667	-19.32
4400	9.634	87.175	78.238	39.323	43.928	-20.24
4500	9.636	87.391	78.439	40.287	44.199	-21.15
4600	9.638	87.603	78.636	41.251	44.478	-22.05
4700	9.640	87.810	78.829	42.214	44.770	-22.94
4800	9.642	88.013	79.018	43.179	45.071	-23.82
4900	9.644	88.212	79.203	44.143	45.383	-24.69
5000	9.646	88.407	79.386	45.108	45.705	-25.55
5100	9.651	88.598	79.564	46.072	46.037	-26.40
5200	9.654	88.786	79.740	47.038	46.379	-27.24
5300	9.658	88.969	79.912	48.003	46.732	-28.07
5400	9.661	89.150	80.082	48.969	47.096	-28.89
5500	9.663	89.327	80.248	49.936	47.469	-29.70
5600	9.669	89.501	80.412	50.902	47.853	-30.50
5700	9.673	89.673	80.573	51.869	48.247	-31.29
5800	9.678	89.841	80.731	52.837	48.651	-32.07
5900	9.682	89.999	80.887	53.805	49.065	-32.84
6000	9.687	90.159	81.040	54.773	49.488	-33.60

June 30, 1965

IRON MONOCHLORIDE (FeCl)

(IDEAL GAS)

MOL. WT. = 91.300

Ground State Configuration $6^5\Sigma$
 $S_{298.15}^o = [61.537] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = 60 \pm 20 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o = 60 \pm 20 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

ϵ_i , cm ⁻¹	$\frac{g_i}{6}$
0	[200]
[200]	[8]
[1000]	[8]
[4000]	[8]

 $\omega_e x_e = 1.19 \text{ cm.}^{-1}$ $\sigma = 1$ $\omega_e = 404.92 \text{ cm.}^{-1}$ $r_e = [2.09]$ $\omega_e = [0.00075] \text{ cm.}^{-1}$

Heat of Formation.

The dissociation energy (D_0^o) of FeCl(g) was reported as $3 \pm 2 \text{ e.v.}$ ($69 \pm 46 \text{ kcal. mole}^{-1}$) by A. O. Ceylan, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The corresponding ΔH_f^o 298.15 (FeCl, g) was evaluated to be $56 \pm 46 \text{ kcal. mole}^{-1}$. By comparing $D(\text{Fe-O}) = 101 \text{ kcal. mole}^{-1}$ in FeO(g) with the coordinate bond energies obtained in organic complexes and iron carbonyl halides of $E(\text{Fe-O}) = 59.4$ and $E(\text{Fe-Cl}) = 37.3 \text{ kcal. mole}^{-1}$, reported by M. M. Jones, B. J. Yow and M. R. May, Inorg. Chem. 1, 166 (1962), the $D(\text{Fe-Cl})$ in FeCl(g) was estimated as $101 \times (37.3/59.4) = 63.3 \text{ kcal. mole}^{-1}$, yielding ΔH_f^o 298.15 (FeCl, g) = $64 \text{ kcal. mole}^{-1}$. The adopted value of ΔH_f^o 298.15 for FeCl(g) is $60 \pm 20 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The ground state configuration, ω_e and $\omega_e x_e$ (corrected to the average isotopic species) were obtained from O. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950. The Fe-Cl bond distance was assumed to be the same as that in FeCl₂(g). Hence the values of B_e and ω_e were calculated. The electronic levels and quantum weights were estimated by comparison with the electronic levels in Fe²⁺(g) reported by C. E. Moore, "Atomic Energy Levels", Circular of the National Bureau of Standards 467, Vol. II, 1952, using the reasoning suggested by J. T. Hougen, O. E. Leroi and T. C. James, J. Chem. Phys. 34, 1670 (1961). The total 30 for the quantum weight was obtained from the ground multiplet of Fe²⁺ and was split arbitrarily. The entropy values may be in error by a few entropy units due to the uncertainties in the low lying electronic levels. The principal moment of inertia is $1.5728 \times 10^{-38} \text{ g. cm.}^2$.

Hydrogen Chloride (HCl)

(Ideal Gas) Mol. Wt. = 36.465

T, °K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔF°	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	6.959	37.041	2.065	-22.019	-22.019	∞.000	∞.000
200	6.961	41.865	2.065	-22.063	-22.063	48.709	1.485
298	6.964	44.685	2.065	-22.063	-22.063	44.685	1.656
300	6.964	44.688	2.065	-22.064	-22.064	16.596	1.656
400	6.973	46.693	2.065	-22.064	-22.064	12.573	1.656
500	7.004	48.252	2.065	-22.064	-22.064	10.151	1.656
600	7.069	49.534	2.065	-22.064	-22.064	8.320	1.656
700	7.167	50.630	2.065	-22.064	-22.064	7.368	1.656
800	7.289	51.595	2.065	-22.064	-22.064	6.494	1.656
900	7.423	52.461	2.065	-22.064	-22.064	5.812	1.656
1000	7.559	53.250	2.065	-22.064	-22.064	5.205	1.656
1100	7.693	53.977	2.065	-22.064	-22.064	4.616	1.656
1200	7.819	54.652	2.065	-22.064	-22.064	4.042	1.656
1300	7.936	55.283	2.065	-22.064	-22.064	3.484	1.656
1400	8.043	55.875	2.065	-22.064	-22.064	2.942	1.656
1500	8.141	56.431	2.065	-22.064	-22.064	2.416	1.656
1600	8.229	56.961	2.065	-22.064	-22.064	1.905	1.656
1700	8.310	57.461	2.065	-22.064	-22.064	1.408	1.656
1800	8.382	57.940	2.065	-22.064	-22.064	1.025	1.656
1900	8.449	58.395	2.065	-22.064	-22.064	0.756	1.656
2000	8.509	58.830	2.065	-22.064	-22.064	0.500	1.656
2100	8.564	59.246	2.065	-22.064	-22.064	0.256	1.656
2200	8.614	59.646	2.065	-22.064	-22.064	0.025	1.656
2300	8.660	60.030	2.065	-22.064	-22.064	0.000	1.656
2400	8.703	60.399	2.065	-22.064	-22.064	0.000	1.656
2500	8.742	60.755	2.065	-22.064	-22.064	0.000	1.656
2600	8.778	61.099	2.065	-22.064	-22.064	0.000	1.656
2700	8.812	61.431	2.065	-22.064	-22.064	0.000	1.656
2800	8.844	61.752	2.065	-22.064	-22.064	0.000	1.656
2900	8.874	62.063	2.065	-22.064	-22.064	0.000	1.656
3000	8.902	62.364	2.065	-22.064	-22.064	0.000	1.656
3100	8.928	62.656	2.065	-22.064	-22.064	0.000	1.656
3200	8.953	62.940	2.065	-22.064	-22.064	0.000	1.656
3300	8.976	63.216	2.065	-22.064	-22.064	0.000	1.656
3400	8.999	63.484	2.065	-22.064	-22.064	0.000	1.656
3500	9.020	63.745	2.065	-22.064	-22.064	0.000	1.656
3600	9.041	64.000	2.065	-22.064	-22.064	0.000	1.656
3700	9.061	64.248	2.065	-22.064	-22.064	0.000	1.656
3800	9.079	64.490	2.065	-22.064	-22.064	0.000	1.656
3900	9.096	64.726	2.065	-22.064	-22.064	0.000	1.656
4000	9.115	64.956	2.065	-22.064	-22.064	0.000	1.656
4100	9.132	65.182	2.065	-22.064	-22.064	0.000	1.656
4200	9.148	65.402	2.065	-22.064	-22.064	0.000	1.656
4300	9.164	65.617	2.065	-22.064	-22.064	0.000	1.656
4400	9.180	65.828	2.065	-22.064	-22.064	0.000	1.656
4500	9.195	66.035	2.065	-22.064	-22.064	0.000	1.656
4600	9.210	66.237	2.065	-22.064	-22.064	0.000	1.656
4700	9.224	66.435	2.065	-22.064	-22.064	0.000	1.656
4800	9.238	66.629	2.065	-22.064	-22.064	0.000	1.656
4900	9.252	66.820	2.065	-22.064	-22.064	0.000	1.656
5000	9.265	67.007	2.065	-22.064	-22.064	0.000	1.656
5100	9.278	67.191	2.065	-22.064	-22.064	0.000	1.656
5200	9.291	67.371	2.065	-22.064	-22.064	0.000	1.656
5300	9.304	67.548	2.065	-22.064	-22.064	0.000	1.656
5400	9.316	67.722	2.065	-22.064	-22.064	0.000	1.656
5500	9.329	67.893	2.065	-22.064	-22.064	0.000	1.656
5600	9.341	68.061	2.065	-22.064	-22.064	0.000	1.656
5700	9.353	68.227	2.065	-22.064	-22.064	0.000	1.656
5800	9.365	68.390	2.065	-22.064	-22.064	0.000	1.656
5900	9.376	68.550	2.065	-22.064	-22.064	0.000	1.656
6000	9.388	68.707	2.065	-22.064	-22.064	0.000	1.656

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1964

HYDROGEN CHLORIDE (HCl)

(IDEAL GAS)

Ground State Configuration	$1\Sigma^+$	$1\Sigma^+ +$	Electronic Levels and Quantum Weights	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	ϵ_6	ϵ_7	ϵ_8	ϵ_9	ϵ_{10}	ϵ_{11}	ϵ_{12}	ϵ_{13}	ϵ_{14}	ϵ_{15}	ϵ_{16}	ϵ_{17}	ϵ_{18}	ϵ_{19}	ϵ_{20}	ϵ_{21}	ϵ_{22}	ϵ_{23}	ϵ_{24}	ϵ_{25}	ϵ_{26}	ϵ_{27}	ϵ_{28}	ϵ_{29}	ϵ_{30}	ϵ_{31}	ϵ_{32}	ϵ_{33}	ϵ_{34}	ϵ_{35}	ϵ_{36}	ϵ_{37}	ϵ_{38}	ϵ_{39}	ϵ_{40}	ϵ_{41}	ϵ_{42}	ϵ_{43}	ϵ_{44}	ϵ_{45}	ϵ_{46}	ϵ_{47}	ϵ_{48}	ϵ_{49}	ϵ_{50}	ϵ_{51}	ϵ_{52}	ϵ_{53}	ϵ_{54}	ϵ_{55}	ϵ_{56}	ϵ_{57}	ϵ_{58}	ϵ_{59}	ϵ_{60}	ϵ_{61}	ϵ_{62}	ϵ_{63}	ϵ_{64}	ϵ_{65}	ϵ_{66}	ϵ_{67}	ϵ_{68}	ϵ_{69}	ϵ_{70}	ϵ_{71}	ϵ_{72}	ϵ_{73}	ϵ_{74}	ϵ_{75}	ϵ_{76}	ϵ_{77}	ϵ_{78}	ϵ_{79}	ϵ_{80}	ϵ_{81}	ϵ_{82}	ϵ_{83}	ϵ_{84}	ϵ_{85}	ϵ_{86}	ϵ_{87}	ϵ_{88}	ϵ_{89}	ϵ_{90}	ϵ_{91}	ϵ_{92}	ϵ_{93}	ϵ_{94}	ϵ_{95}	ϵ_{96}	ϵ_{97}	ϵ_{98}	ϵ_{99}	ϵ_{100}	ϵ_{101}	ϵ_{102}	ϵ_{103}	ϵ_{104}	ϵ_{105}	ϵ_{106}	ϵ_{107}	ϵ_{108}	ϵ_{109}	ϵ_{110}	ϵ_{111}	ϵ_{112}	ϵ_{113}	ϵ_{114}	ϵ_{115}	ϵ_{116}	ϵ_{117}	ϵ_{118}	ϵ_{119}	ϵ_{120}	ϵ_{121}	ϵ_{122}	ϵ_{123}	ϵ_{124}	ϵ_{125}	ϵ_{126}	ϵ_{127}	ϵ_{128}	ϵ_{129}	ϵ_{130}	ϵ_{131}	ϵ_{132}	ϵ_{133}	ϵ_{134}	ϵ_{135}	ϵ_{136}	ϵ_{137}	ϵ_{138}	ϵ_{139}	ϵ_{140}	ϵ_{141}	ϵ_{142}	ϵ_{143}	ϵ_{144}	ϵ_{145}	ϵ_{146}	ϵ_{147}	ϵ_{148}	ϵ_{149}	ϵ_{150}	ϵ_{151}	ϵ_{152}	ϵ_{153}	ϵ_{154}	ϵ_{155}	ϵ_{156}	ϵ_{157}	ϵ_{158}	ϵ_{159}	ϵ_{160}	ϵ_{161}	ϵ_{162}	ϵ_{163}	ϵ_{164}	ϵ_{165}	ϵ_{166}	ϵ_{167}	ϵ_{168}	ϵ_{169}	ϵ_{170}	ϵ_{171}	ϵ_{172}	ϵ_{173}	ϵ_{174}	ϵ_{175}	ϵ_{176}	ϵ_{177}	ϵ_{178}	ϵ_{179}	ϵ_{180}	ϵ_{181}	ϵ_{182}	ϵ_{183}	ϵ_{184}	ϵ_{185}	ϵ_{186}	ϵ_{187}	ϵ_{188}	ϵ_{189}	ϵ_{190}	ϵ_{191}	ϵ_{192}	ϵ_{193}	ϵ_{194}	ϵ_{195}	ϵ_{196}	ϵ_{197}	ϵ_{198}	ϵ_{199}	ϵ_{200}	ϵ_{201}	ϵ_{202}	ϵ_{203}	ϵ_{204}	ϵ_{205}	ϵ_{206}	ϵ_{207}	ϵ_{208}	ϵ_{209}	ϵ_{210}	ϵ_{211}	ϵ_{212}	ϵ_{213}	ϵ_{214}	ϵ_{215}	ϵ_{216}	ϵ_{217}	ϵ_{218}	ϵ_{219}	ϵ_{220}	ϵ_{221}	ϵ_{222}	ϵ_{223}	ϵ_{224}	ϵ_{225}	ϵ_{226}	ϵ_{227}	ϵ_{228}	ϵ_{229}	ϵ_{230}	ϵ_{231}	ϵ_{232}	ϵ_{233}	ϵ_{234}	ϵ_{235}	ϵ_{236}	ϵ_{237}	ϵ_{238}	ϵ_{239}	ϵ_{240}	ϵ_{241}	ϵ_{242}	ϵ_{243}	ϵ_{244}	ϵ_{245}	ϵ_{246}	ϵ_{247}	ϵ_{248}	ϵ_{249}	ϵ_{250}	ϵ_{251}	ϵ_{252}	ϵ_{253}	ϵ_{254}	ϵ_{255}	ϵ_{256}	ϵ_{257}	ϵ_{258}	ϵ_{259}	ϵ_{260}	ϵ_{261}	ϵ_{262}	ϵ_{263}	ϵ_{264}	ϵ_{265}	ϵ_{266}	ϵ_{267}	ϵ_{268}	ϵ_{269}	ϵ_{270}	ϵ_{271}	ϵ_{272}	ϵ_{273}	ϵ_{274}	ϵ_{275}	ϵ_{276}	ϵ_{277}	ϵ_{278}	ϵ_{279}	ϵ_{280}	ϵ_{281}	ϵ_{282}	ϵ_{283}	ϵ_{284}	ϵ_{285}	ϵ_{286}	ϵ_{287}	ϵ_{288}	ϵ_{289}	ϵ_{290}	ϵ_{291}	ϵ_{292}	ϵ_{293}	ϵ_{294}	ϵ_{295}	ϵ_{296}	ϵ_{297}	ϵ_{298}	ϵ_{299}	ϵ_{300}	ϵ_{301}	ϵ_{302}	ϵ_{303}	ϵ_{304}	ϵ_{305}	ϵ_{306}	ϵ_{307}	ϵ_{308}	ϵ_{309}	ϵ_{310}	ϵ_{311}	ϵ_{312}	ϵ_{313}	ϵ_{314}	ϵ_{315}	ϵ_{316}	ϵ_{317}	ϵ_{318}	ϵ_{319}	ϵ_{320}	ϵ_{321}	ϵ_{322}	ϵ_{323}	ϵ_{324}	ϵ_{325}	ϵ_{326}	ϵ_{327}	ϵ_{328}	ϵ_{329}	ϵ_{330}	ϵ_{331}	ϵ_{332}	ϵ_{333}	ϵ_{334}	ϵ_{335}	ϵ_{336}	ϵ_{337}	ϵ_{338}	ϵ_{339}	ϵ_{340}	ϵ_{341}	ϵ_{342}	ϵ_{343}	ϵ_{344}	ϵ_{345}	ϵ_{346}	ϵ_{347}	ϵ_{348}	ϵ_{349}	ϵ_{350}	ϵ_{351}	ϵ_{352}	ϵ_{353}	ϵ_{354}	ϵ_{355}	ϵ_{356}	ϵ_{357}	ϵ_{358}	ϵ_{359}	ϵ_{360}	ϵ_{361}	ϵ_{362}	ϵ_{363}	ϵ_{364}	ϵ_{365}	ϵ_{366}	ϵ_{367}	ϵ_{368}	ϵ_{369}	ϵ_{370}	ϵ_{371}	ϵ_{372}	ϵ_{373}	ϵ_{374}	ϵ_{375}	ϵ_{376}	ϵ_{377}	ϵ_{378}	ϵ_{379}	ϵ_{380}	ϵ_{381}	ϵ_{382}	ϵ_{383}	ϵ_{384}	ϵ_{385}	ϵ_{386}	ϵ_{387}	ϵ_{388}	ϵ_{389}	ϵ_{390}	ϵ_{391}	ϵ_{392}	ϵ_{393}	ϵ_{394}	ϵ_{395}	ϵ_{396}	ϵ_{397}	ϵ_{398}	ϵ_{399}	ϵ_{400}	ϵ_{401}	ϵ_{402}	ϵ_{403}	ϵ_{404}	ϵ_{405}	ϵ_{406}	ϵ_{407}	ϵ_{408}	ϵ_{409}	ϵ_{410}	ϵ_{411}	ϵ_{412}	ϵ_{413}	ϵ_{414}	ϵ_{415}	ϵ_{416}	ϵ_{417}	ϵ_{418}	ϵ_{419}	ϵ_{420}	ϵ_{421}	ϵ_{422}	ϵ_{423}	ϵ_{424}	ϵ_{425}	ϵ_{426}	ϵ_{427}	ϵ_{428}	ϵ_{429}	ϵ_{430}	ϵ_{431}	ϵ_{432}	ϵ_{433}	ϵ_{434}	ϵ_{435}	ϵ_{436}	ϵ_{437}	ϵ_{438}	ϵ_{439}	ϵ_{440}	ϵ_{441}	ϵ_{442}	ϵ_{443}	ϵ_{444}	ϵ_{445}	ϵ_{446}	ϵ_{447}	ϵ_{448}	ϵ_{449}	ϵ_{450}	ϵ_{451}	ϵ_{452}	ϵ_{453}	ϵ_{454}	ϵ_{455}	ϵ_{456}	ϵ_{457}	ϵ_{458}	ϵ_{459}	ϵ_{460}	ϵ_{461}	ϵ_{462}	ϵ_{463}	ϵ_{464}	ϵ_{465}	ϵ_{466}	ϵ_{467}	ϵ_{468}	ϵ_{469}	ϵ_{470}	ϵ_{471}	ϵ_{472}	ϵ_{473}	ϵ_{474}	ϵ_{475}	ϵ_{476}	ϵ_{477}	ϵ_{478}	ϵ_{479}	ϵ_{480}	ϵ_{481}	ϵ_{482}	ϵ_{483}	ϵ_{484}	ϵ_{485}	ϵ_{486}	ϵ_{487}	ϵ_{488}	ϵ_{489}	ϵ_{490}	ϵ_{491}	ϵ_{492}	ϵ_{493}	ϵ_{494}	ϵ_{495}	ϵ_{496}	ϵ_{497}	ϵ_{498}	ϵ_{499}	ϵ_{500}	ϵ_{501}	ϵ_{502}	ϵ_{503}	ϵ_{504}	ϵ_{505}	ϵ_{506}	ϵ_{507}	ϵ_{508}	ϵ_{509}	ϵ_{510}	ϵ_{511}	ϵ_{512}	ϵ_{513}	ϵ_{514}	ϵ_{515}	ϵ_{516}	ϵ_{517}	ϵ_{518}	ϵ_{519}	ϵ_{520}	ϵ_{521}	ϵ_{522}	ϵ_{523}	ϵ_{524}	ϵ_{525}	ϵ_{526}	ϵ_{527}	ϵ_{528}	ϵ_{529}	ϵ_{530}	ϵ_{531}	ϵ_{532}	ϵ_{533}	ϵ_{534}	ϵ_{535}	ϵ_{536}	ϵ_{537}	ϵ_{538}	ϵ_{539}	ϵ_{540}	ϵ_{541}	ϵ_{542}	ϵ_{543}	ϵ_{544}	ϵ_{545}	ϵ_{546}	ϵ_{547}	ϵ_{548}	ϵ_{549}	ϵ_{550}	ϵ_{551}	ϵ_{552}	ϵ_{553}	ϵ_{554}	ϵ_{555}	ϵ_{556}	ϵ_{557}	ϵ_{558}	ϵ_{559}	ϵ_{560}	ϵ_{561}	ϵ_{562}	ϵ_{563}	ϵ_{564}	ϵ_{565}	ϵ_{566}	ϵ_{567}	ϵ_{568}	ϵ_{569}	ϵ_{570}	ϵ_{571}	ϵ_{572}	ϵ_{573}	ϵ_{574}	ϵ_{575}	ϵ_{576}	ϵ_{577}	ϵ_{578}	ϵ_{579}	ϵ_{580}	ϵ_{581}	ϵ_{582}	ϵ_{583}	ϵ_{584}	ϵ_{585}	ϵ_{586}	ϵ_{587}	ϵ_{588}	ϵ_{589}	ϵ_{590}	ϵ_{591}	ϵ_{592}	ϵ_{593}	ϵ_{594}	ϵ_{595}	ϵ_{596}	ϵ_{597}	ϵ_{598}	ϵ_{599}	ϵ_{600}	ϵ_{601}	ϵ_{602}	ϵ_{603}	ϵ_{604}	ϵ_{605}	ϵ_{606}	ϵ_{607}	ϵ_{608}	ϵ_{609}	ϵ_{610}	ϵ_{611}	ϵ_{612}	ϵ_{613}	ϵ_{614}	ϵ_{615}	ϵ_{616}	ϵ_{617}	ϵ_{618}	ϵ_{619}	ϵ_{620}	ϵ_{621}	ϵ_{622}	ϵ_{623}	ϵ_{624}	ϵ_{625}	ϵ_{626}	ϵ_{627}	ϵ_{628}	ϵ_{629}	ϵ_{630}	ϵ_{631}	ϵ_{632}	ϵ_{633}	ϵ_{634}	ϵ_{635}	ϵ_{636}	ϵ_{637}	ϵ_{638}	ϵ_{639}	ϵ_{640}	ϵ_{641}	ϵ_{642}	ϵ_{643}	ϵ_{644}	ϵ_{645}	ϵ_{646}	ϵ_{647}	ϵ_{648}	ϵ_{649}	ϵ_{650}	ϵ_{651}	ϵ_{652}	ϵ_{653}	ϵ_{654}	ϵ_{655}	ϵ_{656}	ϵ_{657}	ϵ_{658}	ϵ_{659}	ϵ_{660}	ϵ_{661}	ϵ_{662}	ϵ_{663}	ϵ_{664}	ϵ_{665}	ϵ_{666}	ϵ_{667}	ϵ_{668}	ϵ_{669}	ϵ_{670}	ϵ_{671}	ϵ_{672}	ϵ_{673}	ϵ_{674}	ϵ_{675}	ϵ_{676}	ϵ_{677}	ϵ_{678}	ϵ_{679}	ϵ_{680}	ϵ_{681}	ϵ_{682}	ϵ_{683}	ϵ_{684}	ϵ_{685}	ϵ_{686}	ϵ_{687}	ϵ_{688}	ϵ_{689}	ϵ_{690}	ϵ_{691}	ϵ_{692}	ϵ_{693}	ϵ_{694}	ϵ_{695}	ϵ_{696}	ϵ_{697}	ϵ_{698}	ϵ_{699}	ϵ_{700}	ϵ_{701}	ϵ_{702}	ϵ_{703}	ϵ_{704}	ϵ_{705}	ϵ_{706}	ϵ_{707}	ϵ_{708}	ϵ_{709}	ϵ_{710}	ϵ_{711}	ϵ_{712}	ϵ_{713}	ϵ_{714}	ϵ_{715}	ϵ_{716}	ϵ_{717}	ϵ_{718}	ϵ_{719}	ϵ_{720}	ϵ_{721}	ϵ_{722}	ϵ_{723}	ϵ_{724}	ϵ_{725}	ϵ_{726}	ϵ_{727}	ϵ_{728}	ϵ_{729}	ϵ_{730}	ϵ_{731}	ϵ_{732}	ϵ_{733}	ϵ_{734}	ϵ_{735}	ϵ_{736}	ϵ_{737}	ϵ_{738}	ϵ_{739}	ϵ_{740}	ϵ_{741}	ϵ_{742}	ϵ_{743}	ϵ_{744}	ϵ_{745}	ϵ_{746}	ϵ_{747}	ϵ_{748}	ϵ_{749}	ϵ_{750}	ϵ_{751}	ϵ_{752}	ϵ_{753}	ϵ_{754}	ϵ_{755}	ϵ_{756}	ϵ_{757}	ϵ_{758}	ϵ_{759}	ϵ_{760}	ϵ_{761}	ϵ_{762}	ϵ_{763}	ϵ_{764}	ϵ_{765}	ϵ_{766}	ϵ_{767}	ϵ_{768}	ϵ_{769}	ϵ_{770}	ϵ_{771}	ϵ_{772}	ϵ_{773}	ϵ_{774}	ϵ_{775}	ϵ_{776}	ϵ_{777}	ϵ_{778}	ϵ_{779}	ϵ_{780}	ϵ_{781}	ϵ_{782}	ϵ_{783}	ϵ_{784}	ϵ_{785}	ϵ_{786}	ϵ_{787}	ϵ_{788}	ϵ_{789}	ϵ_{790}	ϵ_{791}	ϵ_{792}	ϵ_{793}	ϵ_{794}	ϵ_{795}	ϵ_{796}	ϵ_{797}	ϵ_{798}	ϵ_{799}	ϵ_{800}	ϵ_{801}	ϵ_{802}	ϵ_{803}	ϵ_{804}	ϵ_{805}	ϵ_{806}	ϵ_{807}	ϵ_{808}	ϵ_{809}	ϵ_{810}	ϵ_{811}	ϵ_{812}	ϵ_{813}	ϵ_{814}	ϵ_{815}	ϵ_{816}	ϵ_{817}	ϵ_{818}	ϵ_{819}	ϵ_{820}	ϵ_{821}	ϵ_{822}	ϵ_{823}	ϵ_{824}	ϵ_{825}	ϵ_{826}	ϵ_{827}	ϵ_{828}	ϵ_{829}	ϵ_{830}	ϵ_{831}	ϵ_{832}	ϵ_{833}	ϵ_{834}	ϵ_{835}	ϵ_{836}	ϵ_{837}	ϵ_{838}	ϵ_{839}	ϵ_{840}	ϵ_{841}	ϵ_{842}	ϵ_{843}	ϵ_{844}	ϵ_{845}	ϵ_{846}	ϵ_{847}	ϵ_{848}	ϵ_{849}	ϵ_{850}	ϵ_{851}	ϵ_{852}	ϵ_{853}	ϵ_{854}	ϵ_{855}	ϵ_{856}	ϵ_{857}	ϵ_{858}	ϵ_{859}	ϵ_{860}	ϵ_{861}	ϵ_{862}	ϵ_{863}	ϵ_{864}	ϵ_{865}	ϵ_{866}	ϵ_{867}	ϵ_{868}	ϵ_{869}	ϵ_{870}	ϵ_{871}	ϵ_{872}	ϵ_{873}	ϵ_{874}	ϵ_{875}	ϵ_{876}	ϵ_{877}	ϵ_{878}	ϵ_{879}	ϵ_{880}	ϵ_{881}	ϵ_{882}	ϵ_{883}	ϵ_{884}	ϵ_{885}	ϵ_{886}	$\epsilon_{887}</$
----------------------------	-------------	---------------	---------------------------------------	--------------	--------------	--------------	--------------	--------------	--------------	--------------	--------------	--------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	-----------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	------------------	--------------------

Hypochlorous Acid (HClO)

(Ideal Gas) Mol. Wt. = 52.465

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	7.954	0.000	INFINITE	INFINITE	2.440	21.294	21.294	INFINITE
100	8.256	47.566	64.019	1.845	1.845	21.595	20.767	85.428
200	8.484	51.139	57.237	1.680	1.680	21.902	19.456	13.655
298	8.594	52.936	56.136	1.600	1.600	22.000	18.558	13.655
300	8.697	56.601	56.547	1.616	1.616	22.004	18.939	13.764
400	9.553	59.253	56.904	1.840	1.840	22.198	17.887	9.773
500	10.070	61.445	57.599	1.923	1.923	22.356	16.790	7.339
600	10.509	63.323	58.400	2.054	2.054	22.488	15.644	5.705
700	10.844	64.949	59.223	2.142	2.142	22.598	14.517	4.532
800	11.125	66.436	60.035	2.200	2.200	22.695	13.356	3.649
900	11.370	67.761	60.821	2.240	2.240	22.778	12.185	2.959
1000	11.589	68.970	61.576	2.268	2.268	22.849	11.004	2.405
1100	11.787	70.084	62.300	2.288	2.288	22.911	9.816	1.990
1200	11.967	71.118	62.992	2.301	2.301	22.964	8.623	1.570
1300	12.131	72.082	63.655	2.308	2.308	23.011	7.427	1.248
1400	12.279	72.987	64.289	2.312	2.312	23.051	6.226	0.972
1500	12.413	73.839	64.894	2.315	2.315	23.086	5.023	0.732
1600	12.534	74.644	65.462	2.317	2.317	23.122	3.818	0.52
1700	12.643	75.407	66.004	2.318	2.318	23.152	2.609	0.325
1800	12.742	76.132	66.518	2.319	2.319	23.181	1.401	0.170
1900	12.831	76.824	67.005	2.319	2.319	23.209	0.189	0.022
2000	12.911	77.484	67.468	2.319	2.319	23.237	1.022	0.112
2100	12.983	78.116	67.903	2.318	2.318	23.264	2.236	0.233
2200	13.049	78.721	68.319	2.317	2.317	23.293	3.451	0.343
2300	13.108	79.303	68.707	2.315	2.315	23.322	4.667	0.443
2400	13.162	79.862	69.077	2.313	2.313	23.354	5.886	0.536
2500	13.211	80.400	69.489	2.311	2.311	23.389	7.103	0.621
2600	13.256	80.919	70.299	2.309	2.309	23.424	8.325	0.700
2700	13.296	81.420	70.701	2.307	2.307	23.463	9.546	0.773
2800	13.334	81.904	71.093	2.305	2.305	23.505	10.770	0.841
2900	13.368	82.373	71.474	2.303	2.303	23.549	11.996	0.904
3000	13.399	82.826	71.845	2.301	2.301	23.597	13.221	0.963
3100	13.428	83.264	72.204	2.300	2.300	23.648	14.448	1.019
3200	13.456	83.693	72.558	2.299	2.299	23.701	15.678	1.071
3300	13.479	84.107	72.902	2.298	2.298	23.761	16.910	1.120
3400	13.502	84.510	73.238	2.297	2.297	23.822	18.143	1.166
3500	13.523	84.902	73.565	2.296	2.296	23.886	19.378	1.210
3600	13.542	85.284	73.884	2.295	2.295	23.957	20.616	1.252
3700	13.560	85.654	74.199	2.294	2.294	24.030	21.851	1.291
3800	13.577	86.016	74.503	2.293	2.293	24.106	23.097	1.328
3900	13.593	86.369	74.805	2.292	2.292	24.186	24.340	1.364
4000	13.607	86.713	75.098	2.291	2.291	24.270	25.585	1.398
4100	13.621	87.050	75.385	2.290	2.290	24.357	26.832	1.430
4200	13.634	87.378	75.667	2.289	2.289	24.447	28.082	1.460
4300	13.646	87.699	75.943	2.288	2.288	24.540	29.333	1.491
4400	13.657	88.013	76.214	2.287	2.287	24.636	30.587	1.521
4500	13.667	88.320	76.479	2.286	2.286	24.736	31.843	1.546
4600	13.677	88.620	76.740	2.285	2.285	24.837	33.102	1.571
4700	13.687	88.914	76.996	2.284	2.284	24.943	34.365	1.596
4800	13.695	89.203	77.247	2.283	2.283	25.050	35.626	1.622
4900	13.704	89.485	77.494	2.282	2.282	25.159	36.891	1.645
5000	13.711	89.762	77.737	2.281	2.281	25.271	38.156	1.668
5100	13.719	90.034	77.975	2.280	2.280	25.385	39.430	1.690
5200	13.726	90.300	78.210	2.279	2.279	25.500	40.707	1.710
5300	13.732	90.562	78.440	2.278	2.278	25.619	41.977	1.729
5400	13.739	90.818	78.667	2.277	2.277	25.739	43.249	1.746
5500	13.745	91.071	78.890	2.276	2.276	25.860	44.531	1.769
5600	13.750	91.318	79.110	2.275	2.275	25.985	45.809	1.788
5700	13.754	91.562	79.326	2.274	2.274	26.116	47.086	1.803
5800	13.758	91.801	79.540	2.273	2.273	26.238	48.360	1.816
5900	13.761	92.036	79.749	2.272	2.272	26.367	49.665	1.830
6000	13.770	92.268	79.956	2.271	2.271	26.497	50.956	1.856

HYPOCHLOROUS ACID (HClO)

(IDEAL GAS)

MOL. WT. = 52.465

ClHO

ΔH°_{f0} = [-22] ± 3 kcal. mole⁻¹
 ΔH°_f 298.15 = [-22] ± 3 kcal. mole⁻¹
 S°_{298.15} = 56.546 cal. deg.⁻¹ mole⁻¹

Point Group C_s

Vibrational Levels and Multiplicities

(<i>U</i>), cm. ⁻¹	
739 (1)	
1242 (1)	
3626 (1)	

O-H distance = 0.98 ± 0.01 Å O-Cl distance = 1.72 ± 0.04 Å H-O-Cl angle = 104° ± 3° σ = 1

Product of moments of inertia = 4.54 × 10⁻¹¹⁷ g.² cm.⁶

Heat of Formation

I. E. Fila, K. P. Miahchenko, and N. V. Pakhomova, Zhur. Neorg. Khim. 3, 1772, 1761 (1958), report the following heats of reaction:

ClO⁻(aq) + H⁺(aq) → HOCl(aq)

ΔH°_f 298.15 = -5.84 ± 0.03 kcal.

ΔH°_f 298.15 = -36.93 ± 0.05 kcal.

If the following auxiliary heats of formation are used:

ClO⁻(aq) + H₂O₂(aq) → Cl⁻(aq) + H₂O(l) + O₂(g)

ΔH°_f 298.15 = -40.02 kcal. mole⁻¹ (National Bureau of Standards Circ. 500, 1952)

ΔH°_f 298.15 = -68.32 kcal. mole⁻¹ (National Bureau of Standards Circ. 500, 1952)

ΔH°_f 298.15 = -45.70 ± 0.02 kcal. mole⁻¹ (P. A. Giguère, B. G. Morissette, A. W. Olmos, and O. Knop, Can. J. Chem. 33, 804 (1955), consistent with ΔH°_f 298.15 of H₂O₂(g) in this compilation)

then ΔH°_f 298.15 for HOCl(aq) is found to be -31.35 kcal. mole⁻¹. From the heats of solution in water of other weak acids, ΔH°_{soln} for HClO is estimated to be -8 ± 3 kcal. mole⁻¹. These heats yield -23 ± 3 kcal. mole⁻¹ for ΔH°_f 298.15 of HOCl(g). By averaging the heats of formation of H₂O(g) and Cl₂O(g), ΔH°_f 298.15 of HOCl(g) is estimated to be -20 ± 5 kcal. mole⁻¹. The value -22 ± 5 kcal. mole⁻¹ is adopted here.

Heat Capacity and Entropy

The frequencies are from K. Hadbarg and R. M. Badger, J. Chem. Phys. 19, 508 (1951), and the molecular dimensions from L. V. Gurvich and M. M. Novikov, Optica and Spectroscopy (English translation) 7, 70 (1959).

ClHO

INTERIM TABLE

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H ₂₉₈ °)/T	IF°-H ₂₉₈	ΔF ₁ ⁰	ΔF ₂ ⁰	Log K _p
0	8.000	40.000	INT. NITE	- 2.433	- 45.880	- 45.884	INT. NITE	
100	8.020	40.020	40.020	- 2.433	- 45.880	- 45.884	40.020	
200	9.438	55.559	40.916	- 1.072	- 47.276	- 44.263	40.369	
298	12.199	59.865	46.845	- 1.000	- 48.000	- 42.633	31.249	
300	12.245	59.865	46.845	- 1.000	- 48.000	- 42.633	31.249	
400	12.245	59.865	46.845	- 1.000	- 48.000	- 42.633	31.249	
500	14.256	67.233	61.425	- 2.904	- 49.121	- 38.654	16.605	
600	17.691	70.328	62.655	- 4.604	- 49.479	- 36.525	13.304	
700	18.860	73.147	63.955	- 6.434	- 49.731	- 34.344	10.722	
800	19.871	75.266	65.266	- 8.373	- 49.895	- 32.105	8.776	
900	20.744	76.683	66.583	- 10.422	- 49.982	- 29.812	6.562	
1000	21.384	77.341	67.634	- 12.508	- 50.037	- 27.473	4.066	
1100	21.957	78.207	69.066	- 14.676	- 50.039	- 25.103	5.053	
1200	22.437	78.339	70.259	- 16.896	- 50.008	- 23.200	4.225	
1300	22.839	78.611	71.412	- 19.160	- 49.953	- 20.768	3.525	
1400	23.168	79.023	72.523	- 21.468	- 49.875	- 18.844	2.946	
1500	23.468	79.606	73.603	- 23.795	- 49.800	- 16.519	2.407	
1600	23.714	80.368	74.642	- 26.154	- 49.713	- 14.304	1.954	
1700	23.926	81.333	75.647	- 28.536	- 49.625	- 11.864	1.541	
1800	24.109	82.605	76.616	- 30.939	- 49.566	- 9.065	1.170	
1900	24.266	84.181	77.552	- 33.365	- 49.531	- 6.251	0.834	
2000	24.406	85.962	78.466	- 35.791	- 49.507	- 3.342	0.536	
2100	24.527	87.955	79.347	- 38.237	- 49.496	- 0.343	0.266	
2200	24.634	90.169	80.201	- 40.696	- 49.500	2.550	- 0.253	
2300	24.729	92.603	81.029	- 43.164	- 49.520	5.320	- 0.716	
2400	24.808	95.261	81.826	- 45.642	- 49.560	8.119	- 1.194	
2500	24.855	98.142	82.594	- 48.131	- 49.632	11.194	- 1.682	
2600	24.855	101.255	83.378	- 50.619	- 49.705	14.065	- 2.182	
2700	24.816	104.696	84.112	- 53.117	- 49.780	16.730	- 2.699	
2800	24.727	108.433	84.831	- 55.622	- 49.824	19.169	- 3.235	
2900	24.599	112.461	85.538	- 58.131	- 49.838	21.483	- 3.792	
3000	24.429	116.889	86.214	- 60.645	- 49.838	23.500	- 4.366	
3100	24.205	121.725	86.879	- 63.164	- 49.830	26.349	- 4.959	
3200	23.927	126.956	87.529	- 65.686	- 49.828	31.198	- 5.561	
3300	23.597	132.583	88.162	- 68.212	- 49.730	34.043	- 6.174	
3400	23.216	138.606	88.781	- 70.743	- 49.595	35.881	- 6.800	
3500	22.786	145.029	89.387	- 73.274	- 49.548	39.716	- 7.440	
3600	22.363	151.836	89.978	- 75.809	- 49.439	43.024	- 8.092	
3700	21.947	159.031	90.557	- 78.346	- 49.300	46.508	- 8.755	
3800	21.538	166.616	91.123	- 80.886	- 49.135	50.368	- 9.430	
3900	21.136	174.591	91.673	- 83.431	- 48.948	54.603	- 10.115	
4000	20.750	182.957	92.220	- 85.972	- 48.741	59.226	- 10.818	
4100	20.388	191.713	92.752	- 88.510	- 48.518	64.241	- 11.538	
4200	20.050	199.859	93.273	- 91.046	- 48.278	69.646	- 12.272	
4300	19.736	208.496	93.785	- 93.578	- 48.025	75.431	- 13.020	
4400	19.446	216.626	94.287	- 96.106	- 47.751	81.594	- 13.781	
4500	19.178	225.251	94.778	- 98.631	- 47.454	88.131	- 14.554	
4600	18.932	234.372	95.261	- 101.152	- 47.134	95.044	- 15.340	
4700	18.708	243.989	95.735	- 103.667	- 46.794	102.331	- 16.139	
4800	18.504	254.104	96.201	- 106.168	- 46.438	110.000	- 16.951	
4900	18.319	264.718	96.658	- 108.658	- 46.061	118.031	- 17.775	
5000	18.152	275.831	97.109	- 111.139	- 45.668	126.426	- 18.615	
5100	18.002	287.444	97.551	- 113.615	- 45.261	135.177	- 19.468	
5200	17.868	299.557	97.986	- 116.078	- 44.841	144.286	- 20.334	
5300	17.749	312.170	98.414	- 118.528	- 44.408	153.751	- 21.213	
5400	17.644	325.283	98.836	- 120.966	- 43.964	163.566	- 22.104	
5500	17.552	338.896	99.249	- 123.392	- 43.508	173.726	- 23.007	
5600	17.473	352.999	99.656	- 125.806	- 43.041	184.236	- 23.921	
5700	17.406	367.592	100.056	- 128.206	- 42.564	195.191	- 24.845	
5800	17.350	382.675	100.451	- 130.592	- 42.078	206.596	- 25.778	
5900	17.304	398.248	100.833	- 132.964	- 41.584	218.446	- 26.720	
6000	17.266	414.311	101.228	- 135.325	- 41.084	230.741	- 27.673	

December 31, 1950.

Chlorosilane (H₃SiCl) (Ideal Gas)

Mol. Wt. = 66.571

ΔH_f⁰ 298.15 = [-46 ± 15] kcal. mole⁻¹

S_{298.15} = 59.9 ± 2 cal. deg.⁻¹ mole⁻¹

Point Group C_{3v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ω _{vib} , cm. ⁻¹	Deg.
2201 (1)	2201 (1)
949 (1)	949 (1)
551 (1)	551 (1)
2195 (2)	2195 (2)
954.4(2)	954.4(2)
664 (2)	664 (2)

Moments of Inertia: I_A = .9784 X 10⁻³⁹ g. cm.² I_B = 12.6749 X 10⁻³⁹ g. cm.² I_C = 12.6749 X 10⁻³⁹ g. cm.² ζ = 3

Heat of Formation. ΔH_f⁰ 298.15 was estimated in C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data," January, 1950.

Heat Capacity and Entropy. Vibrational levels and multiplicities were found in C. B. Henderson and R. S. Scheffee, Atlantic Res. Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1950. Moments of Inertia were calculated using the constants found in C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, J. Chem. Phys. 25, 855 (1956).

CH₃Si

Ammonium Chloride (NH₄Cl)

(Crystal) Mol. wt. = 53.49158

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	0.000	INFINITE	5.425	-74.424	-	INFINITE
100	9.480	14.800	59.146	3.328	-74.538	-66.082	144.416
200	16.040	14.281	29.653	2.074	-75.202	-57.336	62.651
298	20.650	22.672	22.672	0.000	-75.180	-48.563	35.596
300	20.780	22.800	22.672	0.038	-75.182	-48.498	35.266
400	24.610	29.812	23.253	2.401	-73.940	-30.279	21.569
500	21.030	30.647	23.432	2.607	-73.940	-30.704	13.420
600	24.300	40.826	27.653	7.904	-73.834	-22.062	8.036
700	26.960	44.772	30.819	10.467	-73.478	-13.457	4.201
800	29.610	48.545	31.926	13.496	-72.876	-4.923	1.345
900	32.260	52.189	33.976	16.732	-72.050	1.850	-0.500
1000	34.930	55.710	35.974	19.735	-70.955	11.861	-2.592
1100	36.500	59.096	37.923	23.490	-69.694	20.084	-3.990
1200	38.200	62.351	39.824	27.033	-68.270	28.186	-5.133
1300	39.000	65.433	41.677	30.884	-66.764	36.162	-6.079
1400	40.870	68.397	43.480	34.983	-65.185	44.011	-6.841
1500	42.000	71.259	45.237	39.035	-63.585	51.757	-7.541

AMMONIUM CHLORIDE (NH₄Cl)

(CRYSTAL)

MOL. WT. = 53.49158



$S_{298.15}^o = 22.7 \pm 1.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 242.6^\circ \text{K.}$
 $T_c = 457.7^\circ \text{K.}$
 $T_m = 795.2^\circ \text{K.}$
 $T_d = 612^\circ \text{K.}$

Heat of Formation.

The equilibrium pressures for the reaction $\text{NH}_4\text{Cl}(c) = \text{NH}_3(g) + \text{HCl}(g)$, at 320-626°K., have been measured by many investigators. A. Smith and W. de Lange, *J. Chem. Soc.*, 2944 (1928), using the densi-tensimeter, determined the vapor pressure of $\text{NH}_4\text{Cl}(c)$ and the density of the saturated vapor simultaneously. The results obtained indicate that within the range 567-626°K. the saturated vapor completely dissociates into gaseous NH_3 and HCl . Based on this conclusion, the reported vapor pressure data were employed to evaluate the heat of dissociation of $\text{NH}_4\text{Cl}(c)$ by both the second and third law methods. The results are presented as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	Drift, e.u.
Smith and Calvert (1)	521.6-619.1	43.18 ± 0.08	42.11	-2.0 ± 0.2
Smith and Lange (2)	527.9-625.6	42.16 ± 0.22	42.14	-0.2 ± 0.4
Braune and Knoke (3)	525.4-615.0	42.05 ± 0.08	42.00	0.5 ± 0.2
Rodebush and Michalek (4)	471.3-557.0	42.33 ± 0.08	42.00	-0.3 ± 0.2
Wegner and Neumann (5)	530.0-612.2	42.83 ± 0.38	42.17	-4.9 ± 1.1
Markowitz and Boryta (6)	503.0-611.4	41.27 ± 0.38	42.12	1.5 ± 0.8

- (1) A. Smith and R. P. Calvert, *J. Am. Chem. Soc.*, 35, 1363 (1914), using isotenoscope.
- (2) A. Smith and W. D. Lange, *J. Chem. Soc.*, 2944 (1928), using densi-tensimeter.
- (3) H. Braune and S. Knoke, *Z. phys. Chem.*, 135, 49 (1928).
- (4) W. H. Rodebush and J. C. Michalek, *J. Am. Chem. Soc.*, 51, 748 (1929), gases diaphragm manometer.
- (5) H. Wegner and K. Neumann, *Z. phys. Chem.*, 28, 51 (1961), torsion-effusion method.
- (6) M. M. Markowitz and D. A. Boryta, *J. Phys. Chem.*, 55, 1477 (1952), differential thermal analysis.

The value of ΔH_f^o 298.15 adopted is 42.15 ± 0.10 kcal. mole⁻¹, yielding ΔH_f^o 298.15 ($\text{NH}_4\text{Cl}, c$) = -75.8 ± 0.20 kcal. mole⁻¹. The corresponding ΔH_f^o 298.15 value evaluated from solution data, selected by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NSRDS-NBS2, National Bureau of Standards, is 42.06 kcal. mole⁻¹.

Heat Capacity and Entropy.

The heat capacities (20.1-523.2°K.) of $\text{NH}_4\text{Cl}(c)$ have been measured by the following investigators: (1) R. Ewald, *Ann. Physik*, 44, 1213 (1914), 138-301°K.; (2) P. Simon, *ibid.*, 69, 241 (1922), 20.1-290.8°K.; (3) H. Klinkhardt, *ibid.*, 84, 167 (1927), 323.2-523.2°K.; (4) P. Simon, C. v. Simon and M. Rühmann, *Z. phys. Chem.*, 129, 339 (1927), 204.5-275.8°K.; (5) W. T. Ziegler and C. E. Messer, *J. Am. Chem. Soc.*, 63, 2694 (1941), 107.2-320.2°K.; (6) R. Extermann and J. Weigle, *Helv. Phys. Acta*, 15, 455 (1942), 228.2-248.2°K.; and (7) M. M. Popov and G. L. Oalchenko, *J. Gen. Chem.*, USSR, 21, 2489 (1951), 373.2-523.2°K. These C_p data were plotted and a smooth C_p curve was drawn and adopted. The C_p values above 523°K. were obtained by graphical extrapolation of the previous C_p curve. $S_{298.15}^o$ was derived from the adopted low temperature data, based on $S_{20.1}^o = 0.114 \text{ e.u.}$

Transition Data.

There are two transitions reported in the literature. The low temperature transition data (T_c and ΔH_c^o) were derived based on the heat capacity (107-320°K.) data reported by W. T. Ziegler and C. E. Messer, loc. cit., in which the other T_c values given by previous investigators were reviewed. The high temperature transition data (T_m and ΔH_m^o) were taken from H. Klinkhardt, loc. cit. However, ΔH_m^o = 1030 and ΔH_m^o = 1059.1 ± 8.0 cal. mole⁻¹ were reported by E. C. Scheffer, *Proc. Acad. Sci. Amsterdam*, 24, 1513 (1915/16), and M. M. Popov and G. L. Oalchenko, loc. cit., respectively. M. M. Markowitz and D. A. Boryta, loc. cit. determined T_m to be 459.5 ± 0.5°K.

Melting Temperature.

T_m was obtained from H. Rasmussen, *Z. anorg. Chem.*, 114, 117 (1920), determined under pressure.

Decomposition Temperature.

The value of T_d was calculated as the temperature at which the vapor pressure of the decomposition products (NH_3 and HCl) equals 1 atm. By differential thermal analysis, T_d for $\text{NH}_4\text{Cl}(c)$ was determined to be 811.4°K. by M. M. Markowitz and D. A. Boryta, loc. cit.



T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞	∞	∞	∞	∞	∞
100	19.400	17.422	67.672	66.301	66.301	INFINITE
200	25.630	32.844	46.654	69.021	53.416	11.6736
298	30.610	44.020	44.020	70.036	37.389	40.855
300	30.700	44.210	44.021	70.699	21.217	15.552
400	35.500	52.154	47.823	70.699	20.911	15.233
500	40.380	57.154	47.823	70.803	12.401	5.229
600	47.220	74.739	51.542	67.750	28.592	10.414
700	52.060	82.381	53.407	66.549	44.561	13.912
800	55.900	89.649	55.236	64.923	60.324	16.479
900	59.640	96.640	57.008	62.458	75.866	18.421
1000	63.380	103.388	58.708	60.376	91.118	19.920
1100	71.599	109.972	70.343	43.592	106.161	21.091
1200	76.000	116.395	73.914	50.977	120.869	22.016
1300	82.984	122.632	77.423	58.772	135.318	22.748
1400	87.970	128.632	80.884	66.568	149.419	23.229
1500	85.500	134.477	84.250	73.341	163.184	23.789

S°_{298.15} = 44.02 ± 0.04 cal. deg.⁻¹ mole⁻¹
ΔH°_f = 2.3 ± 0.2 kcal. mole⁻¹

ΔH°_f 298.15 = -70.69 ± 0.30 kcal. mole⁻¹
T_g = 513.15°K
T_d = [513]°K.

Heat of Formation.

A. A. Gilliland and W. H. Johnson, J. Research Natl. Bur. Standards 65A, 67 (1961), and M. M. Birky and L. O. Hepler, J. Phys. Chem. 64, 586 (1960), have derived the heat of formation for NH₄ClO₄(c) from solution-calorimetric measurements. Their values are -70.74 ± 0.32 and -70.63 kcal. mole⁻¹, respectively. The mean of these is adopted here.

Heat Capacity and Entropy.

B. H. Justice and E. F. Westrum, private communication, April 1961, have measured the heat capacity from 5° to 350°K. The C_p values above 350°K were extrapolated. From the partial molar entropies of NH₄⁺(aq) and ClO₄⁻(aq) and the entropy of solution, Birky and Hepler, loc. cit., calculated a value of 43.6 cal. deg.⁻¹ mole⁻¹ for S°_{298.15}. The fair agreement of this value with that derived from C_p suggests that there is no residual entropy at 0°K, as there would be if the NH₄⁺ ion had a random orientation.

Transition and Decomposition Data.

T_g and ΔH°_f were obtained (under a pressure of NH₃) by M. M. Markowitz, Foote Mineral Company, Exton, Pennsylvania (private communication, September 20, 1962). T_d was estimated from the report by M. M. Markowitz, loc. cit.

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 236.067

MERCURY MONOCHLORIDE (HgCl)

(IDEAL GAS)

MOL. WT. = 236.067

CIHG

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	7.000	51.000	INFINITE	-2.353	19.727	19.727	INFINITE
100	7.523	53.156	67.999	-1.684	17.511	17.511	38.269
200	7.959	54.603	64.603	-1.000	15.750	15.750	46.945
298	8.105	55.105	62.105	0.000	13.595	13.595	50.945
300	8.109	55.109	62.109	0.016	13.563	13.563	50.981
400	8.489	56.685	62.448	0.895	12.747	12.747	46.483
500	8.928	58.669	63.101	1.784	12.217	12.217	40.466
600	9.361	60.102	63.536	2.680	11.872	11.872	33.134
700	9.791	61.490	64.576	3.580	11.697	11.697	25.684
800	10.214	62.836	65.292	4.484	11.622	11.622	18.230
900	10.633	64.144	65.775	5.390	11.642	11.642	10.776
1000	11.049	65.413	66.223	6.300	11.750	11.750	3.322
1100	11.463	66.644	66.736	7.212	11.942	11.942	-2.242
1200	11.874	67.836	67.316	8.127	12.206	12.206	-6.776
1300	12.282	68.990	67.960	9.043	12.544	12.544	-11.310
1400	12.687	70.103	68.667	9.962	12.947	12.947	-15.845
1500	13.090	71.176	69.362	10.884	13.419	13.419	-20.379
1600	13.491	72.210	70.085	11.807	13.953	13.953	-24.913
1700	13.890	73.204	70.825	12.732	14.547	14.547	-29.447
1800	14.287	74.158	71.580	13.660	15.201	15.201	-33.981
1900	14.682	75.073	72.348	14.589	15.915	15.915	-38.515
2000	15.075	75.948	73.121	15.521	16.689	16.689	-43.049
2100	15.466	76.783	73.900	16.454	17.524	17.524	-47.583
2200	15.855	77.578	74.684	17.380	18.419	18.419	-52.117
2300	16.242	78.333	75.476	18.307	19.374	19.374	-56.651
2400	16.627	79.048	76.280	19.227	20.389	20.389	-61.185
2500	17.010	79.723	77.093	20.152	21.464	21.464	-65.719
2600	17.391	80.358	77.898	21.080	22.599	22.599	-70.253
2700	17.769	80.953	78.663	22.012	23.794	23.794	-74.787
2800	18.145	81.508	79.388	22.939	25.049	25.049	-79.321
2900	18.519	82.023	80.073	23.871	26.364	26.364	-83.855
3000	18.891	82.500	80.718	24.808	27.739	27.739	-88.389
3100	19.261	82.937	81.323	25.750	29.174	29.174	-92.923
3200	19.629	83.334	81.898	26.705	30.669	30.669	-97.457
3300	19.995	83.691	82.433	27.674	32.224	32.224	-101.991
3400	20.359	84.008	82.938	28.648	33.839	33.839	-106.525
3500	20.721	84.285	83.403	29.627	35.514	35.514	-111.059
3600	21.081	84.522	83.828	30.611	37.249	37.249	-115.593
3700	21.439	84.720	84.213	31.600	39.044	39.044	-120.127
3800	21.795	84.888	84.558	32.584	40.899	40.899	-124.661
3900	22.149	85.026	84.863	33.573	42.814	42.814	-129.195
4000	22.501	85.134	85.128	34.566	44.789	44.789	-133.729
4100	22.851	85.212	85.353	35.564	46.824	46.824	-138.263
4200	23.199	85.261	85.538	36.566	48.919	48.919	-142.797
4300	23.545	85.281	85.683	37.572	51.074	51.074	-147.331
4400	23.889	85.273	85.798	38.582	53.289	53.289	-151.865
4500	24.231	85.247	85.883	39.596	55.564	55.564	-156.399
4600	24.571	85.194	85.938	40.614	57.899	57.899	-160.933
4700	24.909	85.116	85.963	41.636	60.294	60.294	-165.467
4800	25.245	85.014	85.958	42.552	62.749	62.749	-170.001
4900	25.579	84.889	85.923	43.464	65.264	65.264	-174.535
5000	25.911	84.741	85.858	44.362	67.839	67.839	-179.069
5100	26.241	84.569	85.763	45.246	70.474	70.474	-183.603
5200	26.569	84.374	85.638	46.106	73.169	73.169	-188.137
5300	26.895	84.157	85.473	46.952	75.924	75.924	-192.671
5400	27.219	83.919	85.278	47.774	78.739	78.739	-197.205
5500	27.541	83.659	85.053	48.569	81.614	81.614	-201.739
5600	27.861	83.377	84.798	49.338	84.559	84.559	-206.273
5700	28.179	83.073	84.513	50.083	87.574	87.574	-210.807
5800	28.495	82.747	84.198	50.803	90.659	90.659	-215.341
5900	28.809	82.399	83.853	51.498	93.814	93.814	-219.875
6000	29.121	82.029	83.478	52.168	97.039	97.039	-224.409

December 31, 1961

Ground State Configuration 2₂⁺S_{298.15} = 62.105 cal deg⁻¹ mole⁻¹ΔH_f 298.15 = 18.75 ± 2.3 kcal mole⁻¹

Electronic Levels and Multiplicities

$$\frac{g_i}{2}$$

$$\frac{g_i}{2}$$
ω_e = 290.94 cm⁻¹ω_ex_e = 1.5844 cm⁻¹

σ = 1

B_e = [0.1121] cm⁻¹q_e = [0.0007] cm⁻¹r_e = 2.23 Å

Heat of Formation

A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, London 1953, gives 23 ± 2.3 kcal for the heat of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants from K. Wieland Zeits. f. Elektrochemie 64, 761 (1960) were weighted according to their natural isotopic abundances. Rotational constants were estimated using equation III, 123 p. 108, G. Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York 1950. Bond length given by G. Herzberg (loc. cit.).

CIHG

T, °K.	C _p	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$-(F^0 - H^0_{298})/T$ cal. mole ⁻¹	ΔH^0_f kcal. mole ⁻¹	ΔF^0_f	Log K _f
0	0.000	0.000	INFINITE	-2.907	-8.699	INFINITE
100	9.619	10.921	34.181	-2.326	-8.833	15.159
200	11.840	18.406	24.571	-1.233	-8.690	5.557
298	13.200	23.405	23.405	0.000	-8.466	2.464
300	13.223	23.487	23.405	0.024	-8.461	2.426
400	14.387	27.253	23.036	1.406	-10.081	0.872
500	15.387	30.773	24.082	2.896	-14.779	0.420
600	16.287	33.659	26.192	4.480	-14.077	1.473
700	17.086	36.113	27.446	6.150	-13.296	2.187
800	17.785	38.250	28.446	7.792	-12.446	2.690
900	18.383	40.000	29.098	9.703	-11.453	3.054
1000	18.880	42.653	31.086	11.567	-10.569	3.323

Heat of Formation.

The heat of formation is that adopted by O. V. Calder and W. F. Oiaque, J. Phys. Chem. 69, 2443 (1965) from an analysis of the equilibrium data of J. McMorris and D. M. Yost, J. Am. Chem. Soc. 54, 2247 (1932) and C. M. Beeson and D. M. Yost, J. Chem. Phys. 7, 44 (1939). This yielded a heat of formation of ICl(g), from which the heat of formation of ICl(c) was calculated by using the heat of vaporization determined by Calder and Oiaque loc. cit.

Heat Capacity and Entropy.

The heat capacity has been measured by Calder and Oiaque loc. cit. from 17-322°K. The entropy was calculated based on S₁₅ = 0.592 cal. mole⁻¹ deg.⁻¹ Above 300° the heat capacity data was extrapolated smoothly.

Melting Data.

All data were measured by Calder and Oiaque loc. cit.

Iodine Monochloride (ICl)

(Liquid) Mol. Wt. = 162.3574

CII

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	keal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0								
298	24.560	32.544	32.544	-	0.000	- 5.720	- 3.341	2.449
300	24.582	32.696	32.544	-	0.045	- 5.694	- 3.326	2.423
400	23.500	33.849	33.501	-	2.436	- 6.281	- 2.676	1.462
500	22.500	44.785	35.267	-	4.759	- 10.169	- 1.436	.627
600	21.500	48.799	37.200	-	6.959	- 8.852	- 1.185	.067
800	20.500	52.788	39.096	-	11.059	- 7.641	- 1.594	.498
900	19.500	56.716	40.949	-	14.759	- 6.454	- 2.007	.958
1000	18.500	58.847	42.850	-	18.049	- 5.531	- 2.431	1.482
	17.500		44.088	-	14.759	- 4.631	- 4.950	1.082

IODINE MONOCHLORIDE (CLI)

(LIQUID)

MOL. WT. = 162.3574

S°_{298.15} = 32.544 cal. mole⁻¹ deg.⁻¹
T_m = 300.53°K.

ΔH_f^o_{298.15} = -5.72 ± 0.03 kcal. mole⁻¹
ΔH_m^o = 2.773 ± 0.002 kcal. mole⁻¹

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH_m^o and the difference between H°_{300.53}-H°_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity from 300.53 to 317.76°K. has been measured by G. V. Calder and W. F. Giauque, J. Phys. Chem. 69, 2443 (1965). Above 318°K. it was extrapolated in a smooth manner. The entropy was obtained in a manner analogous to the heat of formation.

CII

(Ideal Gas) Mol. Wt. = 162.3574

MOL. WT. = 162.3574

(IDEAL GAS)

IODINE MONOCHLORIDE (ICl)

Mar. 31, 1962; Sept. 30, 1963; Dec. 31, 1963; Sept. 30, 1965

T, °K.	C _p ^o	S ^o - (F ^o -H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H ^o - H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	-	2.284	4.574	4.574	INFINITE	
100	7.400	50.831	50.831	1.816	4.537	4.537	- 5.543	
200	6.275	50.831	50.831	1.816	4.537	4.537	- 5.543	
298	8.497	59.145	59.145	0.000	4.184	- 1.368	1.003	
300	8.502	59.198	59.145	0.016	4.180	- 1.402	1.022	
400	8.700	61.674	59.482	0.877	2.040	- 3.164	1.729	
500	8.808	63.028	60.122	1.755	3.272	- 3.959	1.731	
600	8.873	65.240	60.845	2.637	3.270	- 4.097	1.492	
700	8.918	66.611	61.573	3.527	3.269	- 4.235	1.322	
800	8.952	67.805	62.279	4.420	3.269	- 4.374	1.195	
900	8.978	68.860	62.953	5.317	3.270	- 4.511	1.095	
1000	9.000	69.808	63.592	6.216	3.270	- 4.650	1.016	
1100	9.019	70.666	64.196	7.117	3.271	- 4.788	0.951	
1200	9.036	71.452	64.769	8.020	3.273	- 4.926	0.897	
1300	9.052	72.176	65.311	8.924	3.274	- 5.064	0.851	
1400	9.066	72.847	65.826	9.830	3.276	- 5.200	0.812	
1500	9.080	73.473	66.315	10.737	3.278	- 5.335	0.778	
1600	9.094	74.059	66.781	11.646	3.281	- 5.474	0.748	
1700	9.106	74.611	67.225	12.556	3.283	- 5.611	0.721	
1800	9.119	75.132	67.650	13.467	3.286	- 5.749	0.698	
1900	9.131	75.625	68.057	14.380	3.289	- 5.884	0.677	
2000	9.143	76.094	68.447	15.293	3.293	- 6.023	0.658	
2100	9.155	76.540	68.822	16.208	3.296	- 6.158	0.641	
2200	9.167	76.967	69.183	17.124	3.300	- 6.296	0.625	
2300	9.178	77.374	69.530	18.042	3.304	- 6.430	0.611	
2400	9.190	77.765	69.865	18.960	3.309	- 6.566	0.598	
2500	9.201	78.141	70.189	19.880	3.315	- 6.704	0.586	
2600	9.212	78.502	70.502	20.800	3.321	- 6.839	0.575	
2700	9.223	78.849	70.804	21.722	3.328	- 6.972	0.564	
2800	9.234	79.185	71.098	22.645	3.336	- 7.106	0.555	
2900	9.246	79.509	71.382	23.569	3.345	- 7.241	0.546	
3000	9.257	79.823	71.658	24.494	3.354	- 7.377	0.537	
3100	9.268	80.127	71.927	25.420	3.365	- 7.512	0.530	
3200	9.279	80.421	72.188	26.348	3.377	- 7.644	0.522	
3300	9.290	80.707	72.441	27.276	3.390	- 7.777	0.515	
3400	9.300	80.984	72.689	28.205	3.404	- 7.909	0.508	
3500	9.311	81.254	72.929	29.136	3.418	- 8.042	0.502	
3600	9.322	81.516	73.164	30.068	3.434	- 8.172	0.496	
3700	9.333	81.772	73.394	31.000	3.451	- 8.305	0.491	
3800	9.344	82.021	73.617	31.934	3.468	- 8.437	0.485	
3900	9.355	82.264	73.836	32.869	3.487	- 8.567	0.480	
4000	9.366	82.501	74.050	33.805	3.506	- 8.698	0.475	
4100	9.376	82.732	74.259	34.742	3.526	- 8.825	0.470	
4200	9.387	82.958	74.463	35.681	3.546	- 8.954	0.466	
4300	9.398	83.179	74.663	36.620	3.567	- 9.084	0.462	
4400	9.409	83.396	74.859	37.560	3.589	- 9.214	0.458	
4500	9.419	83.607	75.051	38.502	3.611	- 9.339	0.454	
4600	9.430	83.814	75.240	39.444	3.633	- 9.465	0.450	
4700	9.441	84.017	75.424	40.388	3.654	- 9.593	0.446	
4800	9.452	84.216	75.605	41.332	3.677	- 9.720	0.443	
4900	9.462	84.411	75.783	42.278	3.699	- 9.844	0.439	
5000	9.473	84.602	75.957	43.225	3.721	- 9.969	0.436	
5100	9.484	84.790	76.129	44.173	3.742	- 10.095	0.433	
5200	9.495	84.974	76.297	45.121	3.765	- 10.218	0.429	
5300	9.505	85.155	76.463	46.071	3.786	- 10.342	0.426	
5400	9.516	85.333	76.625	47.022	3.808	- 10.466	0.424	
5500	9.527	85.508	76.785	47.975	3.828	- 10.591	0.421	
5600	9.537	85.680	76.942	48.928	3.849	- 10.718	0.418	
5700	9.548	85.848	77.097	49.882	3.870	- 10.835	0.415	
5800	9.559	86.015	77.249	50.837	3.890	- 10.960	0.413	
5900	9.570	86.178	77.399	51.794	3.909	- 11.081	0.410	
6000	9.580	86.339	77.547	52.751	3.929	- 11.201	0.408	

$\Delta H_f^o = 4.574 \pm 0.025 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o = 4.184 \pm 0.025 \text{ kcal. mole}^{-1}$

$S_{298.15}^o = 59.145 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$
Ground State Configuration $1 \Sigma^+$

Electronic Levels and Quantum Weight

$\frac{E_i, \text{ cm.}^{-1}}{0} \frac{g_i}{1}$

$\omega_e = 382.18 \text{ cm.}^{-1}$
 $\omega_e x_e = 1.450 \text{ cm.}^{-1}$
 $B_e = 0.11298 \text{ cm.}^{-1}$
 $\alpha_e = 0.0005275 \text{ cm.}^{-1}$
 $\sigma^- = 1$
 $r_e = 2.327 \text{ \AA}$

Heat of Formation.

The dissociation energy from spectroscopic measurements of ICl(g) has been summarized by W. H. Evans, T. R. Munson and D. D. Wegman, J. Res. Natl. Bur. Standards, 55, 147 (1955) from which they adopt $D_0^o = 49.64 \text{ kcal. mole}^{-1}$. J. McMorris and D. M. Yost, J. Am. Chem. Soc. 54, 2247 (1932) and C. M. Beeson and D. M. Yost, J. Chem. Phys. 1, 44 (1939) studied the equilibria $\text{NOCl} = \text{NO} + 1/2 \text{ Cl}_2$ and $\text{NO} + \text{ICl} = \text{NOCl} + 1/2 \text{ I}_2(\text{g})$ from which the equilibrium constant of $\text{ICl} = 1/2 \text{ Cl}_2 + 1/2 \text{ I}_2(\text{g})$ can be obtained. O. V. Calder and W. P. Olschue, J. Phys. Chem. 69, 2443 (1965) have used 3rd law analysis to obtain $D_0^o = 49.578 \pm 0.025 \text{ kcal. mole}^{-1}$. This value was adopted yielding $\Delta H_f^o = 4.184 \pm 0.025 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The molecular and vibrational constants were obtained from G. Herzberg "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York 1950. The values were then adjusted for the normal isotopic abundance of chlorine.

Potassium Chloride (KCl)
(Crystal) Mol. Wt. = 74.555

POTASSIUM CHLORIDE (KCl) (CRYSTAL) C/K
MOL. WT. = 74.555

T, °K.	C _p	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	0.000	0.000	INFINITE	2.717	-104.297	-104.297	INFINITE
100	9.369	7.594	20.837	2.249	-104.297	-104.297	10.212
200	11.577	14.969	20.833	1.173	-104.498	-99.619	109.186
298	12.258	19.731	19.731	0.000	-104.370	-97.700	71.616
300	12.268	19.807	19.732	0.023	-104.368	-97.659	71.144
400	12.700	23.598	20.218	1.272	-104.848	-95.329	52.095
500	13.086	26.274	21.131	2.561	-104.728	-92.963	40.634
600	13.460	28.693	22.212	3.889	-104.561	-90.624	33.010
700	13.863	30.797	23.291	5.254	-104.350	-88.317	27.574
800	14.359	32.679	24.349	6.664	-104.095	-86.044	23.506
900	14.906	34.437	25.372	8.132	-103.784	-83.805	20.351
1000	15.506	36.038	26.362	9.652	-103.432	-81.600	17.655
1100	17.200	37.622	27.310	11.343	-121.827	-78.425	15.582
1200	18.200	39.163	28.234	13.115	-121.002	-74.515	13.571
1300	19.000	40.652	29.132	14.977	-120.088	-70.677	11.882
1400	19.600	42.084	30.006	16.908	-119.106	-66.913	10.446
1500	20.000	43.431	30.857	18.890	-118.074	-63.221	9.211

ΔH_f° 0 = -104.30 kcal. mole⁻¹
ΔH_f° 298.15 = -104.37 ± 0.06 kcal. mole⁻¹
ΔH_m° = 6.282 kcal. mole⁻¹
S_{298.15}° = 19.73 ± 0.04 cal. deg.⁻¹ mole⁻¹
T_m = 1044°K.

Heat of Formation.
The heat of formation was calculated from the heat of hydrolysis of K(c), the heats of solution of HCl(g) and KCl(c), and the standard heat of neutralization of a strong acid and strong base. Extensive measurements are available for all these quantities. Values used in the calculation, in addition to the heat of formation for HCl(g), are summarized below.

Source	Reaction	ΔH _f ° 298.15 (kcal.)
1,2,3,4	K(c) + H ₂ O(l) → KOH(∞ H ₂ O) + 1/2 H ₂ (g)	-46.966 ± 0.05
5,2,6	HCl(g) → HCl(∞ H ₂ O)	-17.88 ± 0.015
7	KCl(∞ H ₂ O) → KCl(c)	-4.115 ± 0.010
7	KOH(∞ H ₂ O) + HCl(∞ H ₂ O) → KCl(∞ H ₂ O) + H ₂ O(l)	-13.345 ± 0.025

1. S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1957).
2. S. R. Gunn, UCR-7932, Livermore, Calif., Jul. 1964.
3. C. E. Measer, L. G. Fasolino, and C. E. Thalmer, J. Am. Chem. Soc. 77, 4524 (1955).
4. E. E. Ketchen and W. E. Wallace, J. Am. Chem. Soc. 67, 2521 (1945).
5. C. E. Vanderzee and J. D. Nutter, J. Phys. Chem. 67, 2521 (1963).
6. S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1957).
7. U. S. Government Printing Office, Washington, D.C., 1965.

Heat Capacity and Entropy.

Low temperature heat capacities were obtained from the data (2.8-275°K.) of W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) A242, 487 (1957). Previous measurements scatter around the selected values and are in good agreement. These include P. G. Stralkov, E. S. Itakevich, V. N. Kostyukov, and G. G. Mirskaya (12-298°K.), Zhur. Fiz. Khim. 29, 845 (1954); K. Clusius, J. Ooldman, and A. Perlick (10-273°K.), Z. Naturforsch. 4a, 429 (1949); and J. C. Southard and R. A. Nelson (17-298°K.), J. Am. Chem. Soc. 55, 4865 (1933). For other less extensive data see the review by K. K. Kelley and E. G. King, USNM Bulletin 592, 1961. The entropy is based on the extrapolation S_{2.8}° = 0.0006 cal./deg.-mole.

High temperature values are based on enthalpy data (373-1038°K.) from T. B. Douglas, private communication, U. S. Natl. Bur. Std., May 23, 1961. These values join smoothly with the low temperature values and are in excellent agreement with the enthalpy data (673-933°K.) of S. M. Skuratov and S. A. Lapushkin, J. Gen. Chem. (USSR) 21, 2465 (1951) and the adiabatic heat capacities (334-721°K.) of A. Mustajoki, Ann. Acad. Sci. Fennicae, Series A, I, 28, 7 (1951).

Melting Data.

The melting point and heat of melting are from Douglas, loc. cit. Values of T_m = 1043° and 1045°K. have been reported by E. Aukrust, B. Bjorge, H. Flood, and T. Forland, Ann. New York Acad. Sci. 79, 830 (1960) and J. M. Johnson and M. A. Predig, J. Phys. Chem. 62, 604 (1958), respectively. The heat of melting is confirmed by ΔH_m° = 6.34 kcal./mole obtained from enthalpy data by A. S. Dworkin and M. A. Predig, J. Phys. Chem. 64, 269 (1960) and ΔH_m° = 6.4 and 6.5 kcal./mole based on enthalpy and phase diagram studies of Aukrust et al., loc. cit., respectively.

(Liquid) Mol. Wt. = 74.555

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹		- (F° - H _{298°)/T}		kcal. mole ⁻¹		ΔH ^o		ΔF ^o		Log K _p
		S°				H° - H _{298°}						
0												
100		20.714	20.714			0.000	- 100.810	-	94.433	-	69.221	
200	17.590	20.823	20.714			0.033	- 100.798	-	94.394	-	68.766	
300	17.590	25.883	21.404			1.702	- 100.768	-	92.244	-	50.400	
400	17.590	29.808	22.707			3.551	- 100.178	-	90.180	-	39.418	
500	17.590	33.015	24.166			5.310	- 99.580	-	88.236	-	32.160	
600	17.590	35.727	25.626			7.069	- 98.976	-	86.304	-	26.971	
700	17.590	38.076	27.041			8.828	- 98.372	-	84.639	-	23.122	
800	17.590	40.147	28.385			10.587	- 97.770	-	82.957	-	20.145	
900	17.590	42.001	29.655			12.346	- 97.179	-	81.344	-	17.778	
1000	17.590											
1100	17.590	45.577	31.895			15.109	- 113.205	-	78.760	-	15.943	
1200	17.590	46.207	33.060			17.623	- 113.882	-	72.225	-	12.142	
1300	17.590	46.616	34.075			19.362	- 113.072	-	69.049	-	10.779	
1400	17.590	47.919	35.039			21.141	- 112.263	-	65.933	-	9.606	
1500	17.590	49.133										
1600	17.590	50.268	35.056			22.900	- 111.455	-	62.870	-	8.588	
1700	17.590	51.334	36.829			24.659	- 110.649	-	59.858	-	7.695	
1800	17.590	52.340	37.663			26.418	- 109.843	-	56.895	-	6.908	
1900	17.590	53.291	38.461			28.177	- 109.040	-	53.975	-	6.208	
2000	17.590	54.193	39.225			29.936	- 108.239	-	51.096	-	5.584	

POTASSIUM CHLORIDE (KCl)

(LIQUID)

MOL. WT. = 74.555

$S_{298}^{\circ} = 20.71$ cal. deg.⁻¹ mole⁻¹
 $T_m = 1044^{\circ}\text{K.}$
 $T_b = 1710^{\circ}\text{K.}$ (to equilibrium vapor)
 $T_b = [1750^{\circ}\text{K.}]$ (to monomer only)

$\Delta H_f^{\circ} 298.15 = -100.81$ kcal. mole⁻¹
 $\Delta H_m^{\circ} = 0.282$ kcal. mole⁻¹
 $\Delta H_v^{\circ} = 29.7$ kcal. mole⁻¹ (equilibrium vapor)
 $\Delta H_v^{\circ} = [37.14]$ kcal. mole⁻¹ (monomer)

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH_m° and the difference between ($H_{1044}^{\circ} - H_{298}^{\circ}$) for the crystal and liquid.

Heat Capacity and Entropy.

The constant heat capacity, 17.59 cal./deg.-mole, was derived from enthalpy data (1053-1173°K.) of T. B. Douglas, private communication, U. S. Natl. Bur. Std., May 23, 1961. This value was extrapolated above and below the experimental range. A lower value of 18.7 cal./deg.-mole was derived by A. S. Dworin, private communication, Oak Ridge National Laboratory, Dec. 1, 1964, from enthalpy data (1050-1110°K.) obtained in a heat of melting study. The entropy of the liquid was obtained in a manner analogous to the heat of formation.

Melting Data.

The melting point and heat of melting are from Douglas, loc. cit. Values of $T_m = 1043^{\circ}$ and 1045°K. have been reported by E. Aukrust, B. Bjorge, H. Flood, and T. Forland, Ann. New York Acad. Sci. 79, 830 (1960) and J. W. Johnson and M. A. Bredig, J. Phys. Chem. 82, 804 (1958), respectively. The heat of melting is confirmed by $\Delta H_m^{\circ} = 6.34$ kcal./mole obtained from enthalpy data by A. S. Dworin and M. A. Bredig, J. Phys. Chem. 84, 289 (1960) and $\Delta H_m^{\circ} = 6.4$ and 6.5 kcal./mole based on enthalpy and phase diagram studies of Aukrust et al., loc. cit., respectively.

Vaporization Data.

T_b (to equilibrium vapor) is the temperature resulting in unit total pressure based on the calculated partial pressures of KCl(g) and $K_2Cl_2(g)$. This value may be compared with boiling points of 1688° and 1690°K. observed respectively by O. Ruff and S. Mugdan, Z. anorg. allgem. Chem. 117, 147 (1921), and H. von Wartenburg and F. Albrecht, Z. Elektrochem. 27, 162 (1921). ΔH_v° (equilibrium vapor) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 22.5 mole percent of dimer. According to the selected functions, the amount of dimer at lower temperatures increases gradually to about 32 mole percent at the melting point then decreases rapidly over the crystal. T_b (to monomer only) is taken as the temperature at which the calculated free energy change is zero for $KCl(l) \rightarrow KCl(g)$, while ΔH_v° (monomer) is the corresponding heat of reaction.

Data on vapor pressures and dimer-monomer equilibrium are reviewed on the tables for KCl(g) and $K_2Cl_2(g)$, respectively.

Dec. 31, 1961; Mar. 31, 1966

Potassium Chloride (KCl)

(Ideal Gas) Mol. wt. = 74.555

C/K

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	7.576	48.122	64.639	-1.652	-50.882	-50.882	-50.882	INFINITE
200	8.430	53.687	57.907	-1.844	-50.936	-52.638	-52.638	115.040
298	8.723	57.116	57.116	-0.000	-51.109	-54.274	-54.274	59.307
300	8.726	57.117	57.117	-0.016	-51.314	-55.814	-55.814	40.661
400	8.657	59.701	57.163	-0.866	-52.163	-57.166	-57.166	31.234
500	8.930	61.685	58.114	-1.786	-52.443	-58.384	-58.384	25.520
600	8.979	63.318	58.950	-2.681	-52.708	-59.547	-59.547	21.690
700	9.046	64.915	60.566	-3.584	-52.966	-60.766	-60.766	18.243
800	9.072	66.378	62.089	-4.484	-53.215	-62.001	-62.001	15.250
900	9.097	67.935	63.437	-5.389	-53.467	-63.262	-63.262	13.949
1000	9.119	68.803	64.249	-6.299	-53.726	-64.546	-64.546	12.676
1100	9.162	70.330	65.077	-7.209	-53.991	-65.846	-65.846	11.468
1200	9.182	71.010	65.938	-8.057	-54.261	-67.166	-67.166	10.318
1300	9.198	71.644	66.821	-8.955	-54.536	-68.506	-68.506	9.220
1400	9.202	72.238	67.723	-9.899	-54.816	-69.866	-69.866	8.180
1500	9.221	72.788	68.638	-10.877	-55.101	-71.246	-71.246	7.190
1600	9.259	73.298	69.566	-11.899	-55.391	-72.646	-72.646	6.250
1700	9.278	73.778	70.513	-12.966	-55.686	-74.066	-74.066	5.360
1800	9.297	74.230	71.478	-14.077	-55.986	-75.506	-75.506	4.520
1900	9.316	74.666	72.461	-15.233	-56.291	-76.966	-76.966	3.730
2000	9.335	75.088	73.461	-16.433	-56.601	-78.446	-78.446	2.990
2100	9.353	75.497	74.478	-17.677	-56.916	-79.946	-79.946	2.300
2200	9.372	75.894	75.513	-18.966	-57.236	-81.466	-81.466	1.660
2300	9.390	76.278	76.566	-20.300	-57.561	-82.996	-82.996	1.070
2400	9.408	76.648	77.638	-21.677	-57.891	-84.546	-84.546	0.530
2500	9.426	77.004	78.723	-23.100	-58.226	-86.116	-86.116	0.040
2600	9.445	77.347	79.823	-24.577	-58.566	-87.706	-87.706	-0.410
2700	9.463	77.678	80.938	-26.100	-58.911	-89.316	-89.316	-0.920
2800	9.482	78.000	82.066	-27.677	-59.261	-90.946	-90.946	-1.480
2900	9.500	78.312	83.213	-29.300	-59.616	-92.596	-92.596	-2.090
3000	9.518	78.617	84.378	-31.000	-60.000	-94.266	-94.266	-2.750
3100	9.536	78.912	85.561	-32.777	-60.391	-95.956	-95.956	-3.460
3200	9.555	79.200	86.766	-34.623	-60.786	-97.666	-97.666	-4.220
3300	9.573	79.480	87.991	-36.546	-61.186	-99.396	-99.396	-5.030
3400	9.591	79.757	89.233	-38.546	-61.591	-101.146	-101.146	-5.890
3500	9.609	80.030	90.491	-40.623	-62.000	-102.916	-102.916	-6.800
3600	9.627	80.300	91.766	-42.777	-62.416	-104.706	-104.706	-7.760
3700	9.645	80.567	93.061	-45.000	-62.836	-106.516	-106.516	-8.770
3800	9.663	80.830	94.378	-47.299	-63.261	-108.346	-108.346	-9.830
3900	9.682	81.091	95.713	-49.677	-63.691	-110.196	-110.196	-10.940
4000	9.700	81.347	97.066	-52.146	-64.126	-112.066	-112.066	-12.100
4100	9.718	81.600	98.438	-54.700	-64.566	-113.956	-113.956	-13.310
4200	9.736	81.857	99.823	-57.346	-65.016	-115.866	-115.866	-14.570
4300	9.755	82.110	101.233	-60.077	-65.466	-117.796	-117.796	-15.880
4400	9.773	82.360	102.661	-62.899	-65.926	-119.746	-119.746	-17.240
4500	9.791	82.607	104.113	-65.816	-66.391	-121.716	-121.716	-18.650
4600	9.809	82.850	105.586	-68.833	-66.861	-123.706	-123.706	-20.110
4700	9.827	83.090	107.081	-71.956	-67.336	-125.716	-125.716	-21.620
4800	9.845	83.327	108.596	-75.186	-67.816	-127.746	-127.746	-23.180
4900	9.863	83.561	110.133	-78.523	-68.301	-129.796	-129.796	-24.790
5000	9.881	83.794	111.691	-81.966	-68.791	-131.866	-131.866	-26.450
5100	9.899	84.023	113.273	-85.516	-69.286	-133.956	-133.956	-28.160
5200	9.917	84.249	114.881	-89.173	-69.786	-136.066	-136.066	-29.920
5300	9.935	84.473	116.513	-92.946	-70.291	-138.196	-138.196	-31.730
5400	9.953	84.694	118.166	-96.833	-70.801	-140.346	-140.346	-33.590
5500	9.971	84.913	119.841	-100.836	-71.316	-142.516	-142.516	-35.500
5600	9.989	85.130	121.538	-104.956	-71.836	-144.706	-144.706	-37.460
5700	10.007	85.344	123.261	-109.196	-72.361	-146.916	-146.916	-39.470
5800	10.025	85.557	125.006	-113.556	-72.891	-149.146	-149.146	-41.530
5900	10.043	85.768	126.773	-118.036	-73.426	-151.396	-151.396	-43.640
6000	10.061	85.978	128.561	-122.636	-73.966	-153.666	-153.666	-45.800

Dec. 31, 1961; Mar. 31, 1966

POTASSIUM CHLORIDE (KCl) (IDEAL GAS) MOL. WT. = 74.555

Ground State Configuration $1s^2 \sum$ $\Delta H_f^o = -50.88$ kcal. mole⁻¹
 $S_{298.15}^o = 57.12$ cal. deg⁻¹ mole⁻¹ $\Delta H_f^o = -51.31 \pm 0.1$ kcal. mole⁻¹

Electronic Levels and Quantum Weights

E , cm ⁻¹	g
0	1
$\omega_e = 278.6$ cm ⁻¹	$\omega_e x_e = 1.157$ cm ⁻¹
$B_e = 0.127555$ cm ⁻¹	$\alpha_e = 0.0007799$
	$r_e = 2.6667$ Å

Heat of Formation.

The heat of formation was calculated from that of the liquid based on ΔH_f^o 298.15 = 49.5 kcal./mole as selected from vapor pressure analyses summarized below. Partial pressures for the monomer were obtained from data of the first four sources by combination of total vapor pressures with PVT data or with transpiration data. Mass spectrometric values (source 5) are based on temperature variation of ion intensity. These same five studies were used in selection of ΔH_f^o 298.15 = 45.0 kcal./mole for the dimer-monomer equilibrium (see K₂Cl₂).

The resulting tables were tested by comparison with total pressure data over the range 819-1691°K. Dimer-monomer ratios calculated from the tables were used to convert observed total pressures to the monomer pressures which are analyzed below (sources 6-11). The results are consistent except near the boiling point where the observed pressures (sources 10 and 11) are 6-18 percent larger than those calculated. Knudsen effusion and transpiration studies over the crystal were not analyzed since they are in essential agreement with the total effusion data of source 6.

Source	Method	No. of Points	Temp. °K.	ΔH_{vap}^o kcal./mole	Drift eu
1. Datz (1960)	PVT + Vap. Press. (a)	15	1310-1404	51.040-40	49.67
2. Schrier (1957)	Trans. + Vap. Press. (b)	15	1261-1372	50.7650-77	49.28
3. Barton et al. (1959)	Mass Spectrometry	7	1250-1473	49.670-66	49.48
4. Milne et al. (1960)	Total Vap. Press.	137	774-1016	49.6-1.8	49.57
5. Pugh et al. (1958)	Total Vap. Press.	9	819-945	49.0	49.95
6. Dietz et al. (1956)	Total Vap. Press.	9	847-956	49.0	49.95
7. Dietz (1956)	Total Vap. Press.	9	1170-1466	50.5	49.42
8. Knudsen et al. (1956)	Total Vap. Press.	9	1170-1466	50.5	49.42
9. Knudsen et al. (1956)	Total Vap. Press.	9	1393-1688	53.6	49.48
10. Ruff et al. (1921)	Total Vap. Press.	16	1389-1691	50.2	49.22
11. Wartburg et al. (1921)	Total Vap. Press.	16	1235°K. was omitted.		

(a) Total vapor pressure from sources 2, 3 and 8.

- S. Datz, ORNL-2933, Oak Ridge, Tenn., May 1960.
- E. E. Schrier, Ph.D. Thesis, Rensselaer Polytechnic Inst., Troy, N.Y., Jun 1961.
- C. Beusman, ORNL-2323, Oak Ridge, Tenn., Jun 1957.
- A. Barton and R. P. Pugh, AFOSR TN 60-57, Monro Park, Calif., Jun 1960.
- T. A. Milne and R. P. Pugh, AFOSR TN 60-57, Monro Park, Calif., Jun 1960.
- A. C. P. Pugh and R. P. Pugh, Trans. Faraday Soc. 54, 671 (1958).
- V. Dietz, J. Chem. Phys. 24, 575 (1956).
- E. F. Flock and W. H. Rodenbusch, J. Am. Chem. Soc. 48, 2522 (1926).
- O. I. Novikov and O. O. Polyachenok, Russ. J. Inorg. Chem. 6, 996 (1961).
- O. Ruff and S. Muggen, Z. anorg. allgem. Chem. 111, 145 (1921).
- H. von Wartburg and P. Albrecht, Z. elektrochem. 27, 162 (1921).

Heat Capacity and Entropy.

Rotational and vibrational constants are based on the microwave studies of P. L. Clouser and W. Oordy, Phys. Rev. 134, 4863 (1964). Earlier microwave data of A. Honig, M. Mandel, M. L. Stitt, and C. H. Townes, Phys. Rev. 95, 629 (1954) and electric resonance data of C. A. Lee, B. P. Fabricand, R. O. Carlson, and I. I. Rabi, Phys. Rev. 92, 1395 (1953) are in excellent agreement. Infrared spectra of S. A. Rice and W. Kiempfer, J. Chem. Phys. 21, 575 (1957) yield $\omega_e = 281.6$ cm⁻¹ which is also in good agreement. The constants were adjusted to a natural isotopic composition of 24.47% ³⁷Cl and 6.6% ⁴¹K.

C/K

T, °K.	cal. mole ⁻¹ deg. ⁻¹		-(F° - H ₂₉₈ °) / T		H° - H ₂₉₈ °		Kcal. mole ⁻¹		Log K _p
	C _p	S°	ΔH _f °		ΔH _f °		ΔF _f °		
0	0.000	INFINITE	- 5.036	- 100.896	- 100.896	INFINITE			
100	15.520	14.198	56.248	- 4.205	- 102.256	201.626			
200	21.130	26.835	48.560	- 2.349	- 102.740	89.646			
298	26.805	36.100	0.000	- 102.800	- 71.790	52.621			
300	27.000	36.267	36.101	- 0.050	- 102.797	52.156			
400	33.100	44.927	37.240	3.075	- 102.923	33.405			
500	36.800	52.755	39.575	6.590	- 102.939	22.200			
600	39.500	65.466	42.624	13.705	- 97.595	14.862			
700	41.615	71.715	46.341	17.762	- 96.249	9.816			
800	43.600	77.403	50.874	22.023	- 94.738	6.089			
900	45.288	82.638	53.227	26.469	- 93.077	3.237			
1000	46.800	87.489	56.414	31.075	- 91.293	4.563			
1100	48.138	92.013	59.447	36.823	- 89.300	5.043			
1200	49.300	96.253	62.139	40.697	- 87.078	5.251			
1300	50.440	100.245	65.103	45.684	- 84.553	5.267			
1400	51.507	104.022	67.749	50.782	- 81.332	5.479			
1500	52.500	107.610	70.288	55.983	- 78.823	6.521			

June 30, 1963

$\Delta H_f^\circ 0 = -100.9 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -102.8 \pm 1.0 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 3.29 \text{ kcal. mole}^{-1}$
 $T_t = 572.7^\circ\text{K.}$
 $T_m = 798^\circ\text{K.}$
 $\Delta H_m^\circ = \text{Unknown}$

Heat of Formation.

The heat of decomposition of $\text{KClO}_4(\text{c})$ to $\text{KCl}(\text{c})$ and $\text{O}_2(\text{g})$ was measured by W. H. Johnson and A. A. Gilliland, J. Res. Natl. Bur. Std. 55A, 65 (1961), yielding $\Delta H_f^\circ 298.15 = -103.22 \pm 0.15 \text{ kcal. mole}^{-1}$. K. A. Hofmann and P. H. Martin, Sitzber. preuss. Akad. Wiss. Physik. math. Kl. 448 (1932), burned a mixture of paraffin and potassium perchlorate and obtained $\Delta E_{298.15} = -1.73 \text{ kcal. mole}^{-1}$ for the constant volume process corresponding to the reaction: $\text{KClO}_4(\text{c}) = \text{KCl}(\text{c}) + 2\text{O}_2(\text{g})$. Correction of their value for $\Delta(\text{PV})$ gives $\Delta H_f^\circ 298.15 = -0.55 \text{ kcal. mole}^{-1}$ which agrees reasonably well to the corresponding value, $-0.96 \pm 0.10 \text{ kcal. mole}^{-1}$, reported by W. H. Johnson and A. A. Gilliland, loc. cit. However, for the same reaction, $\Delta H_f^\circ 298.15 = -2.55 \pm 0.18 \text{ kcal. mole}^{-1}$ was determined by S. M. Skuratov, A. P. Vorob'ev and N. M. Privolova, Russ. J. Inorg. Chem. 7, 343 (1962). They measured this quantity by two different methods which gave concordant results. The value of $\Delta H_f^\circ 298.15$ reported was $-101.9 \pm 0.2 \text{ kcal. mole}^{-1}$. The value used here is the average of these four results. M. Berthelot and P. Vieille, Ann. chim. et phys. [5] 21, 225 (1882) determined the difference between the heat of explosion of ammonium picrate and that of an ammonium picrate-potassium perchlorate mixture, and also the difference between the heat of explosion of potassium picrate and that of a potassium picrate-potassium perchlorate mixture. They obtained $\Delta H_f^\circ = 7.5 \text{ kcal. mole}^{-1}$ for the reaction $\text{KClO}_4(\text{c}) = \text{KCl}(\text{c}) + 2\text{O}_2(\text{g})$. From that the value of $\Delta H_f^\circ 298.15$ was calculated to be $-111.9 \text{ kcal. mole}^{-1}$. This value was not used.

Heat Capacity and Entropy.

The low temperature heat capacities ($12.53\text{--}238.07^\circ\text{K.}$) were measured by W. M. Latimer and J. E. Ahlberg, J. Am. Chem. Soc. 52, 549 (1930). The heat capacities above 298°K. were estimated by comparison with those of $\text{NaClO}_4(\text{c})$. $S_{298.15}^\circ$ was reported by K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592 (1961), based on the low temperature heat capacities measured by W. M. Latimer and J. E. Ahlberg, loc. cit., using $S_{12.53}^\circ$ (extrap.) = $0.14 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Transition Data.

T_t and ΔH_t° were obtained from the National Bureau of Standards, Circ. 500, "Selected Values of Chemical Thermodynamic Properties," by F. D. Rossini, et al., 1952.

Temperature of Melting.

T_m was taken from Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use," June 1949.

Lithium Chloride (LiCl)

(Crystal) Mol. Wt. = 42.397

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	Log K _p
0	8.000	3.000	INF	0.000	97.400	12.617
100	8.679	3.247	23.574	-2.233	97.678	12.617
200	10.361	9.810	15.191	-1.076	97.722	102.408
298	11.479	14.173	14.173	0.000	97.758	67.278
300	11.495	14.244	14.173	0.021	97.758	66.837
400	12.182	17.652	14.633	1.207	97.423	61.751
500	12.749	20.432	15.523	2.454	98.023	61.674
600	13.287	22.604	16.344	3.736	97.868	61.657
700	13.790	24.111	17.111	5.111	97.532	61.673
800	14.265	25.769	17.822	6.518	97.188	61.673
900	14.833	28.186	18.486	7.978	96.838	61.673
1000	15.337	30.075	20.590	9.485	96.687	61.673
1100	15.839	31.540	21.521	11.043	96.285	61.673
1200	16.338	32.960	22.376	12.632	95.794	61.673
1300	16.836	34.327	23.179	14.260	95.220	61.673
1400	17.336	35.653	24.011	15.920	94.570	61.673
1500	17.831	36.966	24.814	17.778	94.078	61.673
1600	18.323	38.233	25.692	19.586	93.405	61.673
1700	18.811	39.468	26.475	21.443	92.730	61.673
1800	19.311	40.688	27.279	23.350	91.982	61.673
1900	19.805	41.905	28.187	25.308	91.162	61.673
2000	20.298	42.234	28.579	27.310	90.285	61.673

LITHIUM CHLORIDE (LiCl)

(CRYSTAL)

MOL. WT. = 42.397

$$\Delta H_f^\circ 298.15 = -97.578 \pm 0.273 \text{ kcal mole}^{-1}$$

$$S^\circ_{298.15} = 14.173 \pm 0.015 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$T_m = 883 \pm 2^\circ \text{K}$$

Heat of Formation

The heat of formation was obtained as follows:

- (1) $\text{LiOH} \cdot 100\text{H}_2\text{O} + \text{HCl} \cdot 100\text{H}_2\text{O} \rightarrow \text{LiCl} \cdot 20\text{H}_2\text{O}$
T. W. Richards and A. W. Rowe, *J. Am. Chem. Soc.*, **44**, 684 (1922).
- (2) $\text{Li}(c) + 100\text{H}_2\text{O}(l) \rightarrow \text{LiOH} \cdot 100\text{H}_2\text{O} + 1/2 \text{H}_2(g)$
S. R. Gunn and L. G. Green, *J. Am. Chem. Soc.*, **80**, 4782 (1958).
- (3) $\text{LiOH} \cdot 100\text{H}_2\text{O} \rightarrow \text{LiOH} \cdot 100\text{H}_2\text{O} + 900\text{H}_2\text{O}(l)$
T. W. Richards and A. W. Rowe, *J. Am. Chem. Soc.*, **43**, 770 (1921).
- (4) $1/2 \text{H}_2(g) + 1/2 \text{Cl}_2(g) \rightarrow \text{HCl}(g)$
JANAF Tables.
- (5) $\text{HCl}(g) + 100\text{H}_2\text{O}(l) \rightarrow \text{HCl} \cdot 100\text{H}_2\text{O}$
C. M. Slansky, *J. Am. Chem. Soc.*, **62**, 2430 (1940), and
J. M. Sturtevant, *J. Am. Chem. Soc.*, **62**, 3265 (1940).
- (6) $\text{LiCl} \cdot 20\text{H}_2\text{O} \rightarrow \text{LiCl}(c) + 20\text{H}_2\text{O}(l)$
E. Lange and F. Dürr, *Z. phys. Chem.*, **121**, 361 (1926).

$$(1) + (2) + (3) + (4) + (5) + (6) \text{ gives Li}(c) + 1/2 \text{Cl}_2(g) \rightarrow \text{LiCl}(c)$$

A direct calorimetric determination by H. Siemensen and U. Siemensen, *Z. Electrochem.*, **56**, 643 (1952) gave -94.8 ± 0.6 kcal mole⁻¹. However, the solution route was thought to be inherently more accurate and was adopted.

Heat Capacity and Entropy

The heat capacity between 15° and 325°K has been measured by D. A. Shirley, *J. Am. Chem. Soc.*, **82**, 3841 (1960) and by F. L. Oetting, W. E. Hutton and G. C. Sinke, unpublished work, Thermal Laboratory, Dow Chemical Company. The two sets of data are in substantial agreement and were plotted together and used to evaluate the entropy at 298°. The extrapolation to 0°K was done assuming a T³ law and yielded S₁₅ = 0.019 e.u. Above 298° T. B. Douglas, J. L. Dever and A. W. Harman, quoted in Natl. Bur. Standards Report 6297, have made enthalpy measurements to 1200°K. E. N. Rodigina, K. Z. Gornitski, and V. F. Luginina, *Zhur. Neorg. Khim.*, **4**, 975 (1959) also made enthalpy determinations to 1100°K. These two sets of measurements were averaged and joined smoothly to the low temperature values.

Melting and Transition Data

The melting point has been reported as follows: 880°K., Douglas et al., loc. cit.; 883°K., Rodigina et al., loc. cit.; 883°K., H. M. Haendler, P. S. Bennett, and C. M. Wheeler, *J. Electrochem. Soc.*, **106**, 264 (1959); 879°K., H. Flood, O. Fyke and S. Urnes, *Z. Electrochem.*, **59**, 364 (1955); 879°K., H. von Wartenberg and H. Schulz, *Z. Electrochem.*, **27**, 588 (1921). The highest value of 883°K. was taken as representing the most pure samples. At this temperature the enthalpy equations of Douglas et al. yield a heat of fusion of 4.718 kcal mole⁻¹, those of Rodigina et al., 4.669 kcal mole⁻¹. A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **64**, 263 (1960) report a value of 4.76 ± 0.10 kcal mole⁻¹ and quote 4.83 kcal mole⁻¹ from a private communication from D. F. Smith. The average value ΔH_m = 4.74 ± 0.10 kcal mole⁻¹ was adopted.

A transition at 838°K has been reported by Kislova and Bergman, *Russ. J. Inorg. Chem.*, **5**, 1210 (1960) but is not supported by the enthalpy measurements quoted above.

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹ S° - (F° - H ₂₉₈)/T	H° - H ₂₉₈	cal. mole ⁻¹ ΔH°	Log K _p
0					
100	11.479	19.745	0.000	93.394	65.210
200	11.495	19.816	0.021	93.391	64.786
300	12.748	20.004	2.454	93.639	63.578
400	16.179	27.435	3.792	93.649	64.417
500	15.953	25.912	5.398	93.151	62.917
600	15.727	24.025	6.292	92.732	61.401
700	15.275	23.689	10.082	91.905	78.766
800	15.049	36.934	11.599	91.525	77.471
900	14.822	27.324	13.092	91.170	76.210
1000	14.596	39.411	14.563	90.836	74.977
1100	14.370	40.445	17.031	90.525	72.582
1200	14.143	41.468	18.840	89.967	71.413
1300	13.914	42.374	20.220	89.933	69.892
1400	13.691	43.211	21.378	89.859	68.859
1500	13.467	43.987	22.413	89.768	67.972
1600	13.242	44.709	23.226	89.653	67.177
1700	13.015	45.382			

LITHIUM CHLORIDE (LiCl)

(LIQUID)

MOL. WT. = 42.397

$$\Delta H_f^\circ 298.15 = -93.394 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = 18.745 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^\circ = 4.74 \pm 0.10 \text{ kcal. mole}^{-1}$$

$$T_m = 883 \pm 2^\circ \text{K}$$

$$T_b(\text{monomeric gas}) = 1701^\circ \text{K}$$

$$T_b(\text{equilibrium mixture}) = 1655^\circ \text{K}$$

Heat of Formation.

Obtained from that of the crystal by adding ΔH_m and $H_{883}^\circ - H_{298}^\circ(c)$ and subtracting $H_{883}^\circ - H_{298}^\circ(l)$.

Heat Capacity and Entropy.

The heat capacity from the melting point to 1100°K and 1200°K has been reported by E. N. Rodigina, K. Z. Omel'nik, and V. P. Luginina, Zhur. Neorg. Khim. 4, 975 (1959) and T. B. Douglas, J. L. Dever, and A. W. Harman, quoted in Natl. Bur. of Standards Report 6297. The equation given by the former authors for the enthalpy of the liquid does not agree with their measurements and has been replaced by $H_m - H_{298.15} = 16.000T - 1.5 \times 10^{-5}T^2 - 2279 \text{ cal. mole}^{-1}$, which fits to $\pm 0.5\%$. The two sets of results were averaged and the equations were assumed to hold up to the normal boiling point. The entropy was calculated from that of the crystal in a manner analogous to the heat of formation.

Melting.

See table for crystal.

Boiling.

The equilibrium boiling point was taken from H. von Wartenburg and H. Schultz, Z. Electrochem. 27, 568 (1921) and the boiling point of the monomeric gas is defined as the temperature at which it reaches 1 atm. pressure. This was obtained from the free energy crossover between liquid and monomeric gas. The heat of vaporization to the monomeric gas was found from the tables to be 38.8 kcal. mole⁻¹.

Lithium Chloride (LiCl)

(Ideal Gas) Mol. wt. = 42.397

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	0.000	INFINITE	2.146	-46.742	-46.742	INFINITE
100	6.978	42.659	57.562	-1.470	-46.516	-46.516	105.700
200	7.412	47.800	51.575	-1.755	-46.601	-50.197	54.650
298	7.946	50.864	50.864	-1.000	-46.778	-51.926	38.081
300	7.958	50.913	50.864	-0.15	-46.782	-51.958	37.850
400	8.312	53.255	51.181	-1.839	-47.003	-51.651	29.312
500	8.534	55.135	51.750	-1.673	-48.004	-53.208	24.130
600	8.677	56.705	52.482	-2.534	-48.291	-56.620	20.623
700	8.775	58.050	53.184	-3.407	-48.557	-57.968	18.104
800	8.846	59.197	53.851	-4.280	-48.800	-59.317	16.179
900	8.901	60.272	54.522	-5.175	-49.053	-60.617	14.719
1000	8.945	61.212	55.145	-6.068	-49.304	-61.889	13.525
1100	8.981	62.067	55.736	-6.964	-49.544	-63.135	12.543
1200	9.012	62.859	56.296	-7.864	-49.782	-64.361	11.721
1300	9.040	63.572	56.828	-8.766	-50.016	-65.566	11.022
1400	9.066	64.216	57.332	-9.669	-50.246	-66.748	10.426
1500	9.087	64.789	57.816	-10.576	-50.477	-67.923	9.866
1600	9.108	65.286	58.275	-11.489	-50.702	-69.080	9.335
1700	9.129	65.709	58.714	-12.401	-50.922	-70.221	8.833
1800	9.149	66.059	59.137	-13.310	-51.139	-71.345	8.356
1900	9.165	66.436	59.537	-14.230	-51.354	-72.452	7.902
2000	9.182	66.847	59.923	-15.148	-51.568	-73.542	7.467
2100	9.199	67.295	60.294	-16.067	-51.783	-74.615	7.050
2200	9.215	67.773	60.652	-16.987	-51.998	-75.672	6.652
2300	9.230	68.287	61.000	-17.906	-52.213	-76.715	6.272
2400	9.247	68.837	61.350	-18.825	-52.428	-77.744	5.910
2500	9.263	69.354	61.651	-19.759	-52.642	-78.759	5.564
2600	9.278	69.918	61.962	-20.686	-52.856	-79.752	5.224
2700	9.294	70.266	62.263	-21.615	-53.069	-80.732	4.892
2800	9.309	70.607	62.555	-22.545	-53.281	-81.697	4.566
2900	9.324	70.942	62.840	-23.474	-53.493	-82.648	4.246
3000	9.338	71.250	63.113	-24.410	-53.705	-83.585	3.930
3100	9.353	71.556	63.381	-25.344	-53.916	-84.508	3.618
3200	9.368	71.854	63.641	-26.280	-54.126	-85.418	3.310
3300	9.382	72.142	63.894	-27.216	-54.335	-86.315	3.006
3400	9.397	72.421	64.141	-28.152	-54.543	-87.200	2.706
3500	9.411	72.695	64.382	-29.087	-54.750	-88.073	2.410
3600	9.425	72.960	64.616	-30.039	-54.956	-88.939	2.118
3700	9.440	73.219	64.845	-30.992	-55.161	-89.799	1.830
3800	9.454	73.474	65.071	-31.947	-55.365	-90.652	1.546
3900	9.468	73.714	65.297	-32.902	-55.568	-91.498	1.266
4000	9.482	73.956	65.501	-33.860	-55.770	-92.338	0.990
4100	9.496	74.191	65.710	-34.769	-55.971	-93.172	0.718
4200	9.511	74.420	65.915	-35.720	-56.171	-94.000	0.450
4300	9.525	74.644	66.115	-36.672	-56.370	-94.822	0.186
4400	9.539	74.864	66.313	-37.625	-56.568	-95.638	-0.074
4500	9.553	75.077	66.506	-38.579	-56.765	-96.448	-0.338
4600	9.567	75.287	66.693	-39.535	-56.961	-97.252	-0.606
4700	9.581	75.493	66.878	-40.493	-57.156	-98.050	-0.878
4800	9.595	75.695	67.059	-41.451	-57.350	-98.842	-1.154
4900	9.609	75.895	67.237	-42.410	-57.543	-99.628	-1.434
5000	9.623	76.087	67.413	-43.372	-57.735	-100.408	-1.718
5100	9.636	76.278	67.585	-44.336	-57.927	-101.182	-2.006
5200	9.650	76.465	67.754	-45.300	-58.118	-101.952	-2.298
5300	9.664	76.649	67.920	-46.266	-58.308	-102.718	-2.594
5400	9.678	76.830	68.083	-47.233	-58.497	-103.479	-2.894
5500	9.692	77.008	68.244	-48.202	-58.686	-104.235	-3.198
5600	9.706	77.183	68.402	-49.172	-58.874	-104.986	-3.506
5700	9.720	77.354	68.557	-50.143	-59.061	-105.732	-3.818
5800	9.734	77.523	68.711	-51.116	-59.247	-106.474	-4.134
5900	9.748	77.690	68.861	-52.091	-59.432	-107.211	-4.454
6000	9.761	77.854	69.010	-53.065	-59.616	-107.944	-4.778

CILI

LITHIUM CHLORIDE (LiCl)

(IDEAL GAS)

MOL. WT. = 42.397

$\Delta H_f^\circ = -46.742 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 50.864 \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = 52.998.15 \text{ cal. deg}^{-1} \text{ mole}^{-1}$

Ground State Configuration $1\sum$

$\omega_e = 641.1 \pm 3.0 \text{ cm}^{-1}$
 $\omega_e x_e = 4.2 \pm 0.3 \text{ cm}^{-1}$
 $\omega_e = 0.7053 \text{ cm}^{-1}$
 $\alpha_e = 0.0067 \text{ cm}^{-1}$
 $\sigma = 1$
 $r_e = 2.022 \text{ \AA}$

Heat of Formation.

W. Klemperer, W. G. Norris, A. Büchler and A. G. Emalle, *J. Chem. Phys.* **33**, 1534 (1960) quote a private communication from W. H. Evans at the National Bureau of Standards giving $D_0 = 4.85 \text{ e.v.}$, which corresponds to $\Delta H_f^\circ = -45.3 \pm 2.4 \text{ kcal. mole}^{-1}$. A third law analysis of the vapor pressure data of An. N. Nesmeyanov and L. A. Sazonov, *Zhur. Neorg. Khim.* **5**, 231 (1960) in conjunction with the relative concentration of monomer, dimer, and trimer at 870°K from the work of R. C. Miller and P. Kusch, *J. Chem. Phys.* **25**, 860 (1956) and **27**, 991 (1957) leads to a monomer heat of sublimation at 298° of $52.56 \text{ kcal. mole}^{-1}$, this gives $\Delta H_f^\circ = -45.02 \text{ kcal. mole}^{-1}$. These values lead, however, to partial vapor pressures of the monomer which are less than half of the total vapor pressure near the boiling point. From the data of Miller and Kusch loc. cit. it would be expected that the monomer would be the predominant species near the boiling point, a fact also substantiated by the work of C. Beusman, *AEC Report ORNL-2223* (1957), on the average molecular weight of the vapor. Thus it was decided to change the heat of sublimation as to give the correct normal boiling point and vapor pressures in the region 1400-1600°K and to approximate the relative concentrations of monomer, dimer, and trimer as found by Miller and Kusch at 870°K. A monomer heat of sublimation at 298° of $50.8 \text{ kcal. mole}^{-1}$ was chosen, which gives $\Delta H_f^\circ = -46.778 \text{ kcal. mole}^{-1}$. The normal boiling point was taken as 1656°K as determined by H. von Wartenburg and H. Schulz, *Z. Elektrochem.* **27**, 568 (1921) and the boiling point of $\text{LiCl}(g)$ was found as 1701°K from the free energy crossover between liquid and gas.

Heat Capacity and Entropy.

The spectroscopic constants were taken from Klemperer et al. loc. cit. The value of α_e was calculated from the value of ω_e given by the Rittner potential function and the equation given by Klemperer et al. The value of r_e was taken from the Natl. Bur. of Standards Report 6297 (1959).

CILI

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 58.397

C.I.L.I.O

LITHIUM HYPOCHLORITE (LiClO) (Ideal Gas)

Mol. Wt. = 58.397

 $\Delta_f^\circ 298.15 = [-3.4 \pm 20] \text{ kcal. mole}^{-1}$ $\Delta_f^\circ 298.15 = [61.264] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Vibrational Levels and Multiplicities

$$\frac{\omega \text{ cm.}^{-1}}{[1150](1), [500](1), [700](1)}$$

Li-O-Cl angle 115° , Li-O dist. $1.82 \text{ \AA}$, O-Cl dist. $1.73 \text{ \AA}$ $\sigma = 1$.

Data from D. L. Hildenbrand, Aeronutronic Division of Ford Motor Company, Newport Beach, Calif., "Tables of Thermodynamic Data for Performance Calculations", September, 1959.

T, °K.	C_p°	S°	$\text{ent. mole}^{-1} \text{ deg.}^{-1}$	$-(H^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
100	6.090	51.590	19.741	2.758	2.758	2.758	2.758	19.741
200	9.061	57.615	27.168	.950	3.076	3.076	3.076	27.168
298	10.268	61.284	31.284	.000	3.400	3.400	3.400	31.284
300	10.280	61.328	31.284	.000	3.400	3.400	3.400	31.284
400	11.615	67.010	35.495	2.258	4.768	4.768	4.768	35.495
500	12.367	69.227	36.436	3.474	5.077	4.869	4.869	36.436
600	12.720	71.163	36.405	4.731	5.349	4.603	4.603	36.405
700	12.760	72.876	36.359	6.030	5.598	4.460	4.460	36.359
800	12.770	74.366	36.306	7.361	5.826	4.288	4.288	36.306
900	12.770	75.656	36.250	8.721	6.036	4.088	4.088	36.250
1000	12.770	76.786	36.199	10.111	6.226	3.868	3.868	36.199
1100	12.770	77.776	36.150	11.531	6.396	3.628	3.628	36.150
1200	12.770	78.626	36.101	13.001	6.546	3.368	3.368	36.101
1300	12.770	79.356	36.052	14.521	6.676	3.088	3.088	36.052
1400	12.770	80.006	36.003	16.091	6.786	2.788	2.788	36.003
1500	12.770	80.586	35.954	17.721	6.876	2.468	2.468	35.954
1600	12.770	81.106	35.905	19.411	6.946	2.128	2.128	35.905
1700	12.770	81.566	35.856	21.161	6.996	1.778	1.778	35.856
1800	12.770	81.966	35.806	22.971	7.026	1.418	1.418	35.806
1900	12.770	82.316	35.757	24.841	7.036	1.048	1.048	35.757
2000	12.770	82.616	35.707	26.771	7.026	.668	.668	35.707
2100	12.770	82.866	35.657	28.761	6.996	.278	.278	35.657
2200	12.770	83.066	35.607	30.811	6.946	-.122	-.122	35.607
2300	12.770	83.216	35.557	32.921	6.876	-.512	-.512	35.557
2400	12.770	83.316	35.507	35.091	6.786	-.882	-.882	35.507
2500	12.770	83.366	35.457	37.321	6.676	-1.232	-1.232	35.457
2600	12.770	83.366	35.407	39.611	6.546	-1.562	-1.562	35.407
2700	12.770	83.316	35.357	41.961	6.396	-1.872	-1.872	35.357
2800	12.770	83.216	35.307	44.371	6.226	-2.162	-2.162	35.307
2900	12.770	83.066	35.257	46.841	6.036	-2.432	-2.432	35.257
3000	12.770	82.866	35.207	49.371	5.826	-2.682	-2.682	35.207
3100	12.770	82.616	35.157	51.961	5.598	-2.912	-2.912	35.157
3200	12.770	82.316	35.107	54.611	5.349	-3.122	-3.122	35.107
3300	12.770	81.966	35.057	57.321	5.077	-3.312	-3.312	35.057
3400	12.770	81.566	35.007	60.091	4.786	-3.482	-3.482	35.007
3500	12.770	81.106	34.957	62.921	4.476	-3.632	-3.632	34.957
3600	12.770	80.586	34.907	65.811	4.146	-3.762	-3.762	34.907
3700	12.770	80.006	34.857	68.761	3.796	-3.872	-3.872	34.857
3800	12.770	79.356	34.807	71.771	3.406	-3.962	-3.962	34.807
3900	12.770	78.626	34.757	74.841	2.996	-4.032	-4.032	34.757
4000	12.770	77.776	34.707	77.971	2.566	-4.082	-4.082	34.707
4100	12.770	76.826	34.657	81.161	2.116	-4.112	-4.112	34.657
4200	12.770	75.776	34.607	84.411	1.646	-4.122	-4.122	34.607
4300	12.770	74.626	34.557	87.721	1.156	-4.112	-4.112	34.557
4400	12.770	73.376	34.507	91.091	.646	-4.082	-4.082	34.507
4500	12.770	72.026	34.457	94.521	.116	-4.032	-4.032	34.457
4600	12.770	70.576	34.407	97.911	-.434	-3.962	-3.962	34.407
4700	12.770	69.026	34.357	101.261	-.964	-3.872	-3.872	34.357
4800	12.770	67.376	34.307	104.571	-1.474	-3.762	-3.762	34.307
4900	12.770	65.626	34.257	107.841	-1.954	-3.632	-3.632	34.257
5000	12.770	63.776	34.207	111.071	-2.404	-3.482	-3.482	34.207
5100	12.770	61.826	34.157	114.261	-2.824	-3.312	-3.312	34.157
5200	12.770	59.776	34.107	117.411	-3.214	-3.122	-3.122	34.107
5300	12.770	57.626	34.057	120.521	-3.574	-2.912	-2.912	34.057
5400	12.770	55.376	34.007	123.591	-3.904	-2.682	-2.682	34.007
5500	12.770	53.026	33.957	126.621	-4.204	-2.432	-2.432	33.957
5600	12.770	50.576	33.907	129.611	-4.474	-2.162	-2.162	33.907
5700	12.770	48.026	33.857	132.561	-4.714	-1.872	-1.872	33.857
5800	12.770	45.376	33.807	135.471	-4.924	-1.562	-1.562	33.807
5900	12.770	42.626	33.757	138.341	-5.104	-1.232	-1.232	33.757
6000	12.770	39.776	33.707	141.171	-5.254	-.882	-.882	33.707

December 31, 1960.

C.I.L.I.O

Lithium Perchlorate (LiClO₄)
(Crystal) Mol. Wt. = 106.397

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0							
100	25.100	30.000	30.000	0.000	91.060	60.706	44.497
200	25.200	30.156	30.000	0.047	90.098	60.519	44.086
300	31.000	38.181	31.056	2.850	90.652	50.398	27.535
400	34.300	45.699	33.228	6.136	90.673	40.336	17.630
500	36.500	51.965	38.566	13.430	88.752	30.525	11.054
600	38.500	57.233	43.277	21.340	87.553	20.863	6.908
700	39.800	62.952	47.054	28.389	86.268	13.352	3.328
800	41.150	67.719	49.553	35.563	84.885	8.011	1.751
900	42.300	72.116					
1000	43.325	76.197	49.065	49.845	83.417	17.229	3.423
1100	44.200	80.005	51.085	58.423	81.773	26.311	4.792
1200	44.800	83.580	53.119	68.650	80.257	35.221	5.928
1300	45.140	86.960	55.066	78.561	78.561	44.084	6.881
1400	46.073	90.170	56.866	87.904	76.786	52.783	7.690
1500	47.000						

LiClO₄

MOL. WT. = 106.397

(CRYSTAL)

LITHIUM PERCHLORATE (LiClO₄)

ΔH_f° = Unknown

S°_{298.15} = [30 ± 1] cal. deg.⁻¹ mole⁻¹

ΔH_f°_{298.15} = -91.0 ± 0.7 kcal. mole⁻¹

ΔH_m° = [7] kcal. mole⁻¹

T_m = 509°K.

Heat of Formation.
The heats of reaction (ΔH_r°) involving LiClO₄(c) has been determined by several investigators as follows:

Investigator	Chemical Reaction	ΔH _r ° _{298.15} , kcal. mole ⁻¹	ΔH _f ° _{298.15} , kcal. mole ⁻¹
Gilliland and Johnson (1)	LiClO ₄ (c) + KCl(c) → LiCl(c) + KClO ₄ (c)	-5.86 ± 0.06	-90.34
Markowitz, et al. (2)	LiOH(225H ₂ O) + HClO ₄ (225H ₂ O) → LiClO ₄ (451H ₂ O) + H ₂ O(l)	-13.54 ± 0.09	-91.7
Birky and Hepler (3)	LiClO ₄ (c) → Li ⁺ (aq.) + ClO ₄ ⁻ (aq.)	-6.31 ± 0.13	-91.11

(1) A. A. Gilliland and W. H. Johnson, J. Res. Natl. Bur. Std. 65A, 67 (1961).

(2) M. M. Markowitz, R. P. Herra and H. Stewart, Jr., J. Phys. Chem. 63, 1325 (1959).

(3) M. M. Birky and L. G. Hepler, J. Phys. Chem. 64, 686 (1960).

The adopted value, ΔH_f°_{298.15} = -91.0 kcal. mole⁻¹, for LiClO₄(c) is the weighted average of the three values listed.

Heat Capacity and Entropy:

Heat capacities and S°_{298.15} were estimated by comparison with those of KClO₄(c).

Melting Data.

T_m was obtained from T. W. Richards and H. H. Willard, J. Am. Chem. Soc., 32, 4 (1910). The value of ΔH_m°₅₀₉ was estimated by comparison with the value, ΔH_m°₅₂₈ = 5.4 kcal. mole⁻¹, for NaClO₃(c) reported by K. K. Kelley, Contribution to the Data on Theoretical Metallurgy, XIII. High-Temperature Heat-Content, Heat-Capacity and Entropy Data for the Elements and Inorganic Compounds, U. S. Bur. Mines Bull. 584 (1960).

LiClO₄

T. °K.	C _p	$\int_{T_0}^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$\frac{S^0}{T} - (F^0 - H_{298}^0)/T$	$\int_{T_0}^T \frac{C_p}{T^2} dT$ cal. mole ⁻¹ deg. ⁻²	$H^0 - H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K _p
0								
100	38.500	39.245	39.245	-	+0.00	- 85.684	- 58.146	42.620
200	38.500	39.483	39.246	-	+0.71	- 85.657	- 57.976	42.234
300	38.500	39.559	40.756	3.921	- 85.665	- 46.962	- 46.962	26.750
400	38.500	59.150	43.607	7.771	- 83.722	- 40.210	- 40.210	17.575
500	38.500	66.169	46.801	11.621	- 82.529	- 31.620	- 31.620	11.517
600	38.500	72.104	50.002	15.471	- 81.374	- 23.228	- 23.228	7.252
700	38.500	77.234	53.185	19.211	- 80.260	- 16.908	- 16.908	4.066
800	38.500	81.780	56.034	23.171	- 79.169	- 1.065	- 1.065	+2.23
900	38.500	85.836	58.615	27.021	- 78.110	- 77.075	- 77.075	- 1.774
1000	38.500	89.506	61.441	30.871	- 76.921	- 76.921	- 76.921	- 3.042
1100	38.500	92.491	63.921	34.721	- 75.659	- 75.659	- 75.659	- 4.366
1200	38.500	94.937	66.187	38.571	- 74.421	- 74.421	- 74.421	- 5.762
1300	38.500	96.790	68.489	42.421	- 73.203	- 73.203	- 73.203	- 7.162
1400	38.500	98.770	70.599	46.271	- 72.075	- 72.075	- 72.075	- 8.562
1500	38.500	101.447	72.599	50.121	- 71.000	- 71.000	- 71.000	- 9.962

Dec. 31, 1960; Mar. 31, 1964

LITHIUM PERCHLORATE (LiClO₄)

(LIQUID)

MOL. WT. = 106.397

$S_{298.15}^0 = [39.245]$ cal. deg.⁻¹ mole⁻¹
 $T_m = 509^\circ\text{K.}$
 $\Delta H_f^0 298.15 = [-85.574]$ cal. deg.⁻¹ mole⁻¹
 $\Delta G_m^0 = [7]$ kcal. mole⁻¹

Heat of Formation.

$\Delta H_f^0 298.15(1)$ was obtained from $\Delta H_f^0 298.15(c)$ by adding ΔH_m^0 and the difference between $H_{370.6}^0$ and $H_{298.15}^0$ for crystal and liquid.

Heat Capacity and Entropy.

C_p for LiClO₄(l) was estimated by comparison with that for NaClO₃(l). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting temperature (T_m) was obtained from T. W. Richards and H. H. Willard, J. Am. Chem. Soc., **32**, 4 (1910). The value of $\Delta H_m^0 509$ was estimated by comparison with the value, $\Delta H_m^0 528 = 5.4$ kcal. mole⁻¹, for NaClO₃(c) reported by K. K. Kelley, Contribution to the Data on Theoretical Metallurgy, XIII. High-Temperature Heat-Content, Heat-Capacity and Entropy Data for the Elements and Inorganic Compounds, U. S. Bur. Mines Bull. 584 (1960).

Magnesium Monochloride (MgCl)

(Ideal Gas) Mol. wt. = 59.765

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	keal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	Log K _p
0	-0.000	INFINITE	- 2.237	- 10.344	- 10.344	INFINITE
100	7.077	47.399	- 2.801	- 10.152	- 12.405	27.111
200	7.830	52.531	- 3.508	- 10.795	- 16.713	16.077
298	8.324	55.760	- 4.400	- 10.400	- 16.751	12.279
300	8.330	55.812	- 4.403	- 10.403	- 16.701	12.232
400	8.587	58.247	- 5.091	- 10.895	- 18.604	10.523
500	8.730	60.180	- 5.672	- 10.787	- 20.946	9.156
600	8.819	61.780	- 6.136	- 11.013	- 22.959	8.363
700	8.878	63.145	- 6.492	- 11.260	- 24.930	7.784
800	8.915	64.305	- 6.774	- 11.520	- 26.562	7.306
900	8.956	65.336	- 6.994	- 11.840	- 28.084	6.904
1000	8.983	66.331	- 7.158	- 12.218	- 29.442	6.653
1100	9.007	67.188	- 7.279	- 12.609	- 30.688	6.365
1200	9.027	67.973	- 7.361	- 13.045	- 31.802	6.120
1300	9.044	68.700	- 7.415	- 13.525	- 32.795	5.906
1400	9.059	69.387	- 7.450	- 14.049	- 33.672	5.712
1500	9.079	69.993	- 7.466	- 14.618	- 34.420	5.542
1600	9.094	70.580	- 7.465	- 15.229	- 35.066	5.391
1700	9.109	71.151	- 7.448	- 15.884	- 35.612	5.256
1800	9.116	71.706	- 7.415	- 16.584	- 36.058	5.137
1900	9.116	72.146	- 7.361	- 17.328	- 36.402	5.031
2000	9.110	72.615	- 7.288	- 18.118	- 36.545	4.937
2100	9.103	73.062	- 7.198	- 18.958	- 36.488	4.854
2200	9.103	73.488	- 7.095	- 19.850	- 36.232	4.781
2300	9.118	73.888	- 6.978	- 20.795	- 35.676	4.718
2400	9.200	74.288	- 6.850	- 21.795	- 34.820	4.665
2500	9.212	74.664	- 6.728	- 22.840	- 33.564	4.622
2600	9.225	75.025	- 6.600	- 23.930	- 31.908	4.589
2700	9.237	75.373	- 6.468	- 25.064	- 29.852	4.566
2800	9.251	75.703	- 6.332	- 26.242	- 27.396	4.553
2900	9.261	76.034	- 6.193	- 27.464	- 24.540	4.550
3000	9.272	76.349	- 6.050	- 28.728	- 21.284	4.557
3100	9.284	76.653	- 5.903	- 30.044	- 17.628	4.574
3200	9.296	76.948	- 5.752	- 31.418	- 13.572	4.601
3300	9.319	77.232	- 5.597	- 32.846	- 9.116	4.638
3400	9.331	77.512	- 5.438	- 34.328	- 4.260	4.685
3500	9.331	77.782	- 5.275	- 35.864	1.000	4.742
3600	9.343	78.045	- 5.108	- 37.454	6.244	4.809
3700	9.354	78.301	- 4.938	- 39.100	11.484	4.886
3800	9.364	78.551	- 4.763	- 40.802	16.718	4.973
3900	9.377	78.794	- 4.584	- 42.560	21.958	5.070
4000	9.389	79.032	- 4.400	- 44.364	27.204	5.177
4100	9.400	79.264	- 4.212	- 46.214	32.456	5.294
4200	9.412	79.491	- 4.019	- 48.118	37.714	5.421
4300	9.424	79.712	- 3.822	- 50.076	42.978	5.558
4400	9.435	79.929	- 3.621	- 52.088	48.248	5.705
4500	9.446	80.151	- 3.415	- 54.150	53.524	5.862
4600	9.457	80.349	- 3.204	- 56.264	58.806	6.029
4700	9.466	80.522	- 2.988	- 58.430	64.094	6.206
4800	9.474	80.679	- 2.768	- 60.648	69.388	6.393
4900	9.482	80.816	- 2.543	- 62.918	74.688	6.590
5000	9.503	81.139	- 2.314	- 65.240	79.994	6.797
5100	9.515	81.328	- 2.080	- 67.614	85.306	7.014
5200	9.527	81.513	- 1.842	- 69.940	90.624	7.241
5300	9.538	81.694	- 1.599	- 72.318	95.948	7.478
5400	9.549	81.872	- 1.352	- 74.750	101.278	7.725
5500	9.560	82.048	- 1.101	- 77.238	106.614	7.982
5600	9.571	82.220	- 0.846	- 79.782	111.956	8.249
5700	9.583	82.390	- 0.587	- 82.382	117.304	8.526
5800	9.594	82.558	- 0.324	- 85.036	122.658	8.813
5900	9.605	82.721	- 0.057	- 87.744	128.018	9.110
6000	9.617	82.882	0.214	- 90.506	133.384	9.417

Dec. 31, 1960; Mar. 31, 1966

MOL. WT. = 59.765

(IDEAL GAS)

MAGNESIUM MONOCHLORIDE (MgCl)

Ground State Configuration $2\sum$

$\Delta H_f^0 = -10.34 \pm 10$ kcal. mole⁻¹

$S_{298.15}^0 = 55.760$ cal. deg.⁻¹ mole⁻¹

$\Delta H_f^0 298.15 = -10.4 \pm 10$ kcal. mole⁻¹

Electronic Levels and Quantum Weights

$$\frac{\epsilon_l, \text{cm.}^{-1}}{0} \frac{g_l}{2}$$

$\omega_e x_e = 2.02$ cm.⁻¹

$\sigma = 1$

$\alpha_e = [0.0014]$ cm.⁻¹

$r_e = 2.199 \text{ \AA}$

$B_e = [0.2417]$ cm.⁻¹

Heat of Formation.

The heat of formation is calculated from $D_0^0 = 3.2$ e.v. reported by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Co., Inc., New York, 1950. $D_0^0 = 2.7 \pm 0.7$ e.v. reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 2nd Edn., Chapman and Hall, London, 1953, yields $\Delta H_f^0 298$ (MgCl, g) = 1.0 ± 16 kcal. mole⁻¹.

Heat Capacity and Entropy.

Spectroscopic constants were reported by Herzberg loc. cit. and adjusted for natural isotopic abundance. The bond length was reported by E. Morgan and R. F. Barrow, Nature **192**, 1182, (1961). B_e and α_e were estimated by the method suggested by Herzberg loc. cit. The moment of inertia (I) is $11.578 \times 10^{-59} \text{ g. cm.}^2$

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	kcal/mol ΔH ^o	ΔG ^o	Log K _p
100						
200	8.472	54.600	4.000	156.000	148.508	-108.259
298						
300	8.477	54.600	.016	156.006	148.461	-108.154
400	8.493	54.935	.875	156.334	145.895	-70.713
500	8.513	55.078	1.751	156.638	143.251	-62.615
600	8.537	55.197	2.636	156.917	140.546	-51.194
700	8.560	55.296	3.526	157.172	137.787	-43.622
800	8.581	55.376	4.416	157.406	135.003	-39.104
900	8.600	55.446	5.306	157.598	132.204	-32.114
1000	8.614	55.506	6.196	157.752	129.396	-26.314
1100	8.626	55.556	7.086	157.876	126.588	-21.521
1200	8.636	55.600	7.976	157.976	123.780	-17.723
1300	8.644	55.636	8.866	158.056	120.972	-13.925
1400	8.650	55.666	9.756	158.116	118.164	-10.127
1500	8.654	55.690	10.646	158.166	115.356	-6.329
1600	8.656	55.710	11.536	158.206	112.548	-2.531
1700	8.658	55.726	12.426	158.236	109.740	1.267
1800	8.659	55.740	13.316	158.256	106.932	5.065
1900	8.660	55.750	14.206	158.266	104.124	8.863
2000	8.661	55.756	15.096	158.266	101.316	12.661
2100	8.661	55.760	15.986	158.266	98.508	16.459
2200	8.661	55.761	16.876	158.266	95.700	20.257
2300	8.661	55.761	17.766	158.266	92.892	24.055
2400	8.661	55.761	18.656	158.266	90.084	27.853
2500	8.661	55.761	19.546	158.266	87.276	31.651
2600	8.661	55.761	20.436	158.266	84.468	35.449
2700	8.661	55.761	21.326	158.266	81.660	39.247
2800	8.661	55.761	22.216	158.266	78.852	43.045
2900	8.661	55.761	23.106	158.266	76.044	46.843
3000	8.661	55.761	24.000	158.266	73.236	50.641
3100	8.661	55.761	24.890	158.266	70.428	54.439
3200	8.661	55.761	25.780	158.266	67.620	58.237
3300	8.661	55.761	26.670	158.266	64.812	62.035
3400	8.661	55.761	27.560	158.266	62.004	65.833
3500	8.661	55.761	28.450	158.266	59.196	69.631
3600	8.661	55.761	29.340	158.266	56.388	73.429
3700	8.661	55.761	30.230	158.266	53.580	77.227
3800	8.661	55.761	31.120	158.266	50.772	81.025
3900	8.661	55.761	32.010	158.266	47.964	84.823
4000	8.661	55.761	32.900	158.266	45.156	88.621
4100	8.661	55.761	33.790	158.266	42.348	92.419
4200	8.661	55.761	34.680	158.266	39.540	96.217
4300	8.661	55.761	35.570	158.266	36.732	100.015
4400	8.661	55.761	36.460	158.266	33.924	103.813
4500	8.661	55.761	37.350	158.266	31.116	107.611
4600	8.661	55.761	38.240	158.266	28.308	111.409
4700	8.661	55.761	39.130	158.266	25.500	115.207
4800	8.661	55.761	40.020	158.266	22.692	118.999
4900	8.661	55.761	40.910	158.266	19.884	122.797
5000	8.661	55.761	41.800	158.266	17.076	126.595
5100	8.661	55.761	42.690	158.266	14.268	130.393
5200	8.661	55.761	43.580	158.266	11.460	134.191
5300	8.661	55.761	44.470	158.266	8.652	137.989
5400	8.661	55.761	45.360	158.266	5.844	141.787
5500	8.661	55.761	46.250	158.266	3.036	145.585
5600	8.661	55.761	47.140	158.266	0.228	149.383
5700	8.661	55.761	48.030	158.266	-2.580	153.181
5800	8.661	55.761	48.920	158.266	-5.372	156.979
5900	8.661	55.761	49.810	158.266	-8.164	160.777
6000	8.661	55.761	50.700	158.266	-10.956	164.575

June 30, 1968

(IDEAL GAS)

MAGNESIUM MONOCHLORIDE UNIPOSITIVE ION (MgCl⁺)Ground State Configuration {1²}ΔH_f^o = 156 ± 20 kcal/mol

GFW = 59.76445

S_{298.15} = {54.6 ± 2} gibbs/molΔH_f^o_{298.15} = 156 ± 20 kcal/mol

Electronic Levels and Quantum Weights

State	$\epsilon_i, \text{cm}^{-1}$	g_i
1 _g ⁺	0	1
3 _u ⁻	{9000}	6
1 _u ⁻	{11000}	2
3 _g ⁻	{20000}	3
1 _g ⁺	{25000}	2
1 _u ⁻	{30000}	1

 $\omega_e x_e = \{2\} \text{ cm}^{-1}$ $\omega_e = \{400\} \text{ cm}^{-1}$ $B_e = \{0.2415\} \text{ cm}^{-1}$ $\alpha_e = \{0.00164\} \text{ cm}^{-1}$ $r_e = \{2.2\} \text{ \AA}$ $\sigma = 1$

Heat of Formation
The ionization potential of MgCl(g) was reported to be 7.2, 7.5 ± 0.5, and 7 ± 1 eV by Krasnov (1), Hildenbrand (2), and Beckett (2), respectively. The corresponding heats of formation at 298°K for MgCl (g) are derived as 156, 163, and 151 kcal/mol, using ΔH_f^o(MgCl, g) = -10.34 kcal/mol from the JANAF MgCl(g) table (March 31, 1966). The value of ΔH_f^o for MgCl⁺(g) is tentatively selected as 156 ± 20 kcal/mol.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as NaCl(g) which is isoelectronic with MgCl⁺(g). The six electronic states are obtained from Fougere (3). The corresponding electronic levels are estimated by comparison with the isoelectronic molecules BeS (4), BeO (5, 6), and MgO (5, 7). The bond distance is estimated by the method suggested by Krasnov (8). The values of ω_e and $\omega_e x_e$ are estimated by comparison with those for MgCl(g) and NaCl(g). B_e and α_e are calculated by the method recommended by Herzberg (5). The moment of inertia is 1.159 × 10⁻³⁸ g cm². The enthalpy at 0°K is -2.27 kcal/mol.

References

1. K. S. Krasnov, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR 3, 927 (1965).
2. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
3. P. F. Fougere and R. K. Neel, J. Chem. Phys. 44, 285 (1965).
4. G. Verhaegen and W. G. Richards, Proc. Phys. Soc. (London) 90, 979 (1967).
5. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1980.
6. G. Verhaegen and W. G. Richards, J. Chem. Phys. 45, 1428 (1966).
7. L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).
8. K. S. Krasnov, Zh. Strukt. Khim. 1, 209 (1960).
9. D. L. Hildenbrand, McDonnell Douglas Corporation, private communication, July 24, 1968.

Nitrosyl Chloride (NOCl)

(Ideal Gas) Mol. Wt. = 65.4591

T, °K.	C _p ^o	cal. mole ⁻¹ deg ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.009	INFINITE	-	2.713	12.828	12.828	INFINITE	INFINITE
100	8.267	52.217	71.347	-1.913	13.598	13.598	-29.716	-29.716
200	9.731	58.445	67.995	-1.978	11.529	11.529	-15.055	-15.055
298	10.680	62.527	-0.000	-	15.800	15.800	-11.581	-11.581
300	10.694	62.593	62.527	-0.020	15.821	15.821	-11.525	-11.525
400	11.750	68.334	65.781	2.277	12.369	12.369	-7.925	-7.925
500	12.956	72.427	65.693	4.714	12.441	12.441	-7.023	-7.023
600	14.035	75.122	65.122	7.211	13.303	13.303	-3.953	-3.953
700	14.957	77.033	64.438	8.595	13.585	13.585	-3.179	-3.179
800	15.766	78.306	69.278	9.931	12.703	12.703	-4.953	-4.953
900	16.483	79.483	70.080	11.283	12.781	12.781	-4.742	-4.742
1000	17.120	80.578	70.846	12.649	12.862	12.862	-4.562	-4.562
1100	17.688	81.597	71.576	14.033	12.946	12.946	-4.417	-4.417
1200	18.186	82.557	72.278	15.417	13.033	13.033	-4.272	-4.272
1300	18.616	83.459	72.949	16.816	13.121	13.121	-4.153	-4.153
1400	19.000	84.313	73.593	18.224	13.212	13.212	-4.047	-4.047
1500	19.346	85.122	74.211	19.640	13.303	13.303	-3.953	-3.953
1600	19.659	85.895	74.806	21.063	13.396	13.396	-3.868	-3.868
1700	19.944	86.625	75.379	22.493	13.490	13.490	-3.790	-3.790
1800	20.200	87.326	75.931	23.929	13.585	13.585	-3.719	-3.719
1900	20.436	87.997	76.464	25.372	13.680	13.680	-3.655	-3.655
2000	20.651	88.631	76.980	26.821	13.777	13.777	-3.596	-3.596
2100	20.846	89.234	77.476	28.276	13.874	13.874	-3.541	-3.541
2200	21.022	89.806	77.942	29.735	13.970	13.970	-3.490	-3.490
2300	21.180	90.349	78.379	31.200	14.068	14.068	-3.439	-3.439
2400	21.321	90.865	78.785	32.670	14.166	14.166	-3.399	-3.399
2500	21.447	91.356	79.164	34.144	14.263	14.263	-3.368	-3.368
2600	21.560	91.824	79.526	35.621	14.359	14.359	-3.337	-3.337
2700	21.660	92.264	79.766	37.108	14.458	14.458	-3.306	-3.306
2800	21.748	92.684	80.174	38.597	14.556	14.556	-3.274	-3.274
2900	21.824	93.082	80.581	40.090	14.653	14.653	-3.241	-3.241
3000	21.889	93.457	81.164	41.588	14.751	14.751	-3.187	-3.187
3100	21.944	93.809	81.736	43.090	14.848	14.848	-3.133	-3.133
3200	21.989	94.132	82.297	44.597	14.947	14.947	-3.130	-3.130
3300	22.024	94.432	82.841	46.107	15.044	15.044	-3.105	-3.105
3400	22.050	94.708	83.166	47.622	15.143	15.143	-3.080	-3.080
3500	22.068	94.968	83.471	49.141	15.243	15.243	-3.056	-3.056
3600	22.078	95.204	83.756	50.663	15.343	15.343	-3.032	-3.032
3700	22.080	95.418	84.022	52.191	15.443	15.443	-3.012	-3.012
3800	22.074	95.612	84.276	53.722	15.543	15.543	-2.991	-2.991
3900	22.061	95.788	84.517	55.257	15.648	15.648	-2.972	-2.972
4000	22.041	95.946	84.782	56.796	15.752	15.752	-2.953	-2.953
4100	22.014	96.086	85.033	58.338	15.856	15.856	-2.937	-2.937
4200	21.981	96.208	85.267	59.887	15.964	15.964	-2.917	-2.917
4300	21.941	96.312	85.486	61.438	16.074	16.074	-2.894	-2.894
4400	21.895	96.400	85.695	62.993	16.184	16.184	-2.868	-2.868
4500	21.844	96.474	85.886	64.542	16.297	16.297	-2.843	-2.843
4600	21.788	96.535	86.061	66.089	16.407	16.407	-2.818	-2.818
4700	21.727	96.583	86.229	67.631	16.517	16.517	-2.793	-2.793
4800	21.661	96.618	86.376	69.168	16.629	16.629	-2.768	-2.768
4900	21.590	96.641	86.509	70.700	16.734	16.734	-2.743	-2.743
5000	21.514	96.653	86.629	72.227	16.840	16.840	-2.718	-2.718
5100	21.434	96.653	86.736	73.750	16.947	16.947	-2.693	-2.693
5200	21.350	96.641	86.831	75.269	17.054	17.054	-2.668	-2.668
5300	21.261	96.618	86.914	76.783	17.161	17.161	-2.643	-2.643
5400	21.168	96.583	86.986	78.292	17.268	17.268	-2.618	-2.618
5500	21.071	96.535	87.046	79.796	17.374	17.374	-2.593	-2.593
5600	20.970	96.474	87.094	81.295	17.481	17.481	-2.568	-2.568
5700	20.865	96.400	87.131	82.789	17.588	17.588	-2.543	-2.543
5800	20.757	96.312	87.157	84.276	17.694	17.694	-2.518	-2.518
5900	20.646	96.208	87.172	85.756	17.800	17.800	-2.493	-2.493
6000	20.531	96.086	87.176	87.227	17.906	17.906	-2.468	-2.468

June 30, 1961 Dec. 31, 1965

CINO

MOL. WT. = 65.4591

(IDEAL GAS)

NITROSYL CHLORIDE (NOCl)

Point Group C_∞

S_{298.15} = 82.53 cal. deg⁻¹ mole⁻¹

ΔH_f^o = 12.83 ± 0.2 kcal. mole⁻¹

ΔH_f^o 298.15 = 12.37 ± 0.2 kcal. mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies & Degeneracies

ω, cm⁻¹

1800 (1)

594.9 (1)

331.5 (1)

Bond Distance: N-Cl = 1.95 ± 0.06 Å

N-O = 1.17 ± 0.06 Å

Bond Angle: Cl-N-O = 114 ± 3°

Product of the Moments of Inertia: I_AI_BI_C = 2.278778 X 10⁻¹¹⁵ g.³ cm.⁶

σ = 1

Heat of Formation.

The equilibrium constants for the reaction 2NOCl(g) = 2NO(g) + Cl₂(g) have been measured in the temperature range from 372° to 491°K. by C. M. Beeson and D. M. Yost, J. Chem. Phys. **2**, 44 (1936). Using the reported equilibrium constants, the heat of reaction (ΔH_r^o 298) has been calculated by both the second and the third law methods, as 18.33 ± 0.1 kcal. mole⁻¹ and 18.42 ± 0.1 kcal. mole⁻¹, respectively. The third law value is adopted to calculate the heat of formation of nitrosyl chloride (g) as ΔH_f^o 298 = 12.37 ± 0.2 kcal. mole⁻¹.

Heat Capacity and Entropy.

The selected bond distances and angle were obtained from the microwave measurements by J. D. Rogers and D. Williams, J. Chem. Phys. **34**, 2195 (1961). J. A. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. **59**, 2629 (1937), reported the bond distance N-Cl = 1.95 Å and the angle O-N-Cl = 116° by the electron diffraction method. These two are in good agreement. The three principal moments of inertia are I_A = 0.995 X 10⁻⁵⁹, I_B = 14.685 X 10⁻⁵⁹ and I_C = 15.678 X 10⁻⁵⁹ g. cm². The selected vibrational frequencies which were obtained from the infrared spectrum by L. Landau and W. H. Fletcher, J. Mol. Spectry. **4**, 276 (1960), have been modified to natural isotopic mixture. W. G. Burns and J. J. Bernatkin, J. Chem. Phys. **18**, 1669 (1950), reported the vibrational frequencies as 1799, 592 and 332 cm⁻¹.

J. S. Gordon, J. Chem. Eng. Data **7**, 82 (1962), has calculated the thermodynamic functions from 298.15° to 6000°K. by the method of R. E. Fennington and K. A. Kobe, J. Chem. Phys. **22**, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from Landau and Fletcher, loc. cit., and J. D. Rogers, W. J. Pietenpol and D. Williams, Phys. Rev. **83**, 431 (1951). These calculated functions have been adopted in the tabulation. Below 298°K. the rigid-rotator harmonic oscillator method was used to calculate the functions.

CINO

NITRYL CHLORIDE (NO₂Cl)

(IDEAL GAS)

MOL. WT. = 81.4585

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	-0.00	0.00	INFINITE	2.916	4.192	4.192	INFINITE	
100	8.441	53.818	74.938	2.112	3.980	6.525	1.1261	
200	10.744	60.355	66.113	1.156	3.154	9.644	10.538	
298	12.712	65.030	65.030	0.000	2.900	12.889	9.447	
300	12.744	65.108	65.030	0.024	2.897	12.951	9.434	
400	14.444	70.377	67.777	2.483	2.752	19.716	8.617	
500	15.408	72.332	68.577	2.863	2.794	23.106	8.416	
600	16.291	75.193	67.777	4.450	2.877	26.485	8.269	
700	17.066	77.577	69.023	6.114	2.988	29.849	8.154	
800	17.485	80.058	70.261	7.838	3.114	33.197	8.054	
900	17.815	82.411	71.467	9.581	3.263	36.534	7.984	
1000	18.200	84.043	72.931	11.412	3.416	39.853	7.918	
1100	18.448	85.790	73.749	13.245	3.571	43.159	7.860	
1200	18.668	87.404	74.820	15.100	3.731	46.452	7.809	
1300	18.809	88.903	75.847	16.973	3.894	49.735	7.761	
1400	18.941	90.311	76.821	18.867	4.061	53.000	7.712	
1500	19.052	91.613	77.772	20.761	4.214	56.259	7.664	
1600	19.144	92.845	78.676	22.671	4.375	59.508	7.650	
1700	19.222	94.008	79.544	24.589	4.531	62.745	7.618	
1800	19.288	95.109	80.378	26.515	4.686	65.969	7.585	
1900	19.344	96.147	81.165	28.454	4.836	69.197	7.561	
2000	19.394	97.147	81.985	30.383	4.984	72.412	7.536	
2100	19.436	98.094	82.701	32.325	5.125	75.619	7.512	
2200	19.474	98.999	83.422	34.270	5.265	78.817	7.489	
2300	19.506	99.865	84.118	36.219	5.406	82.005	7.467	
2400	19.534	100.694	84.782	38.172	5.546	85.197	7.448	
2500	19.561	101.494	85.444	40.126	5.686	88.390	7.429	
2600	19.584	102.262	86.076	42.084	5.826	91.571	7.412	
2700	19.604	103.001	86.689	44.043	5.966	94.745	7.395	
2800	19.622	103.715	87.284	46.004	6.106	97.914	7.378	
2900	19.638	104.404	87.868	47.967	6.246	101.086	7.364	
3000	19.654	105.070	88.426	49.932	6.386	104.253	7.349	
3100	19.668	105.714	88.973	51.898	6.526	107.412	7.336	
3200	19.680	106.339	89.506	53.866	6.666	110.570	7.322	
3300	19.691	106.945	90.025	55.834	6.806	113.728	7.309	
3400	19.700	107.534	90.534	57.804	6.946	116.880	7.298	
3500	19.711	108.104	91.025	59.774	7.086	120.037	7.287	
3600	19.720	108.659	91.508	61.746	7.226	123.185	7.276	
3700	19.728	109.200	91.978	63.718	7.366	126.335	7.266	
3800	19.735	109.726	92.439	65.692	7.506	129.483	7.256	
3900	19.741	110.241	92.894	67.666	7.646	132.628	7.246	
4000	19.748	110.738	93.339	69.640	7.786	135.772	7.237	
4100	19.754	111.226	93.759	71.615	7.926	138.914	7.228	
4200	19.760	111.702	94.181	73.591	8.066	142.050	7.219	
4300	19.765	112.167	94.596	75.567	8.206	145.186	7.210	
4400	19.770	112.622	95.006	77.544	8.346	148.321	7.204	
4500	19.774	113.066	95.395	79.521	8.486	151.462	7.197	
4600	19.778	113.501	95.784	81.499	8.626	154.602	7.190	
4700	19.782	113.926	96.165	83.477	8.766	157.743	7.183	
4800	19.786	114.344	96.546	85.455	8.906	160.883	7.176	
4900	19.789	114.753	96.921	87.435	9.046	164.029	7.169	
5000	19.793	115.151	97.298	89.413	9.186	167.174	7.164	
5100	19.796	115.562	97.622	91.392	9.326	170.306	7.157	
5200	19.799	115.957	97.971	93.372	9.466	173.449	7.152	
5300	19.802	116.344	98.313	95.352	9.606	176.592	7.147	
5400	19.804	116.724	98.644	97.332	9.746	179.718	7.141	
5500	19.807	117.038	98.981	99.313	9.886	182.848	7.136	
5600	19.809	117.395	99.306	101.294	10.026	185.985	7.131	
5700	19.811	117.745	99.627	103.275	10.166	189.125	7.126	
5800	19.813	118.090	99.942	105.256	10.306	192.267	7.121	
5900	19.815	118.431	100.258	107.237	10.446	195.402	7.117	
6000	19.817	118.762	100.558	109.219	10.586	198.532	7.117	

Dec. 31, 1962; Dec. 31, 1965

Point Group C_{2v}

$$\Delta H_f^0 = 4.20 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 2.90 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 65.0 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
1293 (1)	1885 (1)
411 (1)	794 (1)
367 (1)	851 (1)

Bond Distances: N-Cl = 1.83 Å

Bond Angle: O-N-O = 129.5°

Product of Moments of Inertia: I_AI_BI_C = 2.36698 X 10⁻¹¹⁴ g.³ cm.⁶

σ = 2

Heat of Formation.

The selected heat of formation was obtained from the recalculation of the heat of reaction ClNO₂ + NO = ClNO + NO₂ which has been measured calorimetrically as -9.27 kcal. mole⁻¹ by J. Ray and R. Ogg, Jr., J. Chem. Phys. 31, 168 (1959). Not only the thermal effects of 2NO₂ = N₂O₄ but also NO + NO₂ = N₂O₃ (a minor one) have been considered in calculation. Using all JANAP auxiliary data for ClNO, NO, NO₂, N₂O₃ and N₂O₄, the recalculation gives ΔH_f²⁹⁸ = 2.90 ± 0.4 kcal. mole⁻¹ for NO₂Cl(g). For the reaction ClNO + N₂O₅ = ClNO₂ + 2NO₂ also measured by Ray and Ogg, loc. cit., the recalculation gives ΔH_f²⁹⁸ (NO₂Cl, g) = 2.56 ± 0.4 kcal. mole⁻¹.

H. Martin and E. Koshlein, Z. physik. Chem. 17, 375 (1958), have determined kinetically the heat of reaction, ΔH_f^{273.15} = 3.10 kcal. mole⁻¹, for the reaction NO₂ + NOCl = NO + NO₂Cl which gives ΔH_f²⁹⁸ = 1.90 ± 1 kcal. mole⁻¹ for NO₂Cl(g). H. Cordas and H. Johnston, J. Am. Chem. Soc., 76, 4284 (1954), have also determined kinetically the ΔH_f⁰ = 29.5 kcal. mole⁻¹ for the reaction NO₂Cl = NO₂ + Cl which gives ΔH_f²⁹⁸ = 6.3 ± 0.3 kcal. mole⁻¹.

Heat Capacity and Entropy.

The selected bond distances and bond angles were obtained from microwave spectrum studies by L. Clayton, Q. Williams and T. L. Weatherly, J. Chem. Phys. 30, 1328 (1959). D. J. Millen and K. M. Simmott, J. Chem. Soc. 350 (1958), reported bond distance N-Cl = 1.840 Å, N-O = 1.202 Å and angle ONO = 130° 35' from the microwave measurement. These two are in good agreement.

The selected vibrational frequencies were obtained from infrared and Raman spectrum measurements by R. Ryerson and M. K. Wilson, J. Chem. Phys. 22, 2000 (1954). However, the assignment of the fundamental frequencies has been revised by R. E. Dodd, J. A. Rolfe and L. A. Woodward, Trans. Faraday Soc. 52, 145 (1956), and Y. Morino and T. Tanaka, J. Mol. Spectry. 15, 179 (1965). Morino and Tanaka's assignment was adopted. The three principal moments of inertia are I_A = 6.3558 X 10⁻³⁹, I_B = 16.3609 X 10⁻³⁹ and I_C = 22.7267 X 10⁻³⁹ g.² cm.²

Sodium Chloride (NaCl)

CINa

(Crystal) Mol. Wt. = 58.448

SODIUM CHLORIDE (NaCl)

(CRYSTAL)

MOL. WT. = 58.448

T. °K.	C _p	S°	(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	8.000	4.000	INFINITE	-2.536	-98.158	-98.158	INFINITE
100	8.349	5.670	27.281	-2.161	-98.454	-96.192	210.218
200	11.203	12.573	18.319	-1.449	-98.389	-93.943	102.051
298	12.072	17.236	17.236	0.000	-98.260	-91.788	67.279
300	12.080	17.311	17.236	0.022	-98.257	-91.748	66.835
400	12.512	20.848	17.716	1.253	-98.786	-89.546	48.023
500	12.892	23.681	18.635	2.523	-98.683	-87.246	38.133
600	13.259	26.064	19.679	3.691	-98.531	-84.972	30.950
700	13.672	28.138	20.743	5.577	-98.334	-80.516	21.999
800	14.039	30.000	21.819	7.868	-97.970	-74.864	15.022
900	14.787	31.659	22.793	8.015	-97.764	-78.339	10.022
1000	15.503	33.293	23.764	9.529	-97.388	-76.200	16.653
1100	16.330	34.809	24.700	11.120	-96.941	-74.104	14.722
1200	17.200	36.268	25.604	12.597	-96.524	-71.967	11.967
1300	18.000	37.680	26.480	14.577	-96.131	-69.831	11.967
1400	18.530	39.029	27.327	16.382	-95.766	-67.714	9.946
1500	18.940	40.322	28.151	18.257	-95.431	-65.620	8.723

$$\Delta H_f^0 = -98.16 \pm 0.08 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -98.26 \pm 0.08 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 6.73 \pm 0.04 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 17.24 \pm 0.05 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1073.8 \pm 1.0^\circ \text{K.}$$

Heat of Formation.

The heat of formation is based on $\Delta H_f^{298.15} = -57.39$ and $-39.95 \text{ kcal. mole}^{-1}$ for $\text{Na}^+(\infty \text{H}_2\text{O})$ and $\text{Cl}^-(\infty \text{H}_2\text{O})$, respectively, and on the heat of solution $\Delta H_{\text{sol}}^{298.15} = 0.922 \text{ kcal. mole}^{-1}$ for NaCl. These values were reported in a private communication from D. D. Wagman, National Bureau of Standards, June, 1964.

Heat Capacity and Entropy.

The low temperature values are based on the heat capacities (3-266°K) reported by T. H. K. Barron, A. J. Leadbetter, J. A. Morrison, Proc. Roy. Soc. (London) A279 (1376), 62 (1964). The earlier work of K. Clausius, J. Goldman, A. Parlick, Z. Naturforsch. 4b, 424 (1949), results in a slightly higher entropy ($S_{298.15}^0 = 17.33 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$) but a lower heat capacity at room temperature ($C_p^{298.15} = 11.9 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$). The high temperature values have been obtained by reanalysis of the enthalpies (672 - 1279°K) of R. Dawson, E. B. Brackett, T. E. Brackett, J. Phys. Chem. 67, 1669 (1963), using the new value for $C_p^{298.15}$. The resulting tables agree within $\pm 0.1 \text{ kcal.}$ with the enthalpies (812 - 1058°K) of W. A. Roth, W. Bertram, Z. Elektrochem. 35, 38 (1929). The enthalpies (540 - 1037°K) of A. Magnus, Physik. Zeitschr. 14, 5 (1913), agree well at the lower temperatures but are about 0.3 kcal. smaller near the melting point.

Melting Data.

The melting temperature was taken from Dawson, Brackett and Brackett, loc. cit., and the heat of melting was obtained by reanalysis of their crystal and liquid enthalpies. Values of $T_m = 1073^\circ \text{K.}$ and $\Delta H_m^0 = 6.69 \pm 0.06 \text{ kcal. mole}^{-1}$ were reported by A. S. Dworkin, M. A. Bredig, J. Phys. Chem. 64, 269 (1960).

Heat of Sublimation.

The vapor in equilibrium with NaCl contains both monomeric and polymeric forms (for details see the tables for NaCl gases).

CINa

Sodium Chloride (NaCl)

CINa

(Liquid) Mol. Wt. = 58.448

SODIUM CHLORIDE (NaCl)

(LIQUID)

MOL. WT. = 58.448

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0								
100								
200								
298	12.072	22.719	22.719		0.000	- 92.237	- 87.400	64.063
300	12.080	22.704	22.719	0.022	- 0.234	- 92.234	- 87.370	63.646
400	12.512	26.331	23.199	1.253	- 92.763	- 92.763	- 85.716	46.831
500	12.892	29.164	24.118	2.523	- 92.660	- 92.660	- 83.064	36.699
600	13.259	31.947	25.162	3.831	- 92.508	- 92.508	- 82.239	29.954
700	13.522	33.571	25.728	5.177	- 92.405	- 92.405	- 81.429	25.116
800	13.740	34.971	26.068	6.568	- 92.053	- 92.053	- 79.879	21.548
900	13.920	36.009	26.501	8.377	- 91.379	- 91.379	- 77.273	18.763
1000	14.070	36.667	26.827	10.140	- 90.754	- 90.754	- 75.740	16.552
1100	14.190	37.000	27.050	11.863	- 90.195	- 90.195	- 74.268	14.755
1200	14.290	37.150	27.183	13.457	- 89.693	- 89.693	- 72.850	12.803
1300	14.370	37.220	27.230	14.932	- 89.240	- 89.240	- 71.480	10.861
1400	14.430	37.260	27.280	16.324	- 88.834	- 88.834	- 70.154	9.103
1500	14.480	37.280	27.300	17.652	- 88.464	- 88.464	- 68.870	7.596
1600	14.520	37.290	27.310	18.925	- 88.129	- 88.129	- 67.624	6.291
1700	14.550	37.290	27.310	20.150	- 87.828	- 87.828	- 66.414	5.155
1800	14.570	37.280	27.300	21.325	- 87.550	- 87.550	- 65.236	4.077
1900	14.580	37.260	27.280	22.450	- 87.294	- 87.294	- 64.090	3.053
2000	14.580	37.230	27.250	23.525	- 87.060	- 87.060	- 62.974	2.076
2100	14.570	37.190	27.200	24.550	- 86.846	- 86.846	- 61.886	1.146
2200	14.550	37.140	27.140	25.525	- 86.652	- 86.652	- 60.824	0.260
2300	14.520	37.080	27.070	26.450	- 86.478	- 86.478	- 59.786	- 0.582
2400	14.480	37.000	26.990	27.325	- 86.324	- 86.324	- 58.772	- 1.407
2500	14.430	36.900	26.890	28.150	- 86.190	- 86.190	- 57.782	- 2.184

$$S_{298.15}^{\circ} = [22.719] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_{f, 298.15}^{\circ} = [-92.237] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 6.73 \pm 0.04 \text{ kcal. mole}^{-1}$$

$$T_m = 1073.8 \pm 1.0^{\circ}\text{K.}$$

Heat of Formation.

$\Delta H_f^{\circ}(1)$ was obtained from $\Delta H_f^{\circ}(c)$ by addition of ΔH_m° and the difference between ($H_{1073.8}^{\circ} - H_{298.15}^{\circ}$) for the crystal and liquid.

Heat Capacity and Entropy.

These were obtained by analysis of the enthalpies (1076 - 1279°K) of R. Dawson, E. B. Brackett, T. E. Brackett, J. Phys. Chem. 67, 1669 (1963). The heat capacity was extrapolated to a constant value of 16.0 at the higher temperatures. A glass transition was assumed at 800°K. and below this temperature C_p° was taken equal to that of the crystal.

Melting Data.

The melting temperature was taken from Dawson, Brackett and Brackett, loc. cit., and the heat of melting was obtained by reanalysis of their crystal and liquid enthalpies. Values of $T_m = 1073^{\circ}\text{K.}$ and $\Delta H_m^{\circ} = 6.69 \pm 0.06 \text{ kcal. mole}^{-1}$ were reported by A. S. Dworkin, M. A. Bredig, J. Phys. Chem. 64, 269 (1960).

Heat of Sublimation.

The vapor in equilibrium with NaCl contains both monomeric and polymeric forms (for details see the tables for NaCl gases).

CINa

(Ideal Gas) Mol. Wt. = 58.448

T, °K.	C _p (cal. mole ⁻¹ deg. ⁻¹)	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ /T	ΔH _f ⁰ (kcal. mole ⁻¹)	ΔF _f ⁰	Log K _p
0	∞	∞	∞	-43.020	-43.020	INFINITE
100	7.258	46.153	2.298	-43.020	-43.020	97.859
200	7.258	46.153	1.827	-43.020	-43.020	97.859
298.15	8.553	54.657	0.000	-43.364	-48.117	35.269
300	8.558	54.657	0.016	-43.364	-48.117	35.269
400	8.769	57.441	0.882	-44.256	-49.653	27.128
500	8.854	59.406	1.763	-44.543	-50.969	22.277
600	8.921	61.026	2.652	-44.810	-52.228	19.023
700	8.969	62.405	3.546	-45.060	-53.446	16.686
800	9.006	63.605	4.445	-45.299	-54.627	14.923
900	9.037	64.668	5.347	-45.532	-55.779	13.544
1000	9.064	65.622	6.252	-45.764	-56.906	12.436
1100	9.088	66.487	7.160	-46.001	-58.010	11.525
1200	9.110	67.278	8.070	-46.248	-59.092	10.678
1300	9.131	68.008	8.982	-46.517	-60.157	9.704
1400	9.152	68.686	9.896	-46.792	-61.209	8.869
1500	9.171	69.318	10.812	-47.076	-62.243	8.165
1600	9.189	69.910	11.730	-47.361	-63.259	7.512
1700	9.209	70.468	12.650	-47.649	-64.259	6.922
1800	9.227	70.995	13.572	-47.940	-65.243	6.455
1900	9.245	71.494	14.506	-48.234	-66.211	6.009
2000	9.263	71.969	15.421	-48.531	-67.166	5.608
2100	9.280	72.421	16.348	-48.831	-68.104	5.245
2200	9.298	72.853	17.277	-49.134	-69.026	4.915
2300	9.315	73.267	18.208	-49.440	-69.932	4.614
2400	9.332	73.664	19.140	-49.749	-70.822	4.337
2500	9.349	74.045	20.074	-50.061	-71.696	4.081
2600	9.367	74.412	21.010	-50.376	-72.555	3.848
2700	9.384	74.766	21.948	-50.694	-73.400	3.630
2800	9.401	75.108	22.887	-51.015	-74.232	3.428
2900	9.418	75.438	23.827	-51.339	-75.052	3.240
3000	9.435	75.757	24.770	-51.666	-75.859	3.064
3100	9.451	76.067	25.715	-51.997	-76.653	2.899
3200	9.468	76.367	26.661	-52.331	-77.434	2.745
3300	9.485	76.659	27.608	-52.668	-78.202	2.600
3400	9.502	76.942	28.558	-53.008	-78.957	2.463
3500	9.519	77.218	29.509	-53.351	-79.700	2.334
3600	9.536	77.486	30.463	-53.696	-80.431	2.212
3700	9.552	77.748	31.419	-54.044	-81.150	2.097
3800	9.569	78.003	32.377	-54.394	-81.857	1.987
3900	9.586	78.252	33.336	-54.746	-82.552	1.884
4000	9.602	78.495	34.296	-55.099	-83.236	1.785
4100	9.619	78.732	35.250	-55.454	-83.909	1.691
4200	9.636	78.964	36.213	-55.810	-84.572	1.601
4300	9.653	79.191	37.177	-56.168	-85.226	1.515
4400	9.669	79.413	38.143	-56.527	-85.871	1.433
4500	9.686	79.630	39.111	-56.887	-86.507	1.355
4600	9.703	79.843	40.080	-57.248	-87.134	1.280
4700	9.719	80.052	41.052	-57.610	-87.752	1.209
4800	9.736	80.257	42.027	-57.974	-88.361	1.139
4900	9.752	80.458	42.999	-58.339	-88.961	1.072
5000	9.769	80.655	43.975	-58.706	-89.552	1.008
5100	9.786	80.849	44.945	-59.074	-90.135	0.946
5200	9.803	81.039	45.912	-59.444	-90.710	0.889
5300	9.819	81.226	46.875	-59.815	-91.277	0.835
5400	9.836	81.410	47.836	-60.187	-91.836	0.773
5500	9.852	81.590	48.793	-60.560	-92.387	0.719
5600	9.869	81.768	49.846	-60.934	-92.931	0.667
5700	9.885	81.943	50.894	-61.309	-93.468	0.617
5800	9.902	82.115	51.937	-61.685	-93.998	0.567
5900	9.919	82.284	52.974	-62.062	-94.521	0.519
6000	9.935	82.451	53.980	-62.440	-95.037	0.473

Heat of Formation.

The heat of formation is based on a heat of sublimation ΔH_g^0 298.15 = 54.9 kcal. mole⁻¹ obtained from the more consistent sets of vapor pressure data by correction for the presence of dimer. Observed vapor pressures were converted to monomer pressures by use of dimer-monomer ratios calculated from JANAF free energy functions and ΔH_f^0 298.15 = 48.6 kcal. for the reaction $(NaCl)_2(g) \rightarrow 2NaCl(g)$. Higher polymeric species were neglected. Analyses of the resulting monomer pressures are summarized below.

Source	Temperature Range (°K)	Heat of Sublimation ΔH_g^0 298.15 (kcal. mole ⁻¹)
Neameyanov & Sazonov(1)	743 - 948*	54.35
Zimm & Mayer(2)	760 - 897*	55.15
Mayer & Mintner(3)	890 - 944*	49.6
Mine(4)	893 - 973*	55.37
Barton & Bloom(5)	1340 - 1540**	52.6
Flock & Rodebush(6)	1250 - 1428**	56.87
Wartenberg & Albrecht(7)	1429 - 1720**	58.65
Ruff & Mugdan(8)	1433 - 1723**	60.0
*Knudsen effusion measurements over crystal		54.45
**total pressures over liquid		54.44

Heat Capacity and Entropy.

The molecular constants are based on molecular beam studies of the rotational spectra by Clouser and Gordy, Bull. Am. Phys. Soc. B, 328 (1963) and on microwave studies by Honig, Mandel, Stinch and Townes, Phys. Rev. 96, 629 (1954).

The infrared spectra of Rice and Kempner, J. Chem. Phys. 21, 573 (1957) give a frequency in close agreement (368 cm.⁻¹).

Sodium Perchlorate (NaClO₄)
(Crystal) Mol. Wt. = 122.448



MOL. WT. = 122.448

(CRYSTAL)

SODIUM PERCHLORATE (NaClO₄)



June 30, 1963

T, °K.	C _p	$\int_0^T C_p dT$	$\int_0^T C_p dT / T$	$H^0 - H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K _f
0							
100	26.600	34.000	0.000	-91.480	-60.785		44.555
200	26.700	34.165	0.049	-91.476	-60.505		44.141
300	32.500	42.622	3.5115	-91.704	-50.300		27.482
400	35.000	50.258	37.395	-90.905	-40.034		17.498
500	38.300	62.774	40.267	13.487	-86.515	-30.065	10.951
600	40.267	68.959	43.958	17.417	-85.285	-20.752	6.479
700	41.848	74.848	47.486	21.403	-84.063	-11.440	3.861
800	43.400	79.350	50.480	25.803	-82.396	-2.681	1.651
900	44.700	83.991	53.782	30.209	-80.782	6.092	1.231
1000	45.900	88.309	56.727	34.740	-79.073	14.604	2.019
1100	47.000	92.350	59.559	34.386	-100.513	23.598	4.798
1200	48.000	96.150	62.320	34.040	-108.442	32.590	7.828
1300	49.000	99.753	64.756	48.996	-96.242	43.950	6.861
1400	50.000	103.170	67.204	53.949	-93.981	53.886	7.851

$\Delta H_f^0 =$ Unknown
 $\Delta H_f^0 298.15 = -91.48 \pm 0.22 \text{ kcal. mole}^{-1}$
 $\Delta H_c^0 = [3.34] \text{ kcal. mole}^{-1}$
 $T_c = 581^\circ\text{K.}$
 $T_m = 755^\circ\text{K.}$
 $\Delta H_m^0 =$ Unknown

Heat of Formation.

A. A. Gilliland and W. H. Johnson, J. Res. Natl. Bur. Std. 65A, 67 (1961) measured the heat of solution of NaClO₄(c) and gave $\Delta H_f^0 298.15 = -91.48 \pm 0.22 \text{ kcal. mole}^{-1}$ for NaClO₄(c). The heat of dilution of NaClO₄(c) was measured by C. E. Vanderveer and J. A. Sorenson, J. Phys. Chem. 67, 285 (1963). The data led to $\Delta H_f^0 298.15 = -91.484 \text{ kcal. mole}^{-1}$ which agrees very well with the data reported by A. A. Gilliland and W. H. Johnson, loc. cit. The value of $\Delta H_f^0 298.15$ was reported to be $-92.18 \text{ kcal. mole}^{-1}$ in the National Bureau of Standards Circ. 500, "Selected Values of Chemical Thermodynamic Properties," 1952, based upon the data prior to 1950. A. F. Vorob'ev, et al., Proc. Acad. Sci. USSR, 135, 1439 (1960) measured the heat of decomposition of NaClO₄(c) into NaCl(c) and O₂(g) and gave $\Delta H_f^0 298.15 = -90.68 \pm 0.3 \text{ kcal. mole}^{-1}$ for NaClO₄(c). This value reported by A. A. Gilliland and W. H. Johnson, loc. cit. was used.

Heat Capacity and Entropy.

Heat capacities and $S_{298.15}^0$ were estimated by comparison with those for NaClO₃(c) and KClO₄(c), respectively.

Transition Data.

T_c was reported in the National Bureau of Standards, Circ. 500, loc. cit. ΔH_c^0 was estimated from that for KClO₄(c).

Temperature of Melting.

T_m was obtained from Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use," June 1949.

Chlorine Monoxide (ClO)

(Ideal Gas) Mol. Wt. = 51.457

CHLORINE MONOXIDE (ClO)

(IDEAL GAS)

MOL. WT. = 51.457

T. °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔG° _f	Log K _p
0	0.000	0.000	INFINITE	2.115	24.211	24.211	INFINITE
100	0.959	46.371	60.573	1.420	23.791	23.791	52.226
200	1.120	71.228	54.145	0.914	24.296	24.296	25.488
298	1.250	94.145	51.457	0.000	24.192	23.298	17.077
300	1.254	94.191	51.445	-0.014	24.192	23.292	16.968
400	1.242	94.419	54.446	1.799	24.197	22.992	12.562
500	0.229	95.224	55.027	1.599	24.214	22.690	9.917
600	0.429	99.743	55.689	2.432	24.236	22.383	8.153
700	0.571	61.054	3.263	24.258	22.072	21.758	6.891
800	0.676	62.205	57.024	4.145	24.279	21.442	5.944
900	0.754	63.232	57.658	5.017	24.296	21.123	5.207
1000	0.816	64.158	58.262	5.895	24.316	20.803	4.616
1100	0.865	65.000	58.837	6.780	24.333	20.482	4.133
1200	0.976	65.773	59.383	7.668	24.347	20.159	3.730
1300	0.921	66.488	59.903	8.561	24.360	19.835	3.389
1400	0.971	67.151	60.397	9.456	24.372	19.511	3.096
1500	0.998	67.771	60.868	10.355	24.382	19.186	2.843
1600	0.922	68.353	61.318	11.256	24.390	18.861	2.621
1700	0.904	68.900	61.748	12.159	24.398	18.535	2.425
1800	0.904	69.418	62.160	13.065	24.404	18.209	2.250
1900	0.903	69.909	62.555	13.972	24.407	17.882	2.094
2000	0.910	70.375	62.934	14.881	24.409	17.556	1.954
2100	0.917	70.819	63.299	15.792	24.410	17.229	1.827
2200	0.913	71.244	63.651	16.704	24.407	16.903	1.711
2300	0.916	71.650	63.990	17.619	24.404	16.578	1.606
2400	0.916	72.040	64.317	18.534	24.398	16.251	1.510
2500	0.917	72.414	64.634	19.451	24.389	15.927	1.421
2600	0.919	72.774	64.940	20.370	24.379	15.602	1.339
2700	0.920	73.122	65.237	21.290	24.366	15.278	1.263
2800	0.921	73.457	65.524	22.211	24.350	14.954	1.192
2900	0.923	73.780	65.803	23.133	24.332	14.631	1.127
3000	0.925	74.094	66.074	24.057	24.312	14.309	1.066
3100	0.928	74.397	66.339	24.982	24.289	13.986	1.009
3200	0.927	74.691	66.595	25.909	24.263	13.666	0.955
3300	0.928	74.976	66.844	26.836	24.235	13.347	0.905
3400	0.929	75.254	67.087	27.765	24.205	13.026	0.858
3500	0.930	75.523	67.325	28.696	24.173	12.710	0.813
3600	0.930	75.786	67.556	29.627	24.139	12.393	0.772
3700	0.932	76.041	67.782	30.559	24.102	12.076	0.732
3800	0.934	76.290	68.003	31.493	24.065	11.761	0.695
3900	0.935	76.533	68.218	32.424	24.025	11.447	0.659
4000	0.936	76.770	68.429	33.364	23.983	11.134	0.625
4100	0.937	77.002	68.635	34.302	23.941	10.821	0.593
4200	0.937	77.228	68.837	35.240	23.897	10.512	0.563
4300	0.940	77.449	69.035	36.180	23.852	10.202	0.534
4400	0.941	77.665	69.229	37.121	23.806	9.892	0.507
4500	0.942	77.877	69.419	38.063	23.759	9.587	0.480
4600	0.943	78.084	69.605	39.006	23.712	9.282	0.455
4700	0.944	78.287	69.787	39.950	23.664	8.974	0.432
4800	0.944	78.486	69.966	40.896	23.616	8.669	0.409
4900	0.947	78.692	70.142	41.843	23.568	8.364	0.387
5000	0.948	78.873	70.315	42.790	23.519	8.064	0.366
5100	0.949	79.061	70.485	43.739	23.471	7.761	0.346
5200	0.950	79.245	70.651	44.689	23.423	7.462	0.326
5300	0.951	79.427	70.815	45.641	23.376	7.159	0.308
5400	0.952	79.605	70.976	46.593	23.328	6.863	0.290
5500	0.954	79.780	71.135	47.546	23.281	6.563	0.273
5600	0.955	79.952	71.291	48.501	23.235	6.263	0.256
5700	0.956	80.121	71.444	49.457	23.188	5.971	0.240
5800	0.957	80.287	71.595	50.414	23.143	5.673	0.225
5900	0.958	80.451	71.744	51.372	23.098	5.380	0.210
6000	0.959	80.612	71.890	52.331	23.054	5.084	0.196

June 30, 1961

$D_0 = 63.33 \pm 0.03$ kcal. mole⁻¹
 $\Delta H_f^\circ 298.15 = 24.19 \pm 0.05$ kcal. mole⁻¹
 $S^\circ_{298.15} = 54.145$ cal. deg.⁻¹ mole⁻¹
Ground State Configuration $2\Pi_{3/2}$

Electronic Level and Multiplicity

E_i , cm. ⁻¹	g_i
0	4

$\omega_e x_e = 7.5$ cm.⁻¹
 $\omega_e = 866 \pm 26$ cm.⁻¹
 $B_e = 0.645(3)$
 $\alpha_e = [0.0069]$ cm.⁻¹
 $D_e = 2(2) \times 10^{-6}$ cm.⁻¹
 $r_e = 1.546$ Å

Heat of Formation

R. A. Durie and D. A. Ramsay, Can. J. Phys. 35, 35 (1958) and G. Herzberg and D. A. Ramsay, Disc. Faraday Soc. 9, 80 (1950) report $D_0 = 22152 \pm 10$ cm.⁻¹ and $D_0 = 22141$ cm.⁻¹ respectively, and these values have been averaged.

Heat Capacity and Entropy

The spectroscopic constants are for the natural mixture of isotopes and are based on measurements by Durie and Ramsay, loc. cit., and by G. Porter, Disc. Faraday Soc. 9, 60 (1950). α_e has been estimated by the method given by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Company, Inc., New York, 1950, p. 108.

Titanium Oxide Chloride (TiOCl)

(Ideal Gas) Mol. Wt. = 99.357

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔF° ₂₉₈	ΔH° ₂₉₈	Log K _p
0	8.750	0.000	INFINITE	2.902	57.998	- 57.998	INFINITE
100	8.756	51.462	73.018	2.156	56.092	- 56.092	128.208
200	11.049	58.318	64.084	1.153	58.248	- 58.248	64.755
298	12.346	62.992	62.992	0.000	58.380	- 58.380	43.779
300	12.345	63.049	62.992	0.023	58.382	- 58.382	43.515
400	13.170	66.744	63.982	1.303	59.493	- 59.493	32.873
500	13.671	69.742	64.449	2.647	58.590	- 60.576	26.476
600	13.993	72.266	65.547	4.031	58.690	- 60.963	22.205
700	14.208	74.440	66.666	5.442	58.802	- 61.335	19.149
800	14.357	76.259	67.759	6.871	58.925	- 61.689	16.832
900	14.479	77.800	68.831	8.324	59.058	- 62.077	14.625
1000	14.543	79.573	69.811	9.762	59.211	- 62.347	13.629
1100	14.602	80.962	70.762	11.220	59.375	- 62.654	12.448
1200	14.649	82.235	71.666	12.682	60.503	- 62.807	11.456
1300	14.715	83.499	72.525	14.149	60.697	- 63.277	9.678
1400	14.778	84.514	74.119	17.092	61.113	- 63.440	8.243
1500	14.758	86.466	74.962	18.567	61.342	- 63.586	8.695
1600	14.774	87.361	75.571	20.043	61.582	- 63.719	8.191
1700	14.800	88.206	76.000	21.501	61.830	- 63.841	7.755
1800	14.810	89.006	76.600	23.001	62.000	- 63.939	6.987
1900	14.810	89.765	77.524	24.481	66.052	- 63.275	5.531
2000	14.819	90.488	78.125	25.963	66.280	- 63.826	6.642
2100	14.826	91.178	78.702	27.445	66.513	- 63.705	6.328
2200	14.833	92.663	79.263	28.927	66.746	- 63.584	5.978
2300	14.844	93.074	80.116	31.806	67.227	- 63.275	5.531
2400	14.848	93.656	80.818	33.380	67.471	- 63.113	5.305
2500	14.852	94.217	81.304	34.865	67.719	- 62.941	5.004
2600	14.856	94.758	81.781	36.351	67.967	- 62.769	4.715
2700	14.859	95.278	82.231	37.837	68.225	- 62.567	4.453
2800	14.862	95.782	82.675	39.323	68.484	- 62.369	4.204
2900	14.865	96.269	83.105	40.809	68.746	- 62.158	4.382
3000	14.867	96.741	83.524	42.296	69.011	- 61.945	4.230
3100	14.871	97.194	83.933	43.783	69.276	- 61.732	4.078
3200	14.871	97.643	84.328	45.269	69.552	- 61.486	3.952
3300	14.873	98.074	84.715	46.757	69.827	- 61.247	3.824
3400	14.875	98.493	85.092	48.244	172.567	- 59.552	3.615
3500	14.877	98.901	85.460	49.732	172.868	- 59.447	3.332
3600	14.879	99.298	85.824	51.220	173.170	- 59.342	3.049
3700	14.881	99.684	86.189	52.707	173.421	- 59.095	2.807
3800	14.881	100.061	86.512	54.195	173.871	- 46.929	2.564
3900	14.882	100.428	86.847	55.683	174.236	- 43.749	2.332
4000	14.883	100.787	87.174	57.172	174.615	- 40.564	2.111
4100	14.884	101.139	87.500	58.660	175.000	- 37.379	1.897
4200	14.885	101.479	87.800	60.148	175.395	- 34.199	1.697
4300	14.886	101.814	88.116	61.637	175.834	- 30.943	1.503
4400	14.886	102.141	88.418	63.125	176.265	- 27.718	1.317
4500	14.887	102.461	88.713	64.614	176.708	- 24.484	1.136
4600	14.888	102.784	89.003	66.102	177.152	- 21.250	0.960
4700	14.888	103.108	89.288	67.592	177.592	- 18.016	0.791
4800	14.889	103.432	89.566	69.080	178.100	- 14.730	0.644
4900	14.890	103.777	89.840	70.569	178.583	- 11.455	0.401
5000	14.890	103.966	90.109	72.058	179.074	- 8.173	0.343
5100	14.891	104.152	90.373	73.547	179.565	- 4.901	0.281
5200	14.891	104.320	90.612	75.035	180.079	- 1.630	0.220
5300	14.892	104.501	90.887	76.526	180.592	- 1.734	0.069
5400	14.892	104.670	91.138	78.015	181.113	- 5.048	0.197
5500	14.893	104.833	91.485	79.504	181.638	- 8.373	0.321
5600	14.893	105.000	91.832	81.000	182.163	- 11.705	0.445
5700	14.893	105.167	92.179	82.493	182.705	- 15.042	0.568
5800	14.894	105.334	92.526	83.972	183.245	- 18.424	0.671
5900	14.894	105.500	92.873	85.460	183.785	- 21.806	0.774
6000	14.894	105.667	93.219	86.948	184.325	- 25.188	0.871

Sept. 30, 1963

TITANIUM OXIDE CHLORIDE (TiOCl)

(IDEAL GAS)

MOL. WT. = 99.357

Point Group [C_{∞v}]ΔF°₀ = [-59.0] kcal. mole⁻¹S°_{298.15} = [62.992] cal. deg.⁻¹ mole⁻¹ΔF°_{298.15} = [-58.4] kcal. mole⁻¹

Ground State Quantum Weight = [2]

Vibrotional Frequencies and Degeneracies

ω, cm.⁻¹

[800] (1)

[230] (2)

[490] (1)

Bond Distances: O-Ti = [1.62] Å Ti-F = [2.17] Å

Bond Angles: O-Ti-Cl = [180°] C = 1

Rotational Constant: B₀ = [0.09225] cm.⁻¹

Heat of Formation.

ΔF°₀ was estimated as -58 kcal. mole⁻¹ by J. S. Gordon, AstroSystems, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. ΔF°_{298.15} was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. Principal moments were: I_A = I_C = 30.34 X 10⁻³⁹ g. cm.²

CIOT:

CIOT:

Chlorine Dioxide (ClO₂)

(Ideal Gas) Mol. Wt. = 67.457

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	INFINITE	25,500	25,500	INFINITE	INFINITE
100	0.000	51.423	1.934	25,500	25,500	25,500	25,500
200	0.000	51.423	1.934	25,500	25,500	25,500	25,500
300	0.000	51.423	1.934	25,500	25,500	25,500	25,500
400	0.000	51.423	1.934	25,500	25,500	25,500	25,500
500	0.000	51.423	1.934	25,500	25,500	25,500	25,500
600	0.000	51.423	1.934	25,500	25,500	25,500	25,500
700	0.000	51.423	1.934	25,500	25,500	25,500	25,500
800	0.000	51.423	1.934	25,500	25,500	25,500	25,500
900	0.000	51.423	1.934	25,500	25,500	25,500	25,500
1000	0.000	51.423	1.934	25,500	25,500	25,500	25,500
1100	0.000	51.423	1.934	25,500	25,500	25,500	25,500
1200	0.000	51.423	1.934	25,500	25,500	25,500	25,500
1300	0.000	51.423	1.934	25,500	25,500	25,500	25,500
1400	0.000	51.423	1.934	25,500	25,500	25,500	25,500
1500	0.000	51.423	1.934	25,500	25,500	25,500	25,500
1600	0.000	51.423	1.934	25,500	25,500	25,500	25,500
1700	0.000	51.423	1.934	25,500	25,500	25,500	25,500
1800	0.000	51.423	1.934	25,500	25,500	25,500	25,500
1900	0.000	51.423	1.934	25,500	25,500	25,500	25,500
2000	0.000	51.423	1.934	25,500	25,500	25,500	25,500
2100	0.000	51.423	1.934	25,500	25,500	25,500	25,500
2200	0.000	51.423	1.934	25,500	25,500	25,500	25,500
2300	0.000	51.423	1.934	25,500	25,500	25,500	25,500
2400	0.000	51.423	1.934	25,500	25,500	25,500	25,500
2500	0.000	51.423	1.934	25,500	25,500	25,500	25,500
2600	0.000	51.423	1.934	25,500	25,500	25,500	25,500
2700	0.000	51.423	1.934	25,500	25,500	25,500	25,500
2800	0.000	51.423	1.934	25,500	25,500	25,500	25,500
2900	0.000	51.423	1.934	25,500	25,500	25,500	25,500
3000	0.000	51.423	1.934	25,500	25,500	25,500	25,500
3100	0.000	51.423	1.934	25,500	25,500	25,500	25,500
3200	0.000	51.423	1.934	25,500	25,500	25,500	25,500
3300	0.000	51.423	1.934	25,500	25,500	25,500	25,500
3400	0.000	51.423	1.934	25,500	25,500	25,500	25,500
3500	0.000	51.423	1.934	25,500	25,500	25,500	25,500
3600	0.000	51.423	1.934	25,500	25,500	25,500	25,500
3700	0.000	51.423	1.934	25,500	25,500	25,500	25,500
3800	0.000	51.423	1.934	25,500	25,500	25,500	25,500
3900	0.000	51.423	1.934	25,500	25,500	25,500	25,500
4000	0.000	51.423	1.934	25,500	25,500	25,500	25,500
4100	0.000	51.423	1.934	25,500	25,500	25,500	25,500
4200	0.000	51.423	1.934	25,500	25,500	25,500	25,500
4300	0.000	51.423	1.934	25,500	25,500	25,500	25,500
4400	0.000	51.423	1.934	25,500	25,500	25,500	25,500
4500	0.000	51.423	1.934	25,500	25,500	25,500	25,500
4600	0.000	51.423	1.934	25,500	25,500	25,500	25,500
4700	0.000	51.423	1.934	25,500	25,500	25,500	25,500
4800	0.000	51.423	1.934	25,500	25,500	25,500	25,500
4900	0.000	51.423	1.934	25,500	25,500	25,500	25,500
5000	0.000	51.423	1.934	25,500	25,500	25,500	25,500
5100	0.000	51.423	1.934	25,500	25,500	25,500	25,500
5200	0.000	51.423	1.934	25,500	25,500	25,500	25,500
5300	0.000	51.423	1.934	25,500	25,500	25,500	25,500
5400	0.000	51.423	1.934	25,500	25,500	25,500	25,500
5500	0.000	51.423	1.934	25,500	25,500	25,500	25,500
5600	0.000	51.423	1.934	25,500	25,500	25,500	25,500
5700	0.000	51.423	1.934	25,500	25,500	25,500	25,500
5800	0.000	51.423	1.934	25,500	25,500	25,500	25,500
5900	0.000	51.423	1.934	25,500	25,500	25,500	25,500
6000	0.000	51.423	1.934	25,500	25,500	25,500	25,500

March 31, 1961

Chlorine Dioxide (ClO₂)

(Ideal Gas)

MOL. WT. = 67.457

ΔH_f⁰ = 25.6 ± 1.5 kcal. mole⁻¹ΔH_f⁰ 298.15 = 25 ± 1.5 kcal. mole⁻¹Point Group C_{2v}S_{298.15}⁰ = 61.453 cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

(ω), cm. ⁻¹
945.3 (1)
447.4 (1)
1109 (1)

Electronic Level and Multiplicity

ε ₁ , cm. ⁻¹	ε ₂
0	2

No α₁ available.

σ = 2

Rotational constants: A₀₀₀ = 1.6005 cm.⁻¹, B₀₀₀ = 0.33283 cm.⁻¹, C₀₀₀ = 0.27553 cm.⁻¹X₁₁ = -4.4 cm.⁻¹X₃₃ = -2.0 cm.⁻¹X₂₂ = 0X₁₂ = -3.0 cm.⁻¹ε₂₂ = 0X₃₁ = -14.4 cm.⁻¹

Heat of Formation

M. H. Evans, T. R. Munson, and D. D. Wagman, J. Research Natl. Bur. Standards **55**, 147 (1955), have evaluated the available data and chosen the above value.

Heat Capacity and Entropy

J. S. Gordon, private communication, February, 1961, has calculated the thermodynamic functions from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. **22**, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from J. B. Coon and E. Ortiz, J. Molec. Spectros. **1**, 61 (1957). The functions below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	Log K _p
0	∞	INFINITE	2.231	34.727	INFINITE
100	7.066	48.446	34.983	34.542	71.117
200	7.799	53.612	35.066	34.850	32.485
298	8.298	56.859	35.000	27.625	20.249
300	8.305	56.891	35.000	27.580	20.091
400	8.566	59.310	34.896	25.121	13.745
500	8.712	61.238	34.763	22.692	9.918
600	8.801	62.835	34.603	20.292	7.391
800	8.961	64.317	34.515	17.921	5.595
900	8.937	66.433	34.788	9.830	2.387
1000	8.964	67.376	13.797	9.389	2.052
1100	8.986	68.232	13.805	8.948	1.778
1200	8.992	68.915	13.812	8.505	1.549
1300	9.000	69.498	13.818	8.062	1.344
1400	9.008	70.005	13.826	7.621	1.150
1500	9.012	70.449	13.830	7.178	1.046
1600	9.016	70.832	13.834	6.734	0.920
1800	9.021	72.184	13.839	5.291	0.509
1900	9.103	73.175	13.849	5.503	0.621
2000	9.114	73.642	13.852	4.957	0.542
2100	9.126	74.087	13.857	4.512	0.470
2200	9.138	74.518	13.860	4.070	0.404
2300	9.148	74.938	13.863	3.629	0.344
2400	9.158	75.348	13.866	3.176	0.289
2500	9.169	75.748	13.870	2.732	0.239
2600	9.179	76.142	13.872	2.285	0.192
2800	9.200	77.023	13.875	1.849	0.109
2900	9.210	77.046	13.875	1.961	0.071
3000	9.220	77.358	13.875	1.503	0.037
3100	9.230	77.661	13.874	0.958	0.004
3200	9.240	77.959	13.871	0.412	0.000
3300	9.250	78.250	13.865	0.082	0.000
3400	9.260	78.515	13.861	1.725	0.108
3500	9.270	78.783	13.856	2.171	0.132
3600	9.280	79.045	13.851	2.616	0.155
3800	9.300	79.297	13.848	3.504	0.196
3900	9.310	79.789	13.838	3.951	0.216
4000	9.319	80.025	13.831	4.384	0.234
4100	9.329	80.255	13.824	4.805	0.252
4200	9.339	80.480	13.815	5.224	0.264
4300	9.348	80.700	13.809	5.642	0.280
4400	9.358	80.915	13.799	6.057	0.294
4500	9.368	81.125	13.790	6.470	0.304
4600	9.378	81.331	13.783	6.881	0.314
4700	9.387	81.531	13.774	7.291	0.324
4800	9.396	81.731	13.765	7.698	0.334
4900	9.405	81.924	13.758	8.104	0.344
5000	9.417	82.115	13.751	8.508	0.354
5100	9.426	82.301	13.744	8.911	0.364
5200	9.436	82.484	13.738	9.314	0.374
5300	9.445	82.664	13.731	9.717	0.384
5400	9.455	82.841	13.724	10.117	0.394
5500	9.465	83.014	13.717	10.517	0.404
5600	9.474	83.185	13.710	10.917	0.414
5700	9.484	83.358	13.703	11.317	0.424
5800	9.493	83.528	13.696	11.717	0.434
5900	9.503	83.698	13.689	12.117	0.444
6000	9.513	83.840	13.682	12.517	0.454

June 30, 1963; Dec. 31, 1963

Ground State Configuration [$3\sum^-$]
 $\Delta H_f^0 = [34.7] \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 298.15 = [56.8] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 298.15 = [35.0] \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

ϵ_i' , cm. ⁻¹	g_i
0	[3]

$$\omega_e = [472] \text{ cm.}^{-1}$$

$$\omega_e x_e = [1.09] \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$B_e = [0.2443]$$

$$\alpha_e = [0.00098]$$

$$r_e = [2.04] \text{ \AA}$$

Heat of Formation.

The selected $\Delta H_f^0 298.15$ was calculated by assuming that the second and third bonds in $\text{PCl}_3(\text{g})$ are of equal strength, and that the first bond has a strength 20% greater than the other two. These assumptions were used by C. B. Henderson and R. S. Scheffer, Survey of Thermochemical Data, Atlantic Research Corporation, Alexandria, Virginia, January 1960. The selected $\Delta H_f^0 298.15$ was calculated using these bond strengths and auxiliary data from JANAP Tables.

A $\Delta H_f^0 298.15$, 40 kcal. mole⁻¹, estimated by C. J. O'Brien and J. R. Perrin, The Marquardt Corporation and J. Perrine, Olin Mathieson Chemical Corp., "Estimation of the Heats of Formation of Gaseous Combustion Product Molecules," WSC/CI Paper 59-4, October, 1959, when adjusted to the red V phosphorus reference state becomes [44.2] kcal. mole⁻¹.

A. A. Sandoval, H. C. Moser, and R. W. Kiser, J. Phys. Chem. 67, 124, (1963) have calculated a $\Delta H_f^0 298.15$ for PCl from an appearance potential. They selected the process $\text{PCl}_3 \rightarrow \text{Cl}^+ + \text{e}^- + \text{PCl} + \text{Cl}$ to explain this potential rather than the process $\text{PCl}_3 \rightarrow \text{Cl}^+ + \text{e}^- + \text{P} + \text{Cl}_2$. The reason for their selection was a calculated $\Delta H_f^0(\text{Cl})$, 10 kcal. lower than the literature value (See National Bureau of Standards "Selected Values of Chemical Thermodynamic Properties" Circular 500). Use of the JANAP $\Delta H_f^0 298.15$ for PCl_3 eliminates this difference.

Therefore, the process of the reported appearance potential would apparently be the second process which does not involve the neutral PCl radical.

Heat Capacity and Entropy.

The molecular constants were estimated by J. S. Gordon, Astrostats International, Livingston, New Jersey, private communication, April 25, 1963.

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 242.67

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	-0.000	0.000	INFINITE	-2.340	3.901	3.901	INFINITE
100	7.4460	53.389	69.716	-1.633	3.835	1.636	3.574
200	8.3335	58.873	63.055	-0.836	3.668	+0.97	+5.43
298	8.658	62.272	62.272	+0.000	3.500	-	2.506
300	8.662	62.325	62.272	+0.16	3.497	-	2.543
400	8.800	65.431	64.243	+0.888	3.389	-	2.424
500	8.881	66.813	65.243	1.775	3.089	-	2.624
600	8.929	68.436	63.994	2.666	2.855	-	3.041
700	8.964	69.816	64.730	3.560	1.441	-	3.124
800	8.991	71.014	65.442	4.458	1.375	-	3.175
900	9.014	72.075	66.121	5.361	1.308	-	3.218
1000	9.034	73.025	66.765	6.261	+0.65	-	3.226
1100	9.054	73.887	67.374	7.165	+0.22	-	3.237
1200	9.075	74.676	67.950	8.071	+0.187	-	3.242
1300	9.098	75.403	68.496	8.980	+0.41	-	3.243
1400	9.121	76.078	69.014	9.891	+0.42	-	3.244
1500	9.144	76.709	69.506	10.805	+0.490	-	3.248
1600	9.168	77.301	69.974	11.722	+0.714	-	3.254
1700	9.222	77.859	70.422	12.643	+0.937	-	3.255
1800	9.275	78.387	70.850	13.567	+1.162	-	3.258
1900	9.328	78.887	71.258	14.494	+1.386	-	3.261
2000	9.358	79.368	71.654	15.430	+1.614	-	3.261
2100	9.408	79.826	72.032	16.368	-	28.124	3.031
2200	9.459	80.265	72.396	17.311	-	28.400	2.821
2300	9.512	80.687	72.748	18.260	-	27.667	2.629
2400	9.565	81.094	73.087	19.214	-	26.935	2.446
2500	9.618	81.484	73.415	20.173	-	26.183	2.289
2600	9.671	81.862	73.733	21.137	-	25.428	2.137
2700	9.723	82.228	74.041	22.107	-	24.666	1.997
2800	9.775	82.582	74.339	23.082	-	23.895	1.862
2900	9.827	82.927	74.627	24.061	-	23.123	1.732
3000	9.871	83.261	74.912	25.047	-	22.357	1.626
3100	9.917	83.585	75.186	26.036	-	21.590	1.518
3200	9.961	83.901	75.454	27.030	-	20.723	1.415
3300	10.003	84.208	75.714	28.028	-	19.906	1.318
3400	10.044	84.507	75.967	29.029	-	19.089	1.224
3500	10.080	84.799	76.217	30.037	-	18.247	1.139
3600	10.115	85.083	76.459	31.046	-	17.401	1.056
3700	10.148	85.361	76.696	32.060	-	16.548	+0.977
3800	10.178	85.632	76.928	33.076	-	15.686	+0.902
3900	10.207	85.897	77.154	34.094	-	14.824	+0.827
4000	10.235	86.155	77.376	35.118	-	13.958	+0.752
4100	10.261	86.408	77.593	36.143	-	13.050	+0.696
4200	10.284	86.656	77.806	37.170	-	12.153	+0.632
4300	10.305	86.898	78.015	38.199	-	11.252	+0.572
4400	10.325	87.135	78.219	39.228	-	10.350	+0.512
4500	10.344	87.368	78.420	40.264	-	9.426	+0.457
4600	10.361	87.595	78.617	41.300	-	8.492	+0.403
4700	10.377	87.818	78.810	42.336	-	7.561	+0.352
4800	10.391	88.037	79.000	43.375	-	6.618	+0.301
4900	10.404	88.251	79.184	44.414	-	5.674	+0.250
5000	10.416	88.461	79.370	45.456	-	4.722	+0.206
5100	10.427	88.668	79.551	46.498	-	3.761	+0.161
5200	10.438	88.870	79.728	47.541	-	2.795	+0.117
5300	10.448	89.069	79.892	48.585	-	1.824	+0.075
5400	10.456	89.265	80.058	49.628	-	+0.851	+0.031
5500	10.464	89.457	80.243	50.676	-	+0.131	+0.005
5600	10.471	89.645	80.409	51.723	-	5.4232	1.117
5700	10.478	89.831	80.573	52.771	-	5.4502	1.204
5800	10.484	90.013	80.734	53.819	-	5.4768	1.289
5900	10.489	90.193	80.894	54.867	-	5.5032	1.372
6000	10.495	90.369	81.049	55.917	-	5.5288	1.456

June 30, 1962

Lead Monochloride (PbCl) (Ideal Gas)

Mol. Wt. = 242.67

 $\Delta H_f^\circ 298.15 = 3.5 \pm 7.2$ kcal. mole⁻¹ $S_{298.15}^\circ = 62.272$ cal. deg.⁻¹ mole⁻¹Ground State Configuration 2π

Electronic Level and Multiplicity

ϵ , cm. ⁻¹	g_1
0	2
[8266]	2

 $\omega_e = 303.6$ cm.⁻¹ $\omega_e x_e = 0.88$ cm.⁻¹ $\alpha_e = [0.00046]$ cm.⁻¹

Heat of Formation. $\Delta H_f^\circ 298.15$ was calculated from the dissociation energy of PbCl(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ω_e , and $\omega_e x_e$ were given by Herzberg, loc. cit. B_e , α_e , and ϵ were estimated by J. S. Gorden, AstroSystems, Inc., private communication, May, 1962.

Silicon Monochloride (SiCl)

SILICON MONOCHLORIDE (SiCl)

(IDEAL GAS)

GFW = 63.539

Ground State Configuration $2\pi_r$

$$\Delta H_f^\circ = 45.2 \pm 15 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 56.82 \text{ gibbs/mol}$$

$$\Delta H_f^\circ_{298.15} = 45.7 \pm 15 \text{ kcal/mol}$$

$$GFW = 63.539$$

(Ideal Gas)

Electronic Levels and Quantum Weights

State	$\epsilon_i, \text{cm}^{-1}$	g_i
$X^2\pi_{1/2}$	0	2
$2\pi_{3/2}$	207.2	2
$A^2\pi^*$	22993.5	2
$B^2\pi^*$	34192	2
$B'^2\pi_{1/2}$	35618	4
$C^2\pi$	41245	4
$D^2\pi$	44940	4

$$\omega_e = 533.75 \text{ cm}^{-1} \quad \sigma = 1$$

$$B_e = 0.25416 \text{ cm}^{-1} \quad r_e = 0.00161 \text{ cm}^{-1}$$

Heat of Formation

The adopted value is based on $D_0^\circ = 90 \pm 15$ kcal/mol which is calculated from $D_0^\circ/D'(LBX) = 1.01$ and $D'(LBX) = 89$ kcal/mol. The latter value comes from linear Birge-Sponer extrapolation of ground state vibrational constants obtained by Verma (1) from the B'-X system. The ratio $D_0^\circ/D'(LBX) = 1.01$ is calculated from an empirical relationship proposed by Hildenbrand (2): $D_0^\circ/D'(LBX) = 0.365(r_e/r_e^\circ) + 0.448$ and $r_e^\circ = 1.40 \text{ \AA}$ (IP-EA), where IP is the ionization potential of the more electronegative element and EA is the electron affinity of the more electronegative element. A similar calculation using $\omega_e/r_e^\circ = 2.1 \text{ cm}^{-1}$ obtained from the B-X system (2) would give $D_0^\circ = 98$ kcal/mol. These values for D_0° may be compared with average (per bond) heats of atomization of 101 kcal/mol for SiCl_2 and 94 kcal/mol for SiCl_4 .

Gaydon (3) selected $D_0^\circ = 7612$ kcal/mol on the assumption that $D_0^\circ/D'(LBX) = 0.8$, but Ovcharenko (4) suggested that this was too low by comparison with $D_0^\circ = 117$ kcal/mol obtained from the B' state. The latter value is calculated from $D'(LBX) = 33$ kcal/mol and presumes that $\text{Si}(\text{D})$ is the excited atomic product. The B and C states could also correlate to give values fairly consistent with $D_0^\circ = 117$. This interpretation seems unlikely, however, because it would involve a crossing of the potential curves for the B and B' states. Since the potential curves may be distorted due to the close proximity of the B and B' states, it seems preferable to obtain D_0° from constants for the ground state.

Heat Capacity and Entropy

Electronic levels of the B and C states are taken from the B-X and C-X systems reported by Ovcharenko et al. (5, 6). The A level is that assigned by Sanii (10) from analysis of the A-X system. The D level is that derived by Herzberg (7) from data of Jevons (2), but it is assigned as π as suggested by Verma (1). The B' level is from Verma and is confirmed by the earlier analysis of Ovcharenko (4). All vibrational and rotational constants for the ground state are those obtained by Verma (1) from the B'-X system. Values only slightly different were obtained from the B-X system by Ovcharenko (5, 6). The adopted constants are adjusted to the natural isotopic abundances of Si and Cl.

References

1. R. D. Verma, Can. J. Phys. 42, 2345 (1964).
2. I. E. Ovcharenko and Yu. Ya. Kuzakov, Opt. Spectry, USSR (English Transl.) 13, 362 (1962).
3. A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.
4. I. E. Ovcharenko, Yu. Ya. Kuzakov and V. M. Tatevskii, Opt. Spectry, USSR (English Transl.), Supplement 2, Molecular Spectroscopy, pp. 6-7 (1968), original Russian published in 1963.
5. I. E. Ovcharenko and Yu. Ya. Kuzakov, Opt. Spectry, USSR (English Transl.) 20, 14 (1968); 13, 362 (1962).
6. I. E. Ovcharenko, L. N. Tunitskii and V. I. Yakutin, Opt. Spectry, USSR (English Transl.) 8, 993 (1960).
7. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
8. W. Jevons, Proc. Phys. Soc. (London) A48, 563 (1936).
9. D. L. Hildenbrand, CPTA Publication No. 146, Vol. 1, 63 (1967).
10. N. Sanii and R. D. Verma, Can. J. Phys. 43, 960 (1965).

CISI

Dec. 31, 1960; Sept. 30, 1967

Titanium Monochloride (TiCl)
(Ideal Gas) $\text{GFW} = 83.353$

TITANIUM MONOCHLORIDE (TiCl)

(IDEAL GAS)

GFW = 83.353

Ground State Configuration $[^4 2]$ $\Delta H_f^\circ = [36.8 \pm 10.0] \text{ kcal/mol}$ $S_{298.15}^\circ = 59.54 \pm 2.0 \text{ gibbs/mol}$ $\Delta H_f^\circ = [36.9 \pm 10.0] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	[4]
[1000]	[4]
[2000]	[4]
[4000]	[4]
[6000]	[4]
[8000]	[4]
[10000]	[4]

 $\omega_e = 379.7 \text{ cm}^{-1}$ $\omega_e x_e = 3.41 \text{ cm}^{-1}$ $\sigma = 1$ $B_e = [0.146] \text{ cm}^{-1}$ $a_e = [0.0013] \text{ cm}^{-1}$ $r_e = [2.3] \text{ \AA}$

Heat of Formation

The heat of formation, ΔH_f° , of TiCl (g) is calculated from the dissociation energy, D_0° , which is estimated as 105 kcal/mol. This estimate is obtained from the relation $D(\text{TiCl}) < D_0^\circ(\text{TiCl}) < D_0^\circ(\text{TiCl}_2)$, where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of $\text{TiF}_2(\text{g})$ by Zmbov and Margrave (1).

Extrapolations of the vibrational levels reported by Shenyavskaya (2), Rao (3) and Mace and Packer (4) yield values of the dissociation energy which are very low when considered with respect to bond energy relations.

Heat Capacity and Entropy

The vibrational frequency, ω_e , and anharmonic vibrational term, $\omega_e x_e$, were reported by Shenyavskaya et al. (2). The interatomic distance is estimated from Guggenheimer's relation (5). B_e is calculated from r_e . The ground state term and electronic levels are estimated from the ground state multiplet of $\text{Ti}^2(\text{g})$. a_e is estimated from the Morse potential function.

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
2. E. A. Shenyavskaya, Yu. Ya. Kuzakov, and V. M. Tatevskii, Opt. Spectrosc. (USSR) **11**, 197 (1962).
3. V. R. Rao, Indian J. Phys. **23**, 535 (1949).
4. K. R. Mace and A. H. Packer, Phys. Rev. **52**, 1150 (1937).
5. K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
6. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

T, °K	C_p°	$S^\circ - (C_p^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	INFINITE	2.314	36.835	36.835	INFINITE
100	7.230	50.812	66.943	34.427	34.427	75.240
200	8.167	60.128	80.331	31.809	31.809	34.759
298	8.915	59.538	59.538	0.000	36.900	29.277
300	8.927	59.583	60.17	36.898	28.229	21.284
400	9.451	62.243	59.886	36.787	26.691	14.583
500	9.683	64.406	60.588	36.685	24.178	10.568
600	10.138	66.232	61.380	36.586	21.665	7.499
700	10.285	67.606	62.169	36.483	19.210	5.098
800	10.316	68.464	62.956	36.378	16.797	3.174
900	10.316	70.410	63.738	36.273	14.307	1.874
1000	10.442	71.509	64.461	36.054	11.880	2.596
1100	10.458	72.505	65.148	35.861	9.473	1.882
1200	10.470	73.416	65.799	35.706	7.121	1.297
1300	10.481	74.251	66.416	35.586	4.849	0.966
1400	10.486	75.031	66.999	35.500	2.562	0.397
1500	10.509	75.756	67.565	34.308	1.267	0.39
1600	10.526	76.434	68.098	34.143	1.996	0.273
1700	10.535	77.073	68.608	33.959	4.249	0.56
1800	10.544	77.678	69.092	33.758	6.721	0.008
1900	10.553	78.254	69.550	33.534	8.721	1.495
2000	10.466	78.792	70.010	28.632	10.788	1.178
2100	10.658	79.310	70.480	28.566	12.759	1.328
2200	10.659	79.805	70.855	28.341	14.723	1.463
2300	10.669	80.273	71.220	28.068	16.681	1.586
2400	10.678	80.719	71.570	27.755	18.614	1.695
2500	10.708	81.170	72.012	27.613	20.546	1.796
2600	10.725	81.590	72.373	27.372	22.468	1.889
2700	10.742	81.995	72.722	27.131	24.380	1.973
2800	10.772	82.368	73.358	26.851	26.277	2.053
2900	10.786	82.719	73.984	26.541	28.177	2.123
3000	10.766	83.129	73.707	26.267	30.064	2.190
3100	10.768	83.483	74.016	26.171	31.942	2.252
3200	10.810	83.856	74.318	26.027	33.816	2.309
3300	10.811	84.182	74.591	25.848	35.687	2.361
3400	10.851	84.482	74.891	25.688	37.552	2.413
3500	10.840	84.756	75.175	25.5206	39.383	2.459
3600	10.869	85.102	75.446	34.759	76.662	2.487
3700	10.857	85.399	75.711	35.844	76.877	2.361
3800	10.864	85.691	75.970	36.010	77.105	2.379
3900	10.871	85.978	76.223	36.171	77.337	2.437
4000	10.878	86.246	76.470	39.105	77.602	2.019
4100	10.884	86.515	76.712	40.193	77.870	1.915
4200	10.891	86.777	76.948	41.282	78.151	1.816
4300	10.903	87.024	77.180	42.371	78.443	1.721
4400	10.903	87.264	77.407	43.461	78.748	1.631
4500	10.909	87.589	77.629	44.552	79.065	1.544
4600	10.915	87.769	77.847	45.643	79.390	1.460
4700	10.921	88.004	78.060	46.735	79.726	1.379
4800	10.923	88.225	78.266	47.827	80.072	1.296
4900	10.933	88.459	78.474	48.920	80.422	1.226
5000	10.939	88.680	78.677	50.013	80.788	1.156
5100	10.953	88.897	78.876	51.108	81.157	1.086
5200	10.952	89.109	79.070	52.203	81.534	1.019
5300	10.952	89.316	79.259	53.298	81.918	0.954
5400	10.966	89.523	79.450	54.398	82.309	0.882
5500	10.973	89.724	79.635	55.491	82.703	0.811
5600	10.980	89.922	79.817	56.589	83.104	0.772
5700	10.987	90.117	79.996	57.687	83.509	0.715
5800	10.993	90.306	80.172	58.786	83.910	0.656
5900	11.003	90.486	80.345	59.886	84.310	0.600
6000	11.011	90.661	80.516	60.987	84.748	0.554

Dec. 31, 1960; Mar. 31, 1964; June 30, 1968; Dec. 31, 1968

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	7.082	54.196	INFINITE	2.240	132.346	132.346	INFINITE
100	7.942	59.335	69.617	1.542	132.540	129.607	-283.257
200	7.942	63.316	79.96	1.000	132.443	126.704	-138.455
298	8.327	62.567	82.567	0.000	132.300	123.917	-90.834
300	8.334	62.619	82.567	0.015	132.297	123.865	-90.235
400	8.582	65.054	82.698	0.861	132.140	121.077	-66.154
500	8.718	66.985	83.529	1.724	131.978	118.130	-51.722
600	8.802	68.583	84.242	2.604	131.809	115.616	-42.113
700	8.843	69.713	84.862	3.474	131.644	113.486	-34.152
800	8.904	70.330	85.366	4.327	131.484	110.272	-30.125
900	8.945	71.181	85.827	5.264	131.250	107.638	-26.138
1000	8.985	73.126	86.961	6.165	131.045	105.025	-22.953
1100	9.027	73.984	87.561	7.065	130.833	102.433	-20.351
1200	9.071	74.793	88.120	7.960	130.623	99.702	-18.359
1300	9.114	75.554	88.641	8.849	130.413	96.934	-16.359
1400	9.164	76.277	89.131	9.794	130.151	94.771	-14.704
1500	9.211	76.810	89.589	10.713	129.809	92.254	-13.441
1600	9.257	77.406	90.134	11.634	129.459	89.752	-12.260
1700	9.303	77.859	90.608	12.547	129.137	87.284	-11.260
1800	9.349	78.509	91.008	13.497	128.795	84.794	-10.295
1900	9.394	79.009	91.412	14.434	128.465	82.337	-9.471
2000	9.439	79.492	91.808	15.375	128.584	79.897	-8.731
2100	9.484	79.953	92.181	16.321	128.995	77.470	-8.062
2200	9.529	80.385	92.545	17.268	128.695	75.062	-7.462
2300	9.572	80.820	92.895	18.228	127.494	72.656	-6.904
2400	9.617	81.229	93.234	19.184	127.384	70.270	-6.399
2500	9.679	81.623	93.562	20.153	127.061	67.896	-5.935
2600	9.734	82.004	93.879	21.126	126.733	65.536	-5.509
2700	9.789	82.372	94.184	22.102	126.393	63.190	-5.115
2800	9.852	82.726	94.486	23.082	126.030	60.854	-4.750
2900	9.918	83.076	94.776	24.071	125.637	58.533	-4.411
3000	9.986	83.414	95.058	25.066	125.209	56.227	-4.096
3100	10.057	83.742	95.333	26.064	124.732	53.934	-3.802
3200	10.131	84.061	95.603	27.064	124.208	51.656	-3.526
3300	10.208	84.374	95.869	28.065	123.613	49.399	-3.272
3400	10.287	84.681	96.117	29.119	122.955	47.164	-3.032
3500	10.368	84.981	96.366	30.152	122.216	44.943	-2.806
3600	10.450	85.274	96.609	31.193	121.369	42.747	-2.595
3700	10.534	85.581	96.849	32.236	120.426	40.577	-2.400
3800	10.613	85.881	97.080	33.296	119.382	38.437	-2.224
3900	10.700	86.120	97.308	34.365	118.248	36.327	-2.061
4000	10.783	86.392	97.532	35.439	117.020	34.262	-1.905
4100	10.865	86.659	97.752	36.522	115.690	32.255	-1.757
4200	10.956	86.918	97.968	37.612	114.266	29.955	-1.626
4300	11.045	87.182	98.176	38.712	112.750	27.266	-1.502
4400	11.133	87.441	98.376	39.817	111.131	25.341	-1.383
4500	11.177	87.685	98.560	40.931	110.109	23.499	-1.233
4600	11.250	87.932	98.740	42.053	109.694	21.499	-1.116
4700	11.315	88.181	98.904	43.184	109.082	19.751	-1.009
4800	11.385	88.412	99.061	44.316	108.285	17.485	-0.908
4900	11.449	88.649	99.372	45.458	107.266	15.022	-0.798
5000	11.508	88.881	99.560	46.606	106.095	13.164	-0.700
5100	11.565	89.109	99.745	47.760	104.910	11.164	-0.607
5200	11.617	89.334	100.000	48.914	103.555	9.054	-0.521
5300	11.667	89.554	100.247	50.083	102.055	6.759	-0.431
5400	11.712	89.775	100.484	51.252	100.384	4.303	-0.368
5500	11.754	89.990	100.658	52.425	104.218	1.759	-0.269
5600	11.792	90.202	100.830	53.603	104.056	4.915	-0.192
5700	11.827	90.411	100.990	54.784	107.741	1.214	-0.145
5800	11.866	90.620	101.133	55.964	107.589	1.597	-0.082
5900	11.906	90.820	101.266	57.155	107.589	1.597	-0.022
6000	11.911	91.020	101.296	58.345	-86.465	-0.347	-0.013

June 30, 1967

(IDEAL GAS)

TUNGSTEN MONOCHLORIDE (WCl)

Ground State Configuration [2]

S°_{298.15} = [62.6] gibbs/molΔH°₀ = [132.3 ± 10] kcal/molΔH°_{298.15} = [132.3 ± 10] kcal/mol

(IDEAL GAS)

C/W

C/W

Electronic Levels and Quantum Weights

ϵ_j , cm ⁻¹	$\frac{g_j}{\epsilon_j}$
0	[4]
[5000]	[2]
[15000]	[20]

 $\omega_e x_e = [1.46] \text{ cm}^{-1}$ $\sigma = 1$ $B_e = [0.11105] \text{ cm}^{-1}$ $r_e = [2.26] \text{ \AA}$

Heat of Formation

The heat of formation, ΔH°_{f298}(WCl, g) = 132.3 kcal/mol, is calculated from the bond dissociation energy, D°₂₉₈(W-Cl) = 100 ± 10 kcal/mol. This estimated D°₂₉₈ is obtained from the average bond dissociation energy for WCl_x(g) + W(g) + xCl(g) where x = 2, 4, 5, 6, using all JANAF values.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in WCl₂(g). This distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental vibrational frequency ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 455 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D_0 + 0.5 \omega_e) = 0.0032$. The rotational constant B_e is calculated from the estimated bond distance. The value of σ_e is calculated from the Morse potential function. The moment of inertia is $25.20 \times 10^{-39} \text{ g cm}^2$.

The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for WF(g). See WF(g) table (March 31, 1967) for details.

Zirconium Monochloride (ZrCl)

(Ideal Gas) GFW = 126.673

ZIRCONIUM MONOCHLORIDE (ZrCl)

(IDEAL GAS)

GFW = 126.673

Ground State Configuration [4]

 $\Delta H_f^\circ = 49.3 \pm 5$ kcal/mol $S_{298.15}^\circ = [60.8 \pm 2]$ gibbs/mol $\Delta H_f^\circ = 49.1 \pm 5$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[4]
[3000]	[4]
[6000]	[4]
[12000]	[4]
[18000]	[4]
[24000]	[4]
[30000]	[4]

 $\omega_e x_e = [4371]$ cm⁻¹ $\sigma = 1$ $r_e = [2.3]$ Å $B_e = [0.1248]$ cm⁻¹ $\omega_e = [0.00042]$ cm⁻¹

Heat of Formation

Potter (1) investigated mass spectrometrically the gaseous equilibria among ZrCl, ZrCl₂, ZrCl₃ and ZrCl₄. Ion intensities were measured 2.5 eV above the ionization threshold. Using the reported equilibrium constants for the reaction ZrCl₃(g) + ZrCl(g) = 2 ZrCl₂(g) in the temperature range 1978-2274°K, second and third law analyses give the heats of reaction at 298°K as -10.36 and -12.63 kcal/mol, respectively. The third law drift is 1.4 ± 2.5 eu. Based on the third law ΔH_{298}° and ΔH_{298}° (ZrCl₂, g) = -44.5 kcal/mol (2), and ΔH_{298}° (ZrCl₃, g) = -125.3 kcal/mol (3), we obtain ΔH_{298}° (ZrCl, g) = 49.1 kcal/mol which is adopted in the tabulation.

Farber et al. (4) also studied mass spectrometrically the reaction Zr(c) + Cl(g) + ZrCl(g). They reported a second law heat of reaction, $\Delta H_{298}^\circ = 8.7 \pm 1.4$ kcal/mol. Using the equilibrium constants $K = (ZrCl)/(Cl)$ which we calculated from their reported ion intensities of run 3 in the temperature range 1667-1896°K, we obtain $\Delta H_{298}^\circ = 20.3$ kcal/mol by the third law method. The third law drift is 6.1 ± 2.4 eu. The heat of formation is derived as ΔH_{298}° (ZrCl, g) = 49.2 kcal/mol.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in ZrCl₄(g). The bond distance is then used with Guggenheimer's relation (5) for polar molecules to calculate the fundamental vibrational frequency ω_e . The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/(v_e^2 + 0.5 \omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of a_e is calculated from the Morse potential function. The moment of inertia is 22.425×10^{-39} g cm².

The ground state configuration is taken from the ground state multiplet of Zr⁺ reported by Moore (6). The electronic levels and the quantum weights are estimated to be the same as those of ZrF(g).

References

1. N. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. JANAF ZrCl₂(g) table dated Dec. 31, 1969.
3. JANAF ZrCl₃(g) table dated Dec. 31, 1969.
4. M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRL-TR-67-244, Contract F04611-67-C-0010, Nov. 1967.
5. K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).
6. C. E. Moore, "Atomic Energy Levels," Vol. II, Natl. Bur. Std. Circ. 467, 1952.

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-2.249	49.269	49.269	INFINITE
100	7.107	52.333	67.866	-1.551	49.407	102.207	1.000
200	7.895	57.533	74.212	-1.111	49.226	148.226	1.000
298	8.356	60.754	80.754	0.000	49.100	171.707	1.000
300	8.372	60.806	80.754	-0.015	49.097	171.661	1.000
400	8.612	63.251	81.086	-0.866	48.909	168.810	1.000
500	8.761	65.169	81.720	-1.735	48.701	166.810	1.000
600	8.888	66.798	82.436	-2.617	48.471	164.810	1.000
700	9.021	68.178	83.160	-3.513	48.221	162.810	1.000
800	9.162	69.392	83.884	-4.422	47.954	160.810	1.000
900	9.309	70.479	84.540	-5.345	47.671	158.810	1.000
1000	9.453	71.468	85.184	-6.284	47.373	156.810	1.000
1100	9.591	72.375	85.797	-7.236	47.060	154.810	1.000
1200	9.720	73.215	86.381	-8.201	46.734	152.810	1.000
1300	9.836	73.998	86.937	-9.179	46.397	150.810	1.000
1400	9.940	74.731	87.468	-10.168	46.050	148.810	1.000
1500	10.031	75.420	87.975	-11.167	45.694	146.810	1.000
1600	10.110	76.070	88.461	-12.176	45.329	144.810	1.000
1700	10.178	76.685	88.927	-13.189	44.956	142.810	1.000
1800	10.235	77.268	89.374	-14.209	44.576	140.810	1.000
1900	10.283	77.823	89.804	-15.235	44.190	138.810	1.000
2000	10.323	78.351	90.218	-16.266	43.799	136.810	1.000
2100	10.355	78.856	90.618	-17.300	43.404	134.810	1.000
2200	10.382	79.338	91.003	-18.337	43.005	132.810	1.000
2300	10.403	79.800	91.376	-19.376	42.602	130.810	1.000
2400	10.420	80.243	91.736	-20.417	42.196	128.810	1.000
2500	10.433	80.669	92.085	-21.460	41.787	126.810	1.000
2600	10.443	81.078	92.423	-22.504	41.374	124.810	1.000
2700	10.451	81.473	92.751	-23.548	40.957	122.810	1.000
2800	10.458	81.853	93.069	-24.594	40.536	120.810	1.000
2900	10.462	82.220	93.379	-25.640	40.111	118.810	1.000
3000	10.466	82.575	93.679	-26.686	39.682	116.810	1.000
3100	10.469	82.918	93.972	-27.733	39.249	114.810	1.000
3200	10.471	83.250	94.259	-28.780	38.812	112.810	1.000
3300	10.473	83.573	94.534	-29.827	38.371	110.810	1.000
3400	10.474	83.885	94.804	-30.874	37.926	108.810	1.000
3500	10.476	84.189	95.068	-31.922	37.477	106.810	1.000
3600	10.478	84.484	95.326	-32.970	37.024	104.810	1.000
3700	10.479	84.771	95.577	-34.018	36.567	102.810	1.000
3800	10.481	85.051	95.823	-35.066	36.107	100.810	1.000
3900	10.483	85.323	96.063	-36.114	35.644	98.810	1.000
4000	10.486	85.588	96.298	-37.162	35.177	96.810	1.000
4100	10.488	85.847	96.527	-38.211	34.706	94.810	1.000
4200	10.491	86.100	96.752	-39.260	34.231	92.810	1.000
4300	10.494	86.347	96.973	-40.309	33.751	90.810	1.000
4400	10.496	86.588	97.188	-41.359	33.266	88.810	1.000
4500	10.502	86.824	97.400	-42.409	32.777	86.810	1.000
4600	10.506	87.055	97.607	-43.459	32.282	84.810	1.000
4700	10.510	87.281	97.811	-44.510	31.782	82.810	1.000
4800	10.515	87.502	98.013	-45.561	31.277	80.810	1.000
4900	10.519	87.719	98.206	-46.613	30.768	78.810	1.000
5000	10.524	87.932	98.399	-47.665	30.254	76.810	1.000
5100	10.530	88.140	98.588	-48.718	29.737	74.810	1.000
5200	10.535	88.345	98.773	-49.771	29.216	72.810	1.000
5300	10.541	88.545	98.956	-50.825	28.691	70.810	1.000
5400	10.546	88.743	99.135	-51.879	28.162	68.810	1.000
5500	10.552	88.938	99.312	-52.934	27.630	66.810	1.000
5600	10.558	89.126	99.485	-53.990	27.095	64.810	1.000
5700	10.564	89.313	99.656	-55.046	26.557	62.810	1.000
5800	10.570	89.497	99.824	-56.102	26.016	60.810	1.000
5900	10.576	89.678	99.990	-57.160	25.472	58.810	1.000
6000	10.582	89.856	100.153	-58.218	24.926	56.810	1.000

T, °K.	cal. mole ⁻¹ deg. ⁻¹		-(F° - H° ₂₉₈)/T		H° - H° ₂₉₈		kcal. mole ⁻¹		ΔF°		Log K _p
	C _p	S°	-(F° - H° ₂₉₈)/T		H° - H° ₂₉₈	ΔH _f	ΔF°				
0	7.001	45.110	INFINITE	-	2.194	0.00	0.00	0.00	0.00	0.00	0.00
100	7.071	45.150	60.130	-	1.498	0.00	0.00	0.00	0.00	0.00	0.00
200	7.576	50.156	54.016	-	.772	0.00	0.00	0.00	0.00	0.00	0.00
298	8.111	53.289	53.289	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00
300	8.119	53.339	53.289	.015	0.00	0.00	0.00	0.00	0.00	0.00	0.00
400	8.437	55.724	53.612	.845	0.00	0.00	0.00	0.00	0.00	0.00	0.00
500	8.624	57.628	54.231	1.698	0.00	0.00	0.00	0.00	0.00	0.00	0.00
600	8.741	59.212	54.033	2.567	0.00	0.00	0.00	0.00	0.00	0.00	0.00
700	8.821	60.565	55.643	3.445	0.00	0.00	0.00	0.00	0.00	0.00	0.00
800	8.878	61.767	56.134	4.231	0.00	0.00	0.00	0.00	0.00	0.00	0.00
900	8.922	62.796	56.095	5.221	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1000	8.956	63.737	57.623	6.115	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1100	8.985	64.592	58.218	7.012	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1200	9.010	65.375	58.782	7.912	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1300	9.032	66.097	59.318	8.814	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1400	9.051	66.767	59.826	9.718	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1500	9.069	67.392	60.310	10.624	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1600	9.086	67.978	60.771	11.532	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1700	9.102	68.530	61.211	12.441	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1800	9.117	69.050	61.636	13.352	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1900	9.133	69.544	62.036	14.264	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2000	9.149	70.013	62.423	15.179	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2100	9.166	70.459	62.795	16.094	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2200	9.184	70.886	63.154	17.012	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2300	9.203	71.296	63.460	17.931	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2400	9.223	71.687	63.832	18.852	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2500	9.245	72.064	64.154	19.776	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2600	9.268	72.427	64.465	20.701	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2700	9.293	72.777	64.766	21.629	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2800	9.319	73.116	65.058	22.560	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2900	9.346	73.443	65.342	23.493	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3000	9.374	73.760	65.617	24.429	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3100	9.403	74.068	65.885	25.368	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3200	9.432	74.367	66.145	26.310	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3300	9.461	74.658	66.399	27.255	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3400	9.490	74.941	66.646	28.202	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3500	9.518	75.216	66.887	29.153	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3600	9.546	75.485	67.122	30.106	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3700	9.573	75.747	67.352	31.062	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3800	9.598	76.002	67.576	32.020	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3900	9.622	76.252	67.795	32.981	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4000	9.645	76.496	68.010	33.945	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4100	9.666	76.734	68.220	34.910	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4200	9.685	76.967	68.425	35.878	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4300	9.702	77.195	68.626	36.847	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4400	9.718	77.419	68.824	37.818	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4500	9.732	77.637	69.017	38.791	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4600	9.743	77.851	69.207	39.764	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4700	9.754	78.061	69.393	40.739	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4800	9.762	78.266	69.576	41.715	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4900	9.768	78.468	69.755	42.692	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5000	9.774	78.665	69.931	43.669	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5100	9.778	78.859	70.105	44.646	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5200	9.783	79.049	70.275	45.624	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5300	9.787	79.235	70.442	46.603	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5400	9.790	79.418	70.607	47.582	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5500	9.792	79.598	70.768	48.561	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5600	9.794	79.774	70.928	49.540	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5700	9.795	79.947	71.084	50.520	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5800	9.797	80.118	71.239	51.499	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5900	9.797	80.285	71.391	52.479	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6000	9.798	80.450	71.540	53.459	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Dec. 31, 1960† Mar. 31, 1961† Sept. 30, 1962

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CHLORINE, DIATOMIC (Cl₂)

MOL. WT. = 70.906

(IDEAL GAS - REFERENCE STATE)

Ground State Configuration 1Σ⁺
S°_{298.15} = 53.29 ± 0.01 cal. deg.⁻¹ mole⁻¹
ΔH°_f 0 = 0
ΔH°_f 298 = 0

Electronic Levels and Multiplicities

State	E cm. ⁻¹	g _i
1Σ ⁺	0	1
3Π ⁺	16,147 ± 500	1
3Π ₁	17,841 ± 500	2
3Π ₂	17,560 ± 500	2

ω_e = 561.1 cm.⁻¹
ω_e x_e = 4.0 cm.⁻¹
B_e = 0.2408 cm.⁻¹
r_e = 1.986 Å
σ = 2

Heat of Formation.

The heat of formation (ΔH°_f) for Cl₂(g) is zero at all temperatures, by definition.

Heat Capacity and Entropy.

The functions adopted here were calculated by R. L. Potter, J. Chem. Phys. 31, 1100 (1959) using a direct summation over the energy levels not including those of non-bonding states. The functions are for the naturally occurring isotopic composition.

The absorption spectrum of chlorine has been observed by A. Elliott, Proc. Roy. Soc. A 127, 638 (1930); C. F. Goodeve and B. A. Stephens, Trans. Faraday Soc. 32, 151.7 (1936); H. Stammreich, R. Fornaria and Y. Tsuarez, Spectrochim. Acta, 17, 775 (1961); Y. V. Rao and P. Venkateswarlu, J. Mol. Spectr. 9, 173 (1962); and A. E. Douglas, C. K. Møller and B. P. Stoicheff, Can. J. Phys. 41, 1174 (1963). There is disagreement over the vibrational assignments. The listed ground state spectroscopic constants for the naturally occurring isotopic composition are based upon the abundances given by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

The molecular structure of gaseous chlorine was determined by the sector-microphotometer method of electron diffraction by S. Shibata, J. Phys. Chem. 57, 2256 (1953). The value of r_e(Cl-Cl) was found to be 1.986 Å. The other r_e values, 1.983 - 1.989 Å, were reported by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., 1950; M. G. Richards and R. F. Barrow, Proc. Chem. Soc., 297 (1962), and L. S. Bartell and K. Kuchitsu, presented at the International Conference on Magnetism and Crystallography, 1961, quoted by S. Shibata, loc. cit.

Cesium Chloride, Dimeric (Cs₂Cl₂)Cl₂Os₂

(Ideal Gas) GFW = 336.716

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^c	Log K ^p
0	-∞	-∞	INFINITE	-	-156.808	-156.808	INFINITE
100	17.135	71.227	106.555	-	-157.277	-157.277	33.686
200	19.063	83.699	93.366	-	-157.446	-157.446	171.750
298	19.507	91.614	83.616	0.000	-157.700	-157.700	115.076
300	19.511	91.734	83.618	0.036	-157.707	-156.986	114.364
400	19.667	97.372	82.382	1.996	-159.101	-156.361	85.431
500	19.740	101.765	83.636	3.867	-159.481	-155.632	68.027
600	19.780	105.372	85.847	5.943	-159.858	-155.025	56.305
700	19.804	108.423	87.164	7.922	-160.237	-154.357	46.047
800	19.820	111.069	88.486	9.904	-160.621	-153.635	37.407
900	19.831	113.404	89.817	11.886	-161.007	-152.862	30.926
1000	19.836	115.484	91.162	13.870	-161.359	-152.047	26.653
1100	19.846	117.385	92.527	15.856	-161.664	-151.195	23.408
1200	19.856	119.112	93.824	17.838	-161.934	-150.303	20.608
1300	19.862	120.700	95.054	19.823	-162.165	-149.368	18.157
1400	19.865	122.172	96.254	21.809	-162.365	-148.398	15.977
1500	19.867	123.542	97.429	23.794	-162.534	-147.394	13.946
1600	19.868	124.823	98.571	25.780	-162.678	-146.356	12.053
1700	19.869	126.027	99.684	27.766	-162.797	-145.285	10.297
1800	19.869	127.162	100.764	29.752	-162.886	-144.186	8.671
1900	19.869	128.236	101.814	31.738	-162.940	-143.058	7.161
2000	19.869	129.255	102.833	33.725	-162.964	-141.899	5.757
2100	19.868	130.224	103.810	35.711	-162.959	-140.710	4.451
2200	19.865	131.148	104.743	37.697	-162.929	-139.492	3.234
2300	19.865	132.031	105.633	39.684	-162.871	-138.246	2.102
2400	19.864	132.877	106.484	41.671	-162.787	-136.973	1.042
2500	19.866	133.688	107.295	43.657	-162.679	-135.673	0.005
2600	19.867	134.462	108.062	45.644	-162.547	-134.346	-0.979
2700	19.867	135.207	108.784	47.630	-162.395	-132.992	-1.973
2800	19.867	135.939	109.464	49.617	-162.225	-131.615	-2.973
2900	19.868	136.637	110.104	51.604	-162.039	-130.216	-3.973
3000	19.868	137.310	110.704	53.591	-161.838	-128.794	-4.973
3100	19.868	137.962	111.274	55.578	-161.614	-127.346	-5.973
3200	19.868	138.592	111.814	57.564	-161.370	-125.873	-6.973
3300	19.869	139.204	121.132	59.551	-161.110	-124.376	-7.973
3400	19.869	139.797	121.627	61.538	-160.832	-122.854	-8.973
3500	19.869	140.373	122.093	63.525	-160.536	-121.307	-9.973
3600	19.869	140.933	122.535	65.512	-160.225	-119.736	-10.973
3700	19.869	141.477	122.954	67.500	-159.900	-118.141	-11.973
3800	19.869	142.007	123.351	69.487	-159.564	-116.523	-12.973
3900	19.869	142.523	123.724	71.474	-159.218	-114.884	-13.973
4000	19.870	143.026	124.081	73.460	-158.862	-113.225	-14.973
4100	19.870	143.517	124.424	75.447	-158.496	-111.546	-15.973
4200	19.870	143.995	124.744	77.434	-158.119	-109.846	-16.973
4300	19.870	144.463	125.053	79.421	-157.732	-108.125	-17.973
4400	19.870	144.920	125.344	81.408	-157.336	-106.384	-18.973
4500	19.870	145.366	125.624	83.395	-156.930	-104.623	-19.973
4600	19.870	145.803	125.894	85.382	-156.514	-102.842	-20.973
4700	19.870	146.230	126.154	87.369	-156.088	-101.041	-21.973
4800	19.870	146.649	126.404	89.356	-155.652	-99.220	-22.973
4900	19.870	147.058	126.644	91.343	-155.206	-97.389	-23.973
5000	19.870	147.460	126.874	93.330	-154.750	-95.548	-24.973
5100	19.870	147.853	127.094	95.317	-154.284	-93.697	-25.973
5200	19.870	148.236	127.304	97.304	-153.808	-91.836	-26.973
5300	19.870	148.611	127.504	99.291	-153.322	-89.965	-27.973
5400	19.870	148.986	127.694	101.278	-152.826	-88.084	-28.973
5500	19.870	149.358	127.874	103.265	-152.320	-86.193	-29.973
5600	19.871	149.712	128.044	105.252	-151.804	-84.292	-30.973
5700	19.871	150.061	128.204	107.239	-151.278	-82.381	-31.973
5800	19.871	150.409	128.354	109.226	-150.742	-80.460	-32.973
5900	19.871	150.759	128.504	111.213	-150.196	-78.529	-33.973
6000	19.871	151.093	128.644	113.200	-149.640	-76.588	-34.973

June 30, 1968

CESIUM CHLORIDE, DIMERIC (Cs₂Cl₂)

(IDEAL GAS)

GFW = 336.716

Point Group [D_{2h}]ΔH_f^o = -156.8 ± 2.5 kcal/molS^o_{298.15} = (91.6 ± 2.1) gibbs/molΔH_f^o_{298.15} = -157.7 ± 2.5 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[140] (1)	[76] (1)
[67] (1)	[151] (1)
[141] (1)	[156] (1)

Bond Distance: Cs-Cl = (3.18) Å

Bond Angle: Cl-Cs-Cl = (93.2)°

Product of the Moments of Inertia: I_AI_BI_C = (3.8076 × 10⁻¹¹¹) g³ cm⁶

σ = [4]

Heat of Formation

Datz (1) studied the molecular association equilibrium in cesium chloride vapors by measuring the temperature dependence of the molecular weight of gaseous CsCl. The molecular weights were determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume. The pressure sensing element was a fused silica manometer containing Au(t). Based on the reported results, we derive the equilibrium constants for the reaction Cs₂Cl₂(g) = 2CsCl(g) in the temperature range 1224 - 1418°K. The enthalpy change of this reaction is evaluated by the second and third law method as 39.3 ± 1.1 and 42.9 ± 0.6 kcal/mol, respectively. The drift in the third law value is equivalent to an entropy error of 2.7 ± 0.8 eu. Using the third law ΔH^o and ΔH_f^o₂₉₈ (CsCl, g) = -57.4 kcal/mol, we obtain ΔH_f^o₂₉₈ = -157.7 ± 2.5 kcal/mol for Cs₂Cl₂(g), which is adopted.

Schrier (2) determined the vapor pressures of molten cesium chloride at temperatures between 1165 and 1387°K by the boiling point or manometric method. The vapor analysis was performed using the transpiration method. An inert gas, N₂, was passed over the CsCl sample at a given temperature. The salt vapor entrained by the carrier gas was collected, weighed and analyzed. The data obtained were combined with the boiling point measurements to yield the average molecular weight of the vapor. Association into dimer was postulated. The mole fraction in the vapor and the partial pressure of CsCl(g) and Cs₂Cl₂(g) were calculated. The equilibrium constants, 1209 - 1350°K, for dissociation of the Cs₂Cl₂ dimer were derived. Using the reported equilibrium constants, we evaluate the enthalpy change (ΔH_f^o₂₉₈) of the reaction Cs₂Cl₂(g) = 2CsCl(g) to be 34.1 ± 2.9 and 43.2 ± 0.9 kcal/mol by the second and third law methods. Based on the third law ΔH_f^o₂₉₈ value and ΔH_f^o₂₉₈ (CsCl, g) = -57.4 kcal/mol, we obtain ΔH_f^o₂₉₈ = -156.0 kcal/mol for Cs₂Cl₂(g), which is in agreement with the adopted value.

Miller and Kusch (3) made an analysis of the velocity distribution of the CsCl molecules which escape through an ideal aperture from an isothermal enclosure. They found that there was no definite evidence that any species other than diatomic molecules were present in the beams in measurable amounts, in other words, the dimerization must be small, e.g. <1.5 per cent. However, according to our calculation the concentration of dimer is 15 - 34 per cent in the temperature range 600 - 900°K, and 33 - 20 per cent at the temperatures 1000 - 1600°K.

Heat Capacity and Entropy

The molecular structure is assumed to be planar, having D_{2h} symmetry. Based on the bond distances of Cs-Cs and Cl-Cl estimated by Berkowitz (4), the Cs-Cl bond distance and Cl-Cs-Cl bond angle are calculated. The vibrational frequencies were calculated by Berkowitz (4), on the basis of the potential function for an ionic model. The three principal moments of inertia are: I_A = 2.105 × 10⁻³⁷, I_B = 6.272 × 10⁻³⁷, and I_C = 2.732 × 10⁻³⁷ g cm².

References

1. S. Datz, Oak Ridge National Laboratory, ORNL-2938, Oak Ridge, Tennessee, May 1960.
2. E. E. Schrier, Ph. D. Thesis, Rensselaer Polytechnic Institute, 1961.
3. R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956).
4. J. Berkowitz, J. Chem. Phys. 29, 1386 (1958).
5. J. Berkowitz, J. Chem. Phys. 32, 1519 (1960).

Cl₂Os₂

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	+000	INFINITE	- 3.581	- 49.392	- 49.392	INFINITE
100	11.180	9.804	3.012	- 49.083	- 45.905	100.326
200	13.616	13.456	1.628	- 49.407	- 42.183	46.095
298	17.180	23.653	+000	- 49.200	- 38.655	28.335
300	17.190	25.939	-032	- 49.194	- 38.590	28.112
400	17.940	30.994	26.517	1.701	- 48.862	35.104
500	18.470	35.057	27.832	3.612	- 48.510	31.704
600	18.830	38.458	29.327	5.478	- 48.146	28.378
700	19.110	41.382	30.845	7.376	- 47.771	25.112
800	19.332	43.946	32.326	9.298	- 47.392	21.803
900	19.516	46.236	33.747	11.240	- 47.007	18.738
1000	19.687	48.301	35.101	13.201	- 46.618	15.618
1100	19.838	50.184	36.388	15.177	- 46.225	12.538
1200	19.983	51.917	37.611	17.168	- 45.830	9.493
1300	20.122	53.522	38.774	19.173	- 45.431	6.480
1400	20.256	55.018	39.881	21.192	- 45.024	3.397
1500	20.384	56.420	40.938	23.224	- 44.638	+031

Mar. 31, 1966

COPPER DICHLORIDE (CuCl₂)

(CRYSTAL)

MOL. WT. = 134.446

$$\Delta H_f^o = -49.39 \pm 1.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -49.2 \pm 1.5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 25.833 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_d = [766]^{\circ}\text{K.}$$

Heat of Formation.

S. A. Shchukarev and M. A. Oranskys, Zhur. Obshchei Khim. 24, 1928 (1954) have reported equilibrium constants for the dissociation $\text{CuCl}_2(\text{c}) \rightarrow \text{CuCl}(\text{c}) + 0.5 \text{ Cl}_2(\text{g})$, which are in general agreement with earlier reports by P. Ephraim, Ber. 50, 1089 (1917) and D. I. Tarasenkov, A. I. Origorovich and A. V. Boroslovskys, Collected Works of the Central State Institute for Non-Ferrous Metallurgy, Part 1, 1, 69 (1929). These data were subjected to third law analysis which revealed a significant trend of $13 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole.}$, indicating that equilibrium conditions were not reached. However an average value of $\Delta H_f^{298} = 16.5 \pm 1.9 \text{ kcal. mole}^{-1}$ yields a heat of formation of $\text{CuCl}_2(\text{c}) = -49.5 \pm 2.5 \text{ kcal. mole}^{-1}$ which is in good agreement with the adopted value taken from Natl. Bureau Std. Circular 500, Washington, 1952.

Heat Capacity and Entropy.

The low temperature heat capacity has been measured from 11-300°K. by J. W. Stout and R. C. Chisholm, J. Chem. Phys. 36, 979 (1962). The integration of this data from $S_{10}^o = 0.111 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ gave $S_{298}^o = 25.833 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. The heat capacity above 298° was obtained by smooth extrapolation of the above data, since the heat capacities of A. N. Krestovnikov and O. A. Karetnikov, Journ. Gen. Chem. (USSR) 5, 955 (1956) were not compatible with the low temperature data.

Decomposition Data.

The temperature of decomposition was estimated from the table for $\text{CuCl}_2(\text{c})$, $\text{CuCl}(\text{l})$ and $\text{Cl}_2(\text{g})$ so that the pressure of Cl_2 is 1 atm.

Phosphoryl Fluoride Dichloride (POCl₂F)
(Ideal Gas) Mol. Wt. = 136.889

PHOSPHORYL FLUORIDE DICHLORIDE (POCl₂F) (IDEAL GAS) MOL. WT. = 136.889

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	10.444	40.000	INFINITE	-3.927	-177.779	-177.779	INFINITE
200	15.843	69.590	91.125	-3.063	-178.410	-175.681	383.932
300	19.003	85.877	78.193	-1.721	-178.797	-172.782	188.799
400	20.951	92.420	76.549	∞	-179.000	-169.762	124.448
500	22.223	97.242	74.836	4.203	-179.131	-163.490	71.458
600	23.083	101.374	80.589	6.471	-179.126	-160.362	58.409
700	23.683	104.981	85.383	8.811	-179.119	-158.256	49.081
800	24.117	108.173	89.677	11.202	-179.112	-156.162	41.580
900	24.435	110.933	93.480	13.631	-179.104	-154.078	35.688
1000	24.674	113.320	96.833	16.087	-179.097	-152.002	30.662
1100	24.859	115.388	99.737	18.564	-179.090	-150.038	26.712
1200	25.000	117.156	102.211	21.064	-179.083	-148.182	23.466
1300	25.119	118.664	104.266	23.584	-179.076	-146.430	20.768
1400	25.212	119.952	105.993	26.080	-179.069	-144.778	18.510
1500	25.289	121.062	107.433	28.606	-179.061	-143.222	16.671
1600	25.352	122.020	108.700	31.138	-179.054	-141.760	15.136
1700	25.401	122.850	109.833	33.671	-179.047	-140.390	13.891
1800	25.435	123.580	110.850	36.218	-179.040	-139.100	12.811
1900	25.468	124.220	111.760	38.765	-179.033	-137.880	11.866
2000	25.501	124.780	112.580	41.316	-179.026	-136.720	11.036
2100	25.529	125.270	113.320	43.869	-179.019	-135.620	10.311
2200	25.552	125.690	113.990	46.431	-179.012	-134.580	9.681
2300	25.570	126.050	114.600	48.994	-179.005	-133.600	9.141
2400	25.583	126.360	115.160	51.564	-179.000	-132.680	8.691
2500	25.592	126.630	115.680	54.140	-179.000	-131.820	8.321
2600	25.600	126.870	116.160	56.717	-179.000	-131.020	8.011
2700	25.600	127.090	116.600	59.294	-179.000	-130.280	7.751
2800	25.600	127.290	117.000	61.869	-179.000	-129.600	7.541
2900	25.600	127.470	117.370	64.431	-179.000	-128.980	7.371
3000	25.600	127.630	117.710	66.980	-179.000	-128.420	7.241
3100	25.600	127.780	118.020	69.520	-179.000	-127.920	7.151
3200	25.600	127.910	118.310	72.050	-179.000	-127.480	7.091
3300	25.600	128.030	118.580	74.570	-179.000	-127.090	7.051
3400	25.600	128.140	118.830	77.080	-179.000	-126.760	7.021
3500	25.600	128.240	119.060	79.580	-179.000	-126.480	7.001
3600	25.600	128.330	119.270	82.070	-179.000	-126.250	6.981
3700	25.600	128.410	119.460	84.550	-179.000	-126.070	6.961
3800	25.600	128.480	119.630	87.020	-179.000	-125.930	6.941
3900	25.600	128.540	119.790	89.480	-179.000	-125.830	6.921
4000	25.600	128.600	119.940	91.930	-179.000	-125.770	6.901
4100	25.600	128.650	120.080	94.370	-179.000	-125.740	6.881
4200	25.600	128.700	120.210	96.800	-179.000	-125.720	6.861
4300	25.600	128.740	120.330	99.220	-179.000	-125.710	6.841
4400	25.600	128.780	120.440	101.630	-179.000	-125.700	6.821
4500	25.600	128.820	120.540	104.030	-179.000	-125.690	6.801
4600	25.600	128.860	120.640	106.420	-179.000	-125.680	6.781
4700	25.600	128.890	120.730	108.800	-179.000	-125.670	6.761
4800	25.600	128.920	120.820	111.170	-179.000	-125.660	6.741
4900	25.600	128.950	120.900	113.540	-179.000	-125.650	6.721
5000	25.600	128.980	120.980	115.900	-179.000	-125.640	6.701
5100	25.600	129.010	121.060	118.250	-179.000	-125.630	6.681
5200	25.600	129.040	121.130	120.590	-179.000	-125.620	6.661
5300	25.600	129.070	121.200	122.920	-179.000	-125.610	6.641
5400	25.600	129.100	121.270	125.240	-179.000	-125.600	6.621
5500	25.600	129.130	121.340	127.550	-179.000	-125.590	6.601
5600	25.600	129.160	121.410	129.850	-179.000	-125.580	6.581
5700	25.600	129.190	121.480	132.140	-179.000	-125.570	6.561
5800	25.600	129.220	121.550	134.420	-179.000	-125.560	6.541
5900	25.600	129.250	121.620	136.690	-179.000	-125.550	6.521
6000	25.600	129.280	121.690	138.950	-179.000	-125.540	6.501

Point Group C_{2v}
S°_{298.15} = 76.548 cal. deg.⁻¹ mole⁻¹
Ground State Multiplicity = {1}

Vibrational Frequencies and Degeneracies	ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
207 (1)	372 (1)	620 (1)	
254 (1)	386 (1)	894 (1)	
330 (1)	547 (1)	1331 (1)	

Bond Distance: P-Cl = 1.99 ± 0.04 Å P-F = 1.50 ± 0.03 Å P-O = 1.54 ± 0.03 Å
Bond Angle: Cl-P-Cl = 103° σ = 1
Product of the Moments of Inertia: I_AI_BI_C = 4.70732540 X 10⁻¹¹³ g.³ cm.⁶

Heat of Formation.

The ΔH°_f 298.15 of POCl₂F was estimated to be -179 kcal. mole⁻¹ from the ΔH°_f 298.15 of POCl₃ by assuming bond energies of 120 kcal. for D(P-F) and 80 kcal. for D(P-Cl). The D(P-F) and D(P-Cl) values were taken from E. Neale and L. T. D. Williams, J. Chem. Soc., 2485 (1955) Part I and E. Neale, L. T. D. Williams, and V. T. Moore, J. Chem. Soc. 422 (1956) Part II.

Essentially the same ΔH°_f 298.15 may be obtained by assuming a ΔH°_f = 0 for the following reaction:
POCl₃(g) + POCl₂F(g) → POCl₃F(g) + POCl₂Cl(g)

Heat Capacity and Entropy.

The molecular constants were determined by L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. 60, 1836 (1938) and by Q. Williams, J. Sheridan, and M. Gordy, J. Chem. Phys., 20, 164 (1952). Brockway and Beach used electron diffraction. Q. Williams et al. measured microwave spectra. Brockway and Beach assumed that the P-P-F and P-P-Cl angles were equal in POCl₂Cl and POCl₂F. An analysis of their data by Q. Williams et al. indicates that the angles in POCl₂Cl, POCl₂F, POCl₃, and POCl₂ should be 103° rather than the reported 106° ± 3°. The principal moments of inertia calculated from these parameters were I_A = 2.69184 X 10⁻³⁸, I_B = 3.79516 X 10⁻³⁸, and I_C = 4.60780 X 10⁻³⁸.

The Raman spectra and vibrational frequencies for POCl₂F were reported by M. L. Delwaule and P. Francois, Compt. Rend. 222, 550 (1946). These frequency assignments are summarized in J. Chim. Phys. 45, 87 (1949) by M. L. Delwaule and P. Francois.

T, °K.	C _p ^a	S ^b	-(F°-H ₂₉₈ °)/T	IF°-H ₂₉₈ °/T	ΔH _f ^c	ΔF ^d	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	12.164	10.703	43.476	3.889	-82.320	-82.320	INFINITE
200	16.806	21.138	29.828	3.277	-82.512	-78.017	172.665
298	18.323	28.190	28.190	1.748	-82.116	-75.452	82.446
300	18.340	28.303	28.100	∞	-81.700	-72.270	52.973
400	19.041	33.681	28.919	-0.934	-81.492	-72.211	52.904
500	19.512	37.083	30.316	1.905	-81.277	-69.115	37.793
600	19.863	41.572	31.001	3.803	-80.506	-63.204	23.021
700	20.166	46.057	33.508	7.804	-80.172	-60.348	18.840
800	20.435	50.542	36.015	11.805	-79.838	-57.492	15.658
900	20.675	55.027	38.522	15.806	-79.504	-54.636	13.486
1000	20.878	59.512	41.029	19.807	-79.170	-51.780	11.314
1100	21.036	63.976	43.536	23.808	-78.836	-48.924	9.142
1200	21.165	68.440	46.043	27.809	-78.502	-46.068	6.970
1300	21.270	72.904	48.550	31.810	-78.168	-43.212	4.800
1400	21.340	77.368	51.057	35.811	-77.834	-40.356	2.630
1500	21.393	81.832	53.564	39.812	-77.500	-37.500	0.460
1600	21.435	86.296	56.071	43.813	-77.166	-34.644	-1.710
1700	21.468	90.760	58.578	47.814	-76.832	-31.788	-3.880
1800	21.492	95.224	61.085	51.815	-76.498	-28.932	-6.050
1900	21.509	99.688	63.592	55.816	-76.164	-26.076	-8.220
2000	21.500	104.152	66.100	59.817	-75.830	-23.220	-10.390

Heat Capacity and Entropy.

The low temperature (53.2-295.0°K.) heat capacities were determined by K. K. Kelley and O. E. Moore, J. Am. Chem. Soc. **65**, 1264 (1943). The high temperature (670.5-941.0°K.) heat capacities were measured by O. E. Moore, J. Am. Chem. Soc. **65**, 1700 (1943). The two sets of C_p data were plotted and joined smoothly at 298°K. The C_p values above 941.0°K. were obtained by graphical extrapolation. The C_p values, 60-500°K., were also reported by F. L. Oetting and N. W. Gregory, J. Phys. Chem. **65**, 138 (1961) which are in good agreement with those determined by O. E. Moore, loc. cit. S_{298}° was derived from the smoothed C_p values, using $S_{53.2}^{\circ} = 4.930$ e.u. The $S_{298.15}^{\circ}$ value was determined by E. F. Westrum, Jr. quoted by L. E. Wilson and N. W. Gregory in J. Phys. Chem. **62**, 437 (1958). The entropy at 298° is assumed to include the uncoupling energy of Fe^{++} which is calculated to be 3.2 e.u. which corresponds to R in 5.

Melting Data.

T_m and ΔH_m° were taken from O. E. Moore, loc. cit.

Heat of Sublimation.

The difference between ΔH_f° 298.15 for $FeCl_2(g)$ and $FeCl_2(c)$ is ΔH_g° 298.15°. The former was obtained by the second and third law analyses on the equilibrium pressure data as described in $FeCl_2(g)$ table.

$$\begin{aligned}\Delta H_f^{\circ} 0 &= -82.32 \pm 0.12 \text{ kcal. mole}^{-1} \\ \Delta H_f^{\circ} 298.15 &= -81.70 \pm 0.12 \text{ kcal. mole}^{-1} \\ \Delta H_m^{\circ} &= 10.28 \pm 0.05 \text{ kcal. mole}^{-1} \\ \Delta H_g^{\circ} 298.15 &= 48.2 \pm 0.7 \text{ kcal. mole}^{-1}\end{aligned}$$

$$S_{298.15}^{\circ} = 28.190 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 950^{\circ}\text{K.}$$

Heat of Formation.

The enthalpy change, ΔH_f° 298.15 = -4.05 ± 0.05 kcal. mole⁻¹, for the reaction $Fe(\infty) + 2(HCl-12.731 H_2O)(l) = FeCl_2(c) + H_2(g) + 25.462 H_2O(l)$ was reported by M. P. Kohler and J. P. Coughlin, J. Phys. Chem. **63**, 605 (1959). The enthalpy change, ΔH_f° 298.15 = -19.5 ± 0.2 kcal. mole⁻¹, for the reaction $FeCl_2(c) = Fe^{++}(aq.) + 2 Cl^{-}(aq.)$ was then derived. The value of ΔH_f° 298.15(FeCl₂, c) was determined by J. C. M. Li and N. W. Gregory, J. Am. Chem. Soc. **74**, 4670 (1952), yielding ΔH_f° 298.15 = -81.4 ± 0.2 kcal. mole⁻¹ which is in agreement with the adopted value reported by M. P. Kohler and J. P. Coughlin. The equilibrium constants for the reaction $FeCl_2(c) + H_2(g) = Fe(c) + 2HCl(g)$ were determined by W. Kangro and E. Petersen, Z. Anorg. Chem. **261**, 157 (1950). By use of the second and third law methods the enthalpy change (ΔH_f° 298.15) of this reaction was evaluated as 37.81 ± 0.68 and 38.24 kcal. mole⁻¹, respectively. Based on the third law value for ΔH_f° 298.15, the value of ΔH_f° 298.15(FeCl₂, c) was derived to be -82.37 kcal. mole⁻¹ which is in reasonable agreement with the adopted value.

Iron Dichloride (FeCl₂)

Mol. Wt. = 126.753

(Liquid)

Cl₂Fe

MOL. WT. = 126.753

(LIQUID)

IRON DICHLORIDE (FeCl₂)

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0								
100	24.420	33.432	33.432	-	0.000	-74.411	-66.544	48.776
200	24.420	33.432	33.432	0.045	-74.392	-66.495	-66.495	48.439
300	24.420	33.432	33.432	0.090	-74.346	-66.406	-66.014	48.094
400	24.420	33.432	33.432	0.135	-74.277	-66.282	-65.790	47.748
500	24.420	33.432	33.432	0.180	-74.188	-66.128	-65.536	47.393
600	24.420	33.432	33.432	0.225	-74.089	-65.945	-65.353	47.038
700	24.420	33.432	33.432	0.270	-73.980	-65.732	-65.140	46.683
800	24.420	33.432	33.432	0.315	-73.861	-65.499	-64.897	46.328
900	24.420	33.432	33.432	0.360	-73.732	-65.246	-64.634	45.973
1000	24.420	33.432	33.432	0.405	-73.593	-64.971	-64.359	45.618
1100	24.420	33.432	33.432	0.450	-73.444	-64.676	-64.064	45.263
1200	24.420	33.432	33.432	0.495	-73.285	-64.361	-63.759	44.908
1300	24.420	33.432	33.432	0.540	-73.116	-64.036	-63.444	44.553
1400	24.420	33.432	33.432	0.585	-72.947	-63.701	-63.119	44.198
1500	24.420	33.432	33.432	0.630	-72.768	-63.356	-62.784	43.843
1600	24.420	33.432	33.432	0.675	-72.589	-63.001	-62.429	43.488
1700	24.420	33.432	33.432	0.720	-72.400	-62.636	-62.064	43.133
1800	24.420	33.432	33.432	0.765	-72.211	-62.261	-61.689	42.778
1900	24.420	33.432	33.432	0.810	-72.022	-61.876	-61.304	42.423
2000	24.420	33.432	33.432	0.855	-71.833	-61.481	-60.919	42.068
2100	24.420	33.432	33.432	0.900	-71.644	-61.076	-60.524	41.713
2200	24.420	33.432	33.432	0.945	-71.455	-60.661	-60.129	41.358
2300	24.420	33.432	33.432	0.990	-71.266	-60.236	-59.724	41.003
2400	24.420	33.432	33.432	1.035	-71.077	-59.801	-59.319	40.648
2500	24.420	33.432	33.432	1.080	-70.888	-59.356	-58.874	40.293
2600	24.420	33.432	33.432	1.125	-70.699	-58.901	-58.419	39.938
2700	24.420	33.432	33.432	1.170	-70.510	-58.436	-57.964	39.583
2800	24.420	33.432	33.432	1.215	-70.321	-57.961	-57.489	39.228
2900	24.420	33.432	33.432	1.260	-70.132	-57.476	-56.994	38.873
3000	24.420	33.432	33.432	1.305	-69.943	-56.981	-56.499	38.518

$\Delta H_f^{298.15} = -74.411 \pm 0.13 \text{ kcal. mole}^{-1}$
 $\Delta H_m^{298.15} = 10.28 \pm 0.05 \text{ kcal. mole}^{-1}$
 $\Delta H_v^{298.15} = 29.83 \text{ kcal. mole}^{-1}$

Heat of Formation.

The value of $\Delta H_f^{298.15}(\text{FeCl}_2, \text{l})$ was obtained from $\Delta H_f^{298.15}(\text{FeCl}_2, \text{c})$ by adding $\Delta H_m^{298.15}$ and the difference between $H_m^{298.15} - H_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity (950-1100°K.) for FeCl₂(l) was reported as 24.42 cal. deg.⁻¹ mole⁻¹ by O. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). A constant C_p was assumed for all the other temperatures. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and $\Delta H_m^{298.15}$ were taken from G. M. Moore, loc. cit.

Vaporization Data.

The boiling point (T_b) is determined as the temperature at which the free energy change ($\Delta F_v^{298.15}$) for the reaction FeCl₂(l) = FeCl₂(g) approaches zero. The corresponding enthalpy change ($\Delta H_v^{298.15}$) at T_b is the heat of vaporization ($\Delta H_v^{298.15}$).

Iron Dichloride (FeCl₂)

(Ideal Gas) Mol. wt. = 126.753

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg ⁻¹	(H ^o - H ₂₉₈)/T	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	0.000	INFINITE	- 3.394	- 35.624	- 35.624	INFINITE
100	10.088	83.128	70.018	- 1.378	- 35.556	- 35.556	40.747
298	14.830	68.710	68.710	0.000	- 35.500	- 38.151	27.964
300	14.854	68.802	68.711	+0.027	- 35.499	- 38.168	27.804
400	15.607	73.596	70.405	1.500	- 35.422	- 38.069	21.746
500	15.887	76.734	70.451	3.181	- 35.304	- 38.008	17.476
600	15.892	79.633	71.747	4.732	- 35.377	- 40.911	14.901
700	15.826	82.078	73.053	6.318	- 35.458	- 41.829	13.059
800	15.750	84.187	74.316	7.867	- 35.633	- 42.730	11.673
900	15.708	86.040	75.518	9.400	- 35.928	- 43.599	10.587
1000	15.675	87.653	76.654	11.078	- 36.408	- 44.450	9.710
1100	15.654	89.186	77.726	12.606	- 37.113	- 45.193	8.979
1200	15.642	90.548	78.739	14.170	- 37.612	- 45.912	8.361
1300	15.635	91.769	79.690	15.734	- 37.773	- 46.596	7.833
1400	15.631	92.858	80.603	17.297	- 37.853	- 47.268	7.379
1500	15.627	93.816	81.463	18.860	- 38.149	- 47.927	6.983
1600	15.624	94.645	82.280	20.423	- 38.363	- 48.573	6.634
1700	15.619	95.392	83.059	21.985	- 38.685	- 49.197	6.324
1800	15.614	96.084	83.803	23.547	- 39.225	- 49.793	6.045
1900	15.608	96.731	84.508	25.109	- 39.884	- 50.361	5.793
2000	15.598	97.329	85.193	26.668	- 40.664	- 50.942	5.523
2100	15.588	97.889	85.848	28.227	- 41.480	- 51.587	5.294
2200	15.576	98.414	86.475	29.785	- 42.504	- 51.187	5.085
2300	15.564	98.906	87.079	31.343	- 43.433	- 51.482	4.892
2400	15.551	99.368	87.661	32.897	- 44.271	- 51.844	4.711
2500	15.538	99.803	88.222	34.453	- 45.816	- 52.014	4.547
2600	15.524	100.212	88.764	36.006	- 46.268	- 52.253	4.392
2700	15.509	100.598	89.288	37.558	- 46.728	- 52.470	4.247
2800	15.495	100.962	89.795	39.108	- 47.197	- 52.680	4.112
2900	15.480	101.303	90.282	40.654	- 47.674	- 52.884	3.984
3000	15.465	101.630	90.762	42.204	- 48.138	- 53.050	3.864
3100	15.451	101.937	91.224	43.750	- 48.651	- 53.193	3.750
3200	15.436	102.227	91.672	45.294	- 49.204	- 53.887	3.544
3300	15.422	102.502	92.109	46.837	- 49.807	- 54.366	3.269
3400	15.408	102.763	92.533	48.378	- 50.454	- 54.841	2.961
3500	15.394	103.008	92.948	49.918	- 51.245	- 55.311	2.701
3600	15.380	103.242	93.348	51.457	- 52.083	- 55.775	2.487
3700	15.367	103.462	93.740	52.994	- 52.933	- 56.256	2.319
3800	15.354	103.671	94.122	54.530	- 53.800	- 56.749	2.112
3900	15.342	103.871	94.495	56.060	- 54.684	- 57.254	1.912
4000	15.330	104.059	94.860	57.590	- 55.586	- 57.770	1.729
4100	15.318	104.238	95.216	59.131	- 56.504	- 58.300	1.551
4200	15.307	104.407	95.563	60.662	- 57.437	- 58.834	1.382
4300	15.295	104.567	95.904	62.193	- 58.384	- 59.381	1.220
4400	15.283	104.718	96.236	63.718	- 59.344	- 59.940	1.065
4500	15.274	104.862	96.562	65.250	- 60.316	- 60.510	0.918
4600	15.264	104.997	96.881	66.776	- 61.300	- 61.090	0.776
4700	15.255	105.124	97.193	68.302	- 62.296	- 61.681	0.640
4800	15.245	105.244	97.499	69.827	- 63.304	- 62.284	0.510
4900	15.236	105.358	97.797	71.347	- 64.324	- 62.898	0.384
5000	15.227	105.469	98.094	72.874	- 65.356	- 63.524	0.264
5100	15.219	105.576	98.382	74.397	- 66.399	- 64.161	0.148
5200	15.211	105.680	98.666	75.918	- 67.454	- 64.810	0.036
5300	15.203	105.781	98.944	77.439	- 68.520	- 65.470	-0.072
5400	15.195	105.879	99.217	78.959	- 69.596	- 66.141	-0.184
5500	15.188	105.974	99.486	80.478	- 70.682	- 66.824	-0.296
5600	15.181	106.067	99.749	81.997	- 71.778	- 67.518	-0.408
5700	15.174	106.160	100.009	83.514	- 72.884	- 68.224	-0.520
5800	15.167	106.254	100.264	85.031	- 73.999	- 68.941	-0.632
5900	15.160	106.348	100.516	86.548	- 75.124	- 69.668	-0.744
6000	15.154	106.443	100.761	88.063	- 76.258	- 70.402	-0.856

June 30, 1965

IRON DICHLORIDE (FeCl₂) (IDEAL GAS)

MOL. WT. = 126.753

Point Group [D_{∞h}] $\Delta H_f^o = -35.83 \pm 2.0$ kcal. mole⁻¹ $\Delta H_f^o = -35.50 \pm 2.0$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

ϵ , cm ⁻¹	ϵ_1
0	[5]
[800]	[10]
[3000]	[5]
[5000]	[5]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹
327 (1)
[135] (2)
492 (1)

Bond Distances Fe-Cl = [2.09] Å

Bond Angles Cl-Fe-Cl = [180]°

Rotational Constant B₀ = [0.05442] cm⁻¹

Heat of Formation

The equilibrium pressures for the reactions: (1) FeCl₂(l) = FeCl₂(g); (2) FeCl₂(c) = FeCl₂(g); and (3) Fe(c) + 2HCl(g) = FeCl₂(g) + H₂(g) were determined by several investigators. Using the reported data, the corresponding enthalpy changes (ΔH_f^o , 298.15°) for these reactions were evaluated by both the second and third law methods. Hence the respective ΔH_f^o , 298.15 values for FeCl₂(g) were derived, based on the third law values for ΔH_f^o , 298.15°. The results obtained are presented as follows.

Investigator	Reaction	Temperature, °K.	Second Law Value	Third Law Value	ΔH_f^o , 298.15° kcal. mole ⁻¹
Beuman ¹	(1)	980.2-1167.2	37.07 ± 0.61	36.42	-35.45 ± 0.30
Schoonmaker and Porten ²	(2)	621.0-701.0	45.61 ± 0.10	46.14	-35.56 ± 0.20
H. Schäfer, et al. ³	(1)	981.0-1107.0	38.95 ± 0.10	37.77	-36.10 ± 0.30
Schäfer and Krehl ⁴	(1)	980.7-1108.7	40.56 ± 1.45	37.78	-39.11 ± 0.50
C. G. Meier ⁵	(1)	972.1-1268.0	38.68 ± 0.18	37.95	-35.92 ± 0.30
Schäfer and Krehl ⁴	(3)	1205.2-1373.2	4.10 ± 0.13	8.01	-36.13 ± 0.50

¹ C. Beuman, "Activities in the KCl-FeCl₂ and LiCl-FeCl₂ Systems", ORNL-2323, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1957.

² R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. **29**, 116 (1956).

³ H. Schäfer, L. Bayer, G. Breil, K. Etzel and K. Krehl, Z. anorg. allgem. Chem. **278**, 300 (1955).

⁴ H. Schäfer and K. Krehl, Z. anorg. allgem. Chem. **266**, 35 (1952).

The value of ΔH_f^o , 298.15 for FeCl₂(g) adopted is -35.5 ± 2.0 kcal. mole⁻¹.

Heat Capacity and Entropy

The molecular structure, bond distance and angle, and two vibrational frequencies (ν_1 and ν_3) were obtained from L. Brewer, G. R. Sonzogni and E. Brackett, Chem. Rev. **63**, 111 (1963). The electronic levels and quantum weights were estimated by comparison with the electronic levels in Fe²⁺(g) reported by C. E. Moore, "Atomic Energy Levels", Circular of the National Bureau of Standards 467, Vol. II, 1952, using the reasoning suggested by J. T. Hougen, O. E. Leroi and T. C. James, J. Chem. Phys. **34**, 1970 (1961). The total 2S for the quantum weight was obtained from the ground multiplet of Fe²⁺ and was split arbitrarily. The bending frequency (ν_2) was derived such that the calculated free energy functions are consistent with the experimental equilibrium data. In other words, the free energy functions were adjusted by choosing a proper value for ν_2 in order to make the second and third law values of ΔH_f^o for the reaction in reasonable agreement. The moment of inertia (I) is 5.1426×10^{-38} g. cm².

Cl₂Fe

Dichlorosilane (SiH₂Cl₂)

(Ideal Gas) Mol. Wt. = 101.02

INTERIM TABLE

T, °K.	C _p ^o	S ^o	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
100	4.000	56.003	14.611	3.498	73.920	73.920	14.611
200	4.183	56.063	14.611	3.498	73.920	73.920	14.611
300	4.366	56.123	14.611	3.498	73.920	73.920	14.611
400	4.549	56.183	14.611	3.498	73.920	73.920	14.611
500	4.732	56.243	14.611	3.498	73.920	73.920	14.611
600	4.915	56.303	14.611	3.498	73.920	73.920	14.611
700	5.098	56.363	14.611	3.498	73.920	73.920	14.611
800	5.281	56.423	14.611	3.498	73.920	73.920	14.611
900	5.464	56.483	14.611	3.498	73.920	73.920	14.611
1000	5.647	56.543	14.611	3.498	73.920	73.920	14.611
1100	5.830	56.603	14.611	3.498	73.920	73.920	14.611
1200	6.013	56.663	14.611	3.498	73.920	73.920	14.611
1300	6.196	56.723	14.611	3.498	73.920	73.920	14.611
1400	6.379	56.783	14.611	3.498	73.920	73.920	14.611
1500	6.562	56.843	14.611	3.498	73.920	73.920	14.611
1600	6.745	56.903	14.611	3.498	73.920	73.920	14.611
1700	6.928	56.963	14.611	3.498	73.920	73.920	14.611
1800	7.111	57.023	14.611	3.498	73.920	73.920	14.611
1900	7.294	57.083	14.611	3.498	73.920	73.920	14.611
2000	7.477	57.143	14.611	3.498	73.920	73.920	14.611
2100	7.660	57.203	14.611	3.498	73.920	73.920	14.611
2200	7.843	57.263	14.611	3.498	73.920	73.920	14.611
2300	8.026	57.323	14.611	3.498	73.920	73.920	14.611
2400	8.209	57.383	14.611	3.498	73.920	73.920	14.611
2500	8.392	57.443	14.611	3.498	73.920	73.920	14.611
2600	8.575	57.503	14.611	3.498	73.920	73.920	14.611
2700	8.758	57.563	14.611	3.498	73.920	73.920	14.611
2800	8.941	57.623	14.611	3.498	73.920	73.920	14.611
2900	9.124	57.683	14.611	3.498	73.920	73.920	14.611
3000	9.307	57.743	14.611	3.498	73.920	73.920	14.611
3100	9.490	57.803	14.611	3.498	73.920	73.920	14.611
3200	9.673	57.863	14.611	3.498	73.920	73.920	14.611
3300	9.856	57.923	14.611	3.498	73.920	73.920	14.611
3400	10.039	57.983	14.611	3.498	73.920	73.920	14.611
3500	10.222	58.043	14.611	3.498	73.920	73.920	14.611
3600	10.405	58.103	14.611	3.498	73.920	73.920	14.611
3700	10.588	58.163	14.611	3.498	73.920	73.920	14.611
3800	10.771	58.223	14.611	3.498	73.920	73.920	14.611
3900	10.954	58.283	14.611	3.498	73.920	73.920	14.611
4000	11.137	58.343	14.611	3.498	73.920	73.920	14.611
4100	11.320	58.403	14.611	3.498	73.920	73.920	14.611
4200	11.503	58.463	14.611	3.498	73.920	73.920	14.611
4300	11.686	58.523	14.611	3.498	73.920	73.920	14.611
4400	11.869	58.583	14.611	3.498	73.920	73.920	14.611
4500	12.052	58.643	14.611	3.498	73.920	73.920	14.611
4600	12.235	58.703	14.611	3.498	73.920	73.920	14.611
4700	12.418	58.763	14.611	3.498	73.920	73.920	14.611
4800	12.601	58.823	14.611	3.498	73.920	73.920	14.611
4900	12.784	58.883	14.611	3.498	73.920	73.920	14.611
5000	12.967	58.943	14.611	3.498	73.920	73.920	14.611
5100	13.150	59.003	14.611	3.498	73.920	73.920	14.611
5200	13.333	59.063	14.611	3.498	73.920	73.920	14.611
5300	13.516	59.123	14.611	3.498	73.920	73.920	14.611
5400	13.699	59.183	14.611	3.498	73.920	73.920	14.611
5500	13.882	59.243	14.611	3.498	73.920	73.920	14.611
5600	14.065	59.303	14.611	3.498	73.920	73.920	14.611
5700	14.248	59.363	14.611	3.498	73.920	73.920	14.611
5800	14.431	59.423	14.611	3.498	73.920	73.920	14.611
5900	14.614	59.483	14.611	3.498	73.920	73.920	14.611
6000	14.797	59.543	14.611	3.498	73.920	73.920	14.611

December 31, 1960.

Dichlorosilane (SiH₂Cl₂) (Ideal Gas)

Mol. Wt. = 101.02

ΔH_f^o 298.15 = [-60 ± 15] kcal. mole⁻¹

S_{298.15}^o = 68.531 cal. deg.⁻¹ mole⁻¹

Point group C_{2v}

Vibrational Frequencies and Degeneracies

cm.⁻¹

2200 (1) 166 (1) 610 (1)

953 (1) 710 (1) 877 (1)

531 (1) 2200 (1) 592 (1)

SI-H distance = 1.48 Å

SI-Cl distance = 2.05 Å

Product of Moments of Inertia: I_AI_BI_C = 7.9175 × 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation. ΔH_f^o 298.15 taken from Henderson and Schaeffer,

"Survey of Thermochemical Data," Atlantic Research Corp.,

Alexandria, Va., January, 1960.

Heat Capacity and Entropy. Molecular constants taken from Janz

and Mikawa, Bull. Chem. Soc. Japan 34, 1495 (1961).

Cl₂H₂Si

Mercury Dichloride (HgCl₂)

INTERIM TABLE

(Crystal) Mol. Wt. = 271.524

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° cal. mole ⁻¹	ΔH _f ⁰ cal. mole ⁻¹	ΔF _f ⁰	Log K _p
0						
100						
298	17.464	34.535	.000	-55.000	-43.991	32.245
300	17.680	34.644	.013	-54.994	-43.972	31.966
400	18.540	35.475	.408	-54.587	-43.565	31.006
500	19.295	36.002	1.258	-54.316	-43.294	30.286
600	19.970	36.372	2.507	-54.086	-43.064	29.726
700	20.590	36.612	4.067	-53.806	-42.784	29.306
800	21.170	36.752	5.867	-53.476	-42.454	29.026
900	21.710	36.802	7.867	-53.096	-42.074	28.846
1000	22.210	36.772	10.017	-52.666	-41.644	28.726
1100	22.680	36.672	12.267	-52.186	-41.164	28.646
1200	23.120	36.502	14.567	-51.656	-40.634	28.606
1300	23.530	36.272	16.867	-51.076	-40.054	28.606
1400	23.910	35.992	19.117	-50.446	-39.424	28.636
1500	24.260	35.662	21.317	-49.766	-38.744	28.686

March 31, 1962

MERCURY DICHLORIDE (HgCl₂)

(Crystal)

Mol. Wt. = 271.524

 $\Delta H_f^{298.15} = -55.000 \pm 1.0$ kcal. mole⁻¹ $S_{298.15}^{298.15} = [34.535] \pm 1.5$ cal. deg.⁻¹ mole⁻¹ $T_m = 550^\circ K$ $\Delta H_m = 4.64 \pm 0.05$ kcal. mole⁻¹

Heat of Formation. Taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," (1952).

Heat Capacity and Entropy. C_p was determined from the heat content data of L. E. Topol and L. D. Ransom, J. Phys. Chem. 54, 1359 (1960) and R. Ewald, Ann. d. Physik u. Chem. (4) 44, 1213 (1914).

Above 550° the curve was smoothly extrapolated. The entropy was estimated by adjusting the value to give the best fit of the melting, sublimation, and vaporization data.

Melting. T_m was taken from National Bureau of Standards Circular 500 (loc. cit.) ΔH_m was given by L. E. Topol and L. D. Ransom (loc. cit.).

Mercury Dichloride (HgCl₂)
(Liquid) Mol. Wt. = 271.524

INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
		cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	cal. mole ⁻¹		
0						
100						
200						
298	17.664	40.721	0.000	- 51.404	- 42.239	30.961
300	17.690	40.830	0.33	- 51.398	- 42.182	30.728
400	24.400	46.550	41.447	- 50.881	- 39.165	24.358
500	24.400	51.995	43.032	- 49.946	- 36.344	15.885
600	24.400	56.464	44.908	- 49.024	- 33.711	12.279
700	24.400	60.205	46.812	- 48.107	- 31.260	9.260
800	24.400	63.445	48.741	- 47.200	- 28.988	6.675
900	24.400	66.317	50.513	- 46.302	- 26.858	4.451
1000	24.400	68.908	52.226	- 45.417	- 24.841	3.571
1100	24.400	71.233	53.850	- 44.541	- 22.931	2.910
1200	24.400	73.329	55.389	- 43.681	- 21.126	2.410
1300	24.400	75.157	56.859	- 42.841	- 19.421	1.959
1400	24.400	76.771	58.231	- 42.020	- 17.807	1.559
1500	24.400	78.101	59.547	- 41.211	- 16.284	1.204
				- 40.411	- 14.848	0.884
				- 39.621	- 13.491	0.594
				- 38.841	- 12.211	0.334
				- 38.071	- 11.001	0.104
				- 37.311	- 9.851	- 0.104
				- 36.561	- 8.751	- 0.354
				- 35.821	- 7.701	- 0.634
				- 35.091	- 6.701	- 0.934
				- 34.371	- 5.741	- 1.254
				- 33.661	- 4.821	- 1.594
				- 32.961	- 3.941	- 1.954
				- 32.271	- 3.101	- 2.334
				- 31.591	- 2.291	- 2.734
				- 30.921	- 1.521	- 3.154
				- 30.261	- 0.791	- 3.594
				- 29.611	- 0.101	- 4.054
				- 28.971	0.541	- 4.534
				- 28.341	1.211	- 5.034
				- 27.721	1.911	- 5.554
				- 27.111	2.641	- 6.094
				- 26.511	3.401	- 6.654
				- 25.921	4.191	- 7.234
				- 25.341	5.011	- 7.834
				- 24.771	5.861	- 8.454
				- 24.211	6.741	- 9.094
				- 23.661	7.651	- 9.754
				- 23.121	8.591	- 10.434
				- 22.591	9.561	- 11.134
				- 22.071	10.561	- 11.854
				- 21.561	11.591	- 12.594
				- 21.061	12.641	- 13.354
				- 20.571	13.711	- 14.134
				- 20.091	14.801	- 14.934
				- 19.621	15.911	- 15.754
				- 19.161	17.041	- 16.594
				- 18.711	18.191	- 17.454
				- 18.271	19.361	- 18.334
				- 17.841	20.551	- 19.234
				- 17.421	21.761	- 20.154
				- 17.011	22.991	- 21.094
				- 16.611	24.241	- 22.054
				- 16.221	25.511	- 23.034
				- 15.841	26.801	- 24.034
				- 15.471	28.111	- 25.054
				- 15.111	29.441	- 26.094
				- 14.761	30.791	- 27.154
				- 14.421	32.161	- 28.234
				- 14.091	33.551	- 29.334
				- 13.771	34.961	- 30.454
				- 13.461	36.391	- 31.594
				- 13.161	37.841	- 32.754
				- 12.871	39.311	- 33.934
				- 12.591	40.801	- 35.134
				- 12.321	42.311	- 36.354
				- 12.061	43.841	- 37.594
				- 11.811	45.391	- 38.854
				- 11.571	46.961	- 40.134
				- 11.341	48.551	- 41.434
				- 11.111	50.161	- 42.754
				- 10.891	51.791	- 44.094
				- 10.681	53.441	- 45.454
				- 10.481	55.111	- 46.834
				- 10.291	56.801	- 48.234
				- 10.111	58.511	- 49.654
				- 9.941	60.241	- 51.094
				- 9.781	62.001	- 52.554
				- 9.631	63.781	- 54.034
				- 9.491	65.581	- 55.534
				- 9.361	67.401	- 57.054
				- 9.241	69.241	- 58.594
				- 9.131	71.101	- 60.154
				- 9.031	72.981	- 61.734
				- 8.941	74.881	- 63.334
				- 8.861	76.801	- 64.954
				- 8.791	78.741	- 66.594
				- 8.731	80.701	- 68.254
				- 8.681	82.681	- 69.934
				- 8.641	84.681	- 71.634
				- 8.611	86.701	- 73.354
				- 8.591	88.741	- 75.094
				- 8.571	90.801	- 76.854
				- 8.561	92.881	- 78.634
				- 8.561	94.981	- 80.434
				- 8.571	97.101	- 82.254
				- 8.591	99.241	- 84.094
				- 8.621	101.401	- 85.954
				- 8.661	103.581	- 87.834
				- 8.711	105.781	- 89.734
				- 8.771	107.991	- 91.654
				- 8.841	110.221	- 93.594
				- 8.921	112.471	- 95.554
				- 9.011	114.741	- 97.534
				- 9.111	117.031	- 99.534
				- 9.221	119.341	- 101.554
				- 9.341	121.671	- 103.594
				- 9.471	124.021	- 105.654
				- 9.611	126.391	- 107.734
				- 9.761	128.781	- 109.834
				- 9.921	131.191	- 111.954
				- 10.091	133.621	- 114.094
				- 10.271	136.071	- 116.254
				- 10.461	138.541	- 118.434
				- 10.661	141.031	- 120.634
				- 10.871	143.541	- 122.854
				- 11.091	146.071	- 125.094
				- 11.321	148.621	- 127.354
				- 11.561	151.191	- 129.634
				- 11.811	153.781	- 131.934
				- 12.071	156.391	- 134.254
				- 12.341	159.021	- 136.594
				- 12.621	161.671	- 138.954
				- 12.911	164.341	- 141.334
				- 13.211	167.031	- 143.734
				- 13.521	169.741	- 146.154
				- 13.841	172.471	- 148.594
				- 14.171	175.221	- 151.054
				- 14.511	177.991	- 153.534
				- 14.861	180.781	- 156.034
				- 15.221	183.591	- 158.554
				- 15.591	186.421	- 161.094
				- 15.971	189.271	- 163.654
				- 16.361	192.141	- 166.234
				- 16.761	195.031	- 168.834
				- 17.171	197.941	- 171.454
				- 17.591	200.871	- 174.094
				- 18.021	203.821	- 176.754
				- 18.461	206.791	- 179.434
				- 18.911	209.781	- 182.134
				- 19.371	212.791	- 184.854
				- 19.841	215.821	- 187.594
				- 20.321	218.871	- 190.354
				- 20.811	221.941	- 193.134
				- 21.311	225.031	- 195.934
				- 21.821	228.141	- 198.754
				- 22.341	231.271	- 201.594
				- 22.871	234.421	- 204.454
				- 23.411	237.591	- 207.334
				- 23.961	240.781	- 210.234
				- 24.521	243.991	- 213.154
				- 25.091	247.221	- 216.094
				- 25.671	250.471	- 219.054
				- 26.261	253.741	- 222.034
				- 26.861	257.031	- 225.034
				- 27.471	260.341	- 228.054
				- 28.091	263.671	- 231.094
				- 28.721	267.021	- 234.154
				- 29.361	270.391	- 237.234
				- 30.011	273.781	- 240.334
				- 30.671	277.191	- 243.454
				- 31.341	280.621	- 246.594
				- 32.021	284.071	- 249.754
				- 32.711	287.541	- 252.934
				- 33.411	291.031	- 256.134
				- 34.121	294.541	- 259.354
				- 34.841	298.071	- 262.594
				- 35.571	301.621	- 265.854
				- 36.311	305.191	- 269.134
				- 37.061	308.781	- 272.434
				- 37.821	312.391	- 275.754
				- 38.591	316.021	- 279.094
				- 39.371	319.671	- 282.454
				- 40.161	323.341	- 285.834
				- 40.961	327.031	- 289.234
				- 41.771	330.741	- 292.654
				- 42.591	334.471	- 296.094
				- 43.421	338.221	- 299.554
				- 44.261	341.991	- 303.034
				- 45.111	345.781	- 306.534
				- 45.971	349.591	- 310.054
				- 46.841	353.421	- 313.594
				- 47.721	357.271	- 317.154
				- 48.611	361.141	- 320.734
				- 49.511	365.031	- 324.334
				- 50.421	368.941	- 327.954
				- 51.341	372.871	- 331.594
				- 52.271	376.821	- 335.254
				- 53.211	380.791	- 338.934
				- 54.161	384.781	- 342.634
				- 55.121	388.791	- 346.354
				- 56.091	392.821	- 350.094
				- 57.071	396.871	- 353.854
				- 58.061	400.941	- 357.634
				- 59.061	405.031	- 361.434
				- 60.071	409.141	- 365.254
				- 61.091	413.271	- 369.094
				- 62.121	417.421	- 372.954
				- 63.161	421.591	- 376.834
			</			

Mercury Dichloride (HgCl₂)
(Ideal Gas) Mol. Wt. = 271.524 INTERIM TABLE

T, °K.	C _p	S° cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	ΔH° _f	Log K _p
0	11.099	56.705	82.117	34.018	INFINITE	
100	13.015	65.049	71.480	34.188	75.286	
200	13.889	70.433	63.965	34.311	37.873	
300	14.290	74.519	58.633	34.365	25.404	
400	14.621	77.794	54.094	34.457	25.246	
500	14.899	80.450	50.236	34.585	25.071	
600	15.129	82.566	46.936	34.740	24.881	
700	15.311	84.275	44.041	34.918	24.678	
800	15.451	85.641	41.517	35.115	24.455	
900	15.558	86.702	39.312	35.325	24.208	
1000	15.633	87.500	37.384	35.545	23.935	
1100	15.678	88.084	35.684	35.770	23.637	
1200	15.699	88.484	34.172	36.000	23.315	
1300	15.699	88.730	32.800	36.230	22.970	
1400	15.678	88.841	31.530	36.460	22.605	
1500	15.633	88.824	30.340	36.690	22.220	
1600	15.558	88.675	29.200	36.920	21.815	
1700	15.451	88.400	28.100	37.150	21.390	
1800	15.311	87.999	27.030	37.380	20.945	
1900	15.129	87.484	26.000	37.610	20.480	
2000	14.899	86.861	25.000	37.840	19.995	
2100	14.621	86.136	24.030	38.070	19.490	
2200	14.290	85.312	23.090	38.300	18.965	
2300	13.889	84.299	22.180	38.530	18.420	
2400	13.415	83.117	21.300	38.760	17.855	
2500	12.889	81.684	20.450	39.000	17.270	
2600	12.311	80.000	19.630	39.230	16.665	
2700	11.684	78.084	18.840	39.460	16.040	
2800	11.015	75.936	18.080	39.690	15.395	
2900	10.300	73.561	17.350	39.920	14.730	
3000	9.536	70.961	16.640	40.150	14.045	
3100	8.730	68.136	15.950	40.380	13.340	
3200	7.884	65.084	15.280	40.610	12.615	
3300	6.999	61.812	14.630	40.840	11.870	
3400	6.075	58.341	14.000	41.070	11.105	
3500	5.112	54.684	13.390	41.300	10.320	
3600	4.109	50.841	12.800	41.530	9.515	
3700	3.075	46.812	12.230	41.760	8.690	
3800	2.012	42.600	11.680	41.990	7.845	
3900	0.919	38.216	11.150	42.220	6.980	
4000	-0.199	33.661	10.640	42.450	6.095	
4100	-1.229	28.946	10.150	42.680	5.190	
4200	-2.275	24.084	9.680	42.910	4.265	
4300	-3.336	19.084	9.230	43.140	3.320	
4400	-4.412	13.946	8.800	43.370	2.355	
4500	-5.494	8.684	8.390	43.600	1.370	
4600	-6.581	3.312	8.000	43.830	0.365	
4700	-7.675	-2.159	7.630	44.060	-0.660	
4800	-8.775	-7.484	7.280	44.290	-1.615	
4900	-9.881	-12.700	6.950	44.520	-2.500	
5000	-10.994	-17.800	6.640	44.750	-3.315	
5100	-12.115	-22.784	6.350	44.980	-4.060	
5200	-13.244	-27.641	6.080	45.210	-4.735	
5300	-14.381	-32.372	5.830	45.440	-5.340	
5400	-15.525	-36.984	5.600	45.670	-5.875	
5500	-16.675	-41.484	5.390	45.900	-6.340	
5600	-17.831	-45.884	5.200	46.130	-6.735	
5700	-18.994	-50.184	5.030	46.360	-7.060	
5800	-20.164	-54.384	4.880	46.590	-7.315	
5900	-21.341	-58.484	4.750	46.820	-7.490	
6000	-22.525	-62.484	4.640	47.050	-7.585	

March 31, 1962

MERCURY DICHLORIDE (HgCl₂) (Ideal Gas)

Mol. Wt. = 271.524
ΔH_f° 298.15 = -34.985 ± 1.5 kcal. mole⁻¹
S° 298.15 = 70.433 cal. deg⁻¹ mole⁻¹
Point Group D_{2h}

Vibrational Levels and Multiplicities

ω, cm.⁻¹
380 { 1
70 { 2
413 { 1

Hg-Cl distance = 2.31 Å

Moment of Inertia = 62.622 X 10⁻³⁹ g. cm.² σ = 2

Heat of Formation. The heat of formation of the crystal as given in National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952 was combined with the 3rd law heat of sublimation at 298°K from the data of K. Nishida and Z. Shibata, J. Fac. Sci. Hokkaido Imp. Univ. Ser. III, 2, 193 (1955); R. Ruf and W. D. Treadwell, Helv. Chim. Acta 37, 1941 (1954) and P. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

Heat Capacity and Entropy. The vibrational constants were given by W. Klemperer and L. Lindeman, J. Chem. Phys. 25, 397 (1956). The bond length is a weighted average of the values given by H. Braune and S. Knoke Naturwiss. 21, 349 (1933); A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton Trans. Farad. Soc. 33, 852, 1937; L. R. Maxwell and V. M. Moulay Phys. Rev. 57, 21 (1946) and P. A. Akshat, V. P. Spiridonov and A. N. Knouchenkov, Zhur. Fiz. Khim. 33, 20 (1959).



Mercury Monochloride, Dimeric (Hg_2Cl_2)

(Crystal) Mol. Wt. = 472.134 INTERIM TABLE

T. °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	18.000	0.000	INFINITE	5.611	62.269	62.269	INFINITE
100	22.820	22.584	46.017	2.423	62.554	59.530	15.143
200	25.820	28.202	46.017	.000	63.319	50.315	36.680
298	24.771	46.017	46.017	.045	63.312	50.234	36.584
300	24.390	46.168	46.017	2.533	62.559	41.705	36.584
400	25.340	53.318	46.017	5.107	62.559	41.705	18.228
500	26.130	59.060	46.017	7.755	62.079	37.580	13.688
600	26.800	63.884	50.940	10.464	62.079	37.580	9.489
700	27.380	68.060	53.111	13.230	62.079	37.580	6.009
800	27.970	71.752	55.215	16.046	62.079	37.580	3.330
900	28.400	75.089	57.240	18.909	62.079	37.580	1.210
1000	28.840	78.084	59.176	21.813	62.079	37.580	.505
1100	29.240	80.852	61.022	24.755	62.079	37.580	1.917
1200	29.600	83.412	62.783	27.732	62.079	37.580	3.097
1300	29.916	85.794	64.462	30.737	62.079	37.580	4.095
1400	30.189	88.021	66.066	33.768	62.079	37.580	4.949
1500	30.420	90.112	67.600		62.079	37.580	

MERCURY MONOCHLORIDE, DIMERIC (Hg_2Cl_2) (CRYSTAL)

MOL. WT. = 472.134

$\Delta H_f^\circ 298.15 = -63.319 \pm 0.05 \text{ kcal mole}^{-1}$

$S_{298.15}^\circ = 46.017 \text{ cal deg}^{-1} \text{ mole}^{-1}$

$T_{\text{sub.}} = 655^\circ \text{K (decomp.)}$

Heat of Formation

Based on the average free energy of formation, $-50.315 \text{ kcal mole}^{-1}$, as measured by R. H. Gerke, J. Am. Chem. Soc. 44, 1684 (1922) and G. J. Hills and D. J. G. Ives, J. Chem. Soc. (London) 318, (1951), and the entropy of formation.

Heat Capacity

The data of F. Pollitzer, Zeits. f. Electrochemie 19, 513 (1913), from 22-199°K was treated by K. K. Kelley, U. S. Bureau of Mines Bulletin 592 (1960). The heat capacities listed by Kelley were raised by 0.05 to match the entropy data of Gerke (loc. cit.). Data above room temperature were obtained by smooth extrapolation.

Entropy

A mean value of the entropy of formation of -46.614 e.u. was adopted from the cell measurements of R. H. Gerke (loc. cit.).

Sublimation

The vapor pressure over mercurous chloride reaches 1 atmosphere at 655°K according to A. Smith and A. W. C. Menzies, J. Am. Chem. Soc. 32, 1541 (1910). At this point the vapor is dissociated into Hg(g) and $\text{HgCl}_2(\text{g})$.

Potassium Chloride, Dimeric (K₂Cl₂)

(Ideal Gas) Mol. Wt. = 149.110

POTASSIUM CHLORIDE, DIMERIC (K₂Cl₂)

(IDEAL GAS)

MOL. WT. = 149.110

T, °K.	C _p	S° cal. mole ⁻¹ deg ⁻¹	(S° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔG _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	16.145	64.482	100.078	- 4.812	- 146.852	- 146.852	INFINITE
200	18.714	76.700	86.062	- 3.650	- 147.219	- 147.219	322.243
298	19.327	84.309	84.309	- 1.872	- 147.402	- 147.597	161.286
300	19.333	84.429	84.310	- 1.836	- 147.420	- 147.652	108.231
400	19.673	94.405	86.516	- 3.965	- 147.625	- 147.652	107.564
500	19.770	101.043	97.998	- 5.915	- 147.652	- 147.652	60.431
600	19.773	103.084	97.998	- 5.915	- 147.652	- 147.652	60.431
700	19.773	105.084	97.998	- 5.915	- 147.652	- 147.652	60.431
800	19.773	107.084	97.998	- 5.915	- 147.652	- 147.652	60.431
900	19.773	109.084	97.998	- 5.915	- 147.652	- 147.652	60.431
1000	19.773	111.084	97.998	- 5.915	- 147.652	- 147.652	60.431
1100	19.830	109.994	95.619	- 5.813	- 146.807	- 146.807	27.980
1200	19.837	111.720	96.889	- 5.717	- 146.807	- 146.807	24.845
1300	19.842	113.708	97.998	- 5.621	- 146.807	- 146.807	22.193
1400	19.845	115.708	99.000	- 5.525	- 146.807	- 146.807	19.541
1500	19.849	117.710	100.000	- 5.429	- 146.807	- 146.807	17.953
1600	19.852	119.724	101.345	- 5.335	- 146.807	- 146.807	16.232
1700	19.854	121.753	102.927	- 5.242	- 146.807	- 146.807	14.714
1800	19.856	123.796	104.746	- 5.150	- 146.807	- 146.807	13.365
1900	19.858	125.843	106.801	- 5.058	- 146.807	- 146.807	12.161
2000	19.859	127.894	109.021	- 4.967	- 146.807	- 146.807	11.073
2100	19.860	129.949	111.416	- 4.876	- 146.807	- 146.807	10.092
2200	19.861	132.009	113.973	- 4.785	- 146.807	- 146.807	9.200
2300	19.862	134.073	116.698	- 4.694	- 146.807	- 146.807	8.385
2400	19.863	136.141	119.581	- 4.603	- 146.807	- 146.807	7.649
2500	19.864	138.213	122.622	- 4.512	- 146.807	- 146.807	6.953
2600	19.864	140.289	125.827	- 4.421	- 146.807	- 146.807	6.319
2700	19.865	142.369	129.196	- 4.330	- 146.807	- 146.807	5.733
2800	19.865	144.453	132.727	- 4.239	- 146.807	- 146.807	5.192
2900	19.866	146.541	136.416	- 4.148	- 146.807	- 146.807	4.692
3000	19.866	148.633	140.263	- 4.057	- 146.807	- 146.807	4.208
3100	19.866	150.729	144.273	- 3.966	- 146.807	- 146.807	3.765
3200	19.867	152.829	148.446	- 3.875	- 146.807	- 146.807	3.350
3300	19.867	154.934	152.781	- 3.784	- 146.807	- 146.807	2.959
3400	19.867	157.043	157.281	- 3.693	- 146.807	- 146.807	2.592
3500	19.868	159.156	161.946	- 3.602	- 146.807	- 146.807	2.245
3600	19.868	161.273	166.781	- 3.511	- 146.807	- 146.807	1.917
3700	19.868	163.394	171.781	- 3.420	- 146.807	- 146.807	1.606
3800	19.869	165.519	176.946	- 3.329	- 146.807	- 146.807	1.312
3900	19.869	167.648	182.281	- 3.238	- 146.807	- 146.807	1.037
4000	19.869	169.781	187.781	- 3.147	- 146.807	- 146.807	0.785
4100	19.869	171.918	193.446	- 3.056	- 146.807	- 146.807	0.511
4200	19.869	174.059	199.281	- 2.965	- 146.807	- 146.807	0.268
4300	19.870	176.204	205.281	- 2.874	- 146.807	- 146.807	0.037
4400	19.870	178.353	211.446	- 2.783	- 146.807	- 146.807	0.000
4500	19.870	180.506	217.781	- 2.692	- 146.807	- 146.807	- 0.398
4600	19.870	182.663	224.281	- 2.601	- 146.807	- 146.807	- 0.603
4700	19.870	184.824	230.946	- 2.510	- 146.807	- 146.807	- 0.799
4800	19.870	186.989	237.781	- 2.419	- 146.807	- 146.807	- 0.986
4900	19.870	189.158	244.781	- 2.328	- 146.807	- 146.807	- 1.162
5000	19.870	191.331	251.946	- 2.237	- 146.807	- 146.807	- 1.347
5100	19.870	193.508	259.281	- 2.146	- 146.807	- 146.807	- 1.518
5200	19.870	195.689	266.781	- 2.055	- 146.807	- 146.807	- 1.683
5300	19.870	197.874	274.446	- 1.964	- 146.807	- 146.807	- 1.842
5400	19.870	199.963	282.281	- 1.873	- 146.807	- 146.807	- 1.996
5500	19.870	202.056	290.281	- 1.782	- 146.807	- 146.807	- 2.148
5600	19.870	204.153	298.446	- 1.691	- 146.807	- 146.807	- 2.295
5700	19.870	206.254	306.781	- 1.600	- 146.807	- 146.807	- 2.438
5800	19.870	208.359	315.281	- 1.509	- 146.807	- 146.807	- 2.577
5900	19.870	210.468	323.946	- 1.418	- 146.807	- 146.807	- 2.710
6000	19.870	212.581	332.781	- 1.327	- 146.807	- 146.807	- 2.847

Dec. 31, 1961 Mar. 31, 1966

Point Group D_{2h}S₂₉₈⁰ = [84.3] cal. deg⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH_f⁰ = -146.85 kcal. mole⁻¹ΔH_f⁰ 298.15 = -147.62 ± 1.0 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[219](1)	[104](1)
[108](1)	[184](1)
[180](1)	[100](1)

Bond Distance: Cl-K = [2.352] Å

Bond Angle: Cl-K-Cl = [100.8°]

Product of the Moments of Inertia: I_AI_BI_C = [2.875 X 10⁻¹¹²] g.³ cm.⁶

σ = 4

Heat of Formation

The heat of formation is calculated from that of KCl(g) using ΔH_f⁰ 298 = 45.0 kcal./mole for K₂Cl₂(g) - 2KCl(g) as selected from data analyses summarized below. The three experimental techniques include PVT measurements (source 1), combination of total vapor pressure and transpiration data (sources 2,3,4), and mass spectrometric studies of the variation of ion intensities with temperature (source 5). The results are reasonably consistent, considering the uncertainties inherent in the problem.

The resulting tables were tested by comparison with other data. Calculated total vapor pressures are in satisfactory agreement with the observed values over the range 820-1500°K.; however, near the boiling point they are lower by 6-18 percent [see KCl(g)]. Knudsen effusion data and transpiration data over KCl(c) have been reviewed by A. C. P. Pugh and R. F. Barron, *Trans. Faraday Soc.* 53, 671 (1958). These data suggest negligible dimer formation when combined with the total vapor pressures of V. Dietz, *J. Chem. Phys.* 4, 575 (1936). Calculated dimer formation (22 mole percent at 900°K.) agrees with the latter combination but calculated total pressures agree with those of Pugh & Barron. Velocity distribution studies of R. C. Miller and P. Kusch, *J. Chem. Phys.* 21, 981 (1957); 25, 860 (1956) suggest about 10 mole percent of dimer at 900°K. Thus, while minor inconsistencies do exist, it is not apparent that they exceed the combined experimental errors.

Source	Method	No. of Points	Temp. Range, °K.	ΔH _f ⁰ 298 kcal./mole	Drift eu
1. Dietz (1936)	PVT data	15	1310-1404	46.70±2.1	-0.5±1.6
2. Schrier (1957)	Trans. + Vap. Press.	10	1253-1372	46.6±1.5	-0.9±1.7
3. Schrier et al. (1959)	Trans. + Vap. Press.	10	1253-1372	44.7±1.5	-0.9±1.7
4. Barton et al. (1960)	Trans. + Vap. Press.	7	1250-1473	42.5±2.9	2.2±2.3
5. Milne et al. (1960)	Mass Spectrometry	—	774-1016	41.9±3.5	—

1. S. Dietz, ORNL-2933, Oak Ridge, Tenn., May 1960.
2. E. Schrier, *Phys. Rev.* 105, 1132 (1957).
3. E. Schrier, *Phys. Rev.* 105, 1132 (1957).
4. J. L. Barton and H. Bloom, *J. Phys. Chem.* 63, 1785 (1959); 60, 1413 (1956).
5. T. A. Milne and H. M. Klein, AFOSR TN 60-512, Menlo Park, Calif., Jun 1960.

Heat Capacity and Entropy

The structure and vibrational frequencies are those calculated from an ionic model by J. Berkowitz, *J. Chem. Phys.* 32, 1519 (1960); 22, 1386 (1958). The sixth fundamental was arbitrarily lowered from 206 to 100 cm⁻¹ since the resulting entropy increase (1.4 eu at 1300°K.) improved the overall agreement with the equilibrium data. Based on electron diffraction studies of the monomer-dimer vapor, P. A. Aklehin and N. O. Rambidi, *Zhur. Neorg. Khim.* 3, 718 (1959) have derived the bond distances and angle to be 2.81 Å and 98°. Interpretation of the diffraction data, however, is complicated by the presence of only about 30 mole percent of dimer at the temperature of measurement. Adoption of this dimer structure would reduce the entropy by 0.23 eu. Principal moments of inertia for the Berkowitz structure are I_A = 45.31 X 10⁻³⁹, I_B = 60.13 X 10⁻³⁹, and I_C = 105.45 X 10⁻³⁹ g. cm.²

Lithium Chloride, Dimeric (LiCl)₂
(Ideal Gas) Mol. Wt. = 84.794 INTERIM TABLE

T, K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	INFINITE	3.701	-142.353	-142.353	INFINITE
100	9.920	53.937	62.557	2.666	-142.557	-142.557	312.466
200	14.975	62.525	70.511	1.597	-142.789	-143.366	156.656
298	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
300	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
400	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
500	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
600	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
700	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
800	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
900	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
1000	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
1100	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
1200	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
1300	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
1400	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
1500	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
1600	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
1700	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
1800	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
1900	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
2000	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
2100	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
2200	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
2300	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
2400	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
2500	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
2600	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
2700	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
2800	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
2900	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
3000	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
3100	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
3200	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
3300	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
3400	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
3500	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
3600	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
3700	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
3800	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
3900	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
4000	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
4100	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
4200	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
4300	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
4400	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
4500	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
4600	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
4700	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
4800	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
4900	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
5000	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
5100	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
5200	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
5300	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
5400	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
5500	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
5600	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
5700	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
5800	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
5900	17.255	68.993	68.993	.000	-143.056	-143.591	105.250
6000	17.255	68.993	68.993	.000	-143.056	-143.591	105.250

June 30, 1962

Cl₂Li₂

Lithium Chloride, Dimeric (LiCl)₂ (Ideal Gas)

Mol. Wt. = 84.794
ΔH_f⁰ 298.15 = -143.056 ± 3.0 kcal. mole⁻¹
S_{298.15} = 68.993 cal. deg.⁻¹ mole⁻¹
Point Group = D_{2h}

Vibrational Levels and Multiplicities
ω, cm.⁻¹ ω, cm.⁻¹
(330) (1) (356) (1)
(298) (1) (335) (1)
(395) (1) (460) (1)

Bond Lengths and Angles Li-Cl distance = 2.23 Å
Li-Li distance = 2.62 Å Cl-Li-Cl angle = 108 ± 4° σ = 4

Moment of Inertia I_AI_BI_C = 6418 × 10⁻¹¹ g.³ cm.⁶

Heat of Formation. A heat of sublimation at 298° of 52.1 kcal. mole⁻¹ was chosen to fit the vapor pressure data and relative concentrations of monomer, dimer and trimer as described in the table for LiCl(g). This value is in reasonable agreement with the value of 53.5 kcal. mole⁻¹ from a 3rd law analysis of the vapor pressure data of An. N. Nesmeyanov and L. A. Sazonov, Zhur. Neorg. Khim. 4, 231 (1960) and the relative concentrations of monomer, dimer, and trimer from the work of R. C. Miller and P. Kuech, J. Chem. Phys. 25, 860 (1956). Also a value of 54.1 kcal. mole⁻¹ was found by T. A. Milne and H. M. Klein, J. Chem. Phys. 33, 1628 (1960), from mass spectrometer studies.

Heat Capacity and Entropy. W. Klemperer and W. G. Norris, J. Chem. Phys. 34, 1071 (1961), observed two bands in the infra-red spectrum and made tentative assignments. The remaining four frequencies were calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960), from a reasonable model. The bond lengths and angles were determined from the electron diffraction experiments of S. H. Bauer, T. Ino and R. F. Porter, J. Chem. Phys. 33, 685 (1960).

Cl₂Li₂

Magnesium Dichloride (MgCl₂)

(Crystal) Mol. wt. = 95.218

MAGNESIUM DICHLORIDE (MgCl₂)

(CRYSTAL)

MOL. WT. = 95.218

$$\Delta H_f^0 = -153.25 \pm 0.11 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -153.35 \pm 0.11 \text{ kcal. mole}^{-1}$$

$$\Delta H_m = 10.30 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^{298.15} = 57.5 \pm 1.5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 21.422 \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

$$T_m = 987^\circ \text{K.}$$

Heat of Formation.

The adopted $\Delta H_f^{298.15} = -153.35 \pm 0.11 \text{ kcal. mole}^{-1}$ is from heat of solution measurements reported by C. H. Shomate and E. H. Huffman, *J. Am. Chem. Soc.* 55, 1625 (1933). Shomate and Huffman's heat of solution of Mg in 1 M HCl ($\Delta H = -111.322 \pm 0.041 \text{ kcal. mole}^{-1}$) has been substantiated for calibration purposes by S. R. Dunn and B. B. Cunningham, *J. Am. Chem. Soc.*, 79, 1553 (1957) ($\Delta H = -111.3 \text{ kcal. mole}^{-1}$) and by E. F. Westrum Jr. and L. Eyring, *J. Am. Chem. Soc.*, 74, 2045 (1952) ($\Delta H = -111.27 \text{ kcal. mole}^{-1}$). Auxiliary heat of dilution and heat of formation data for HCl were taken from V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NBS-RS-2, Nat'l. Bur. Stds., April 1965 and from D. D. Wagman et al., N.B.S. Technical Note 270-1, Oct. 1965.

Heat Capacity and Entropy.

High temperature heat content data by O. E. Moore, *J. Am. Chem. Soc.* 65, 1700 (1943) were joined by Shomate correlation with low temperature heat capacity data reported by K. K. Kelley and O. E. Moore, *J. Am. Chem. Soc.* 65, 1264 (1943). $C_p(c)$ above T_m is a linear extrapolation from 700°K. $S_{298.15}^0$ is derived from the low temperature data and is based on $S_{53.6}^0 = 2.006 \text{ cal. deg}^{-1} \text{ mole}^{-1}$.

Melting Data.

$\Delta H_m = 10.30 \pm 0.05 \text{ kcal. mole}^{-1}$ is taken from heat content measurements of Moore loc. cit. $T_m = 987^\circ \text{K.}$ is from National Bureau of Standards Circular 500, 1952.

Sublimation Data.

The value of $\Delta H_g^{298.15}$ was derived by 2nd and 3rd law analyses of vapor pressure data. See the MgCl₂(g) table for details.

Dec. 31, 1960; Dec. 31, 1965

Cl₂Mg

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S ⁰ -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	-3.288	-153.248	-153.248	INFINITE
100	9.630	6.204	-2.888	-153.703	-149.577	326.884
200	15.195	14.977	-2.926	-153.688	-145.545	159.037
298	17.060	21.422	0.000	-153.350	-141.519	103.731
300	17.688	21.527	-0.932	-153.344	-141.446	103.038
400	18.095	26.594	1.796	-153.024	-137.528	75.138
500	18.677	30.701	3.636	-152.679	-133.692	58.434
600	19.090	34.144	5.525	-152.328	-129.928	47.324
700	19.420	37.111	7.451	-151.973	-126.222	39.406
800	19.680	39.864	9.397	-151.629	-122.566	33.488
900	20.040	42.467	13.417	-151.289	-118.956	28.885
1000	20.350	44.194	15.417	-151.062	-115.700	25.176
1100	20.654	46.148	15.467	-152.731	-111.430	22.138
1200	20.951	47.958	17.547	-152.378	-107.692	19.612
1300	21.242	49.566	19.647	-152.003	-104.380	17.400
1400	21.526	51.231	21.795	-151.603	-101.420	15.582
1500	21.805	52.726	23.962	-151.269	-98.875	13.691
1600	22.076	54.147	26.156	-150.480	-88.182	12.045
1700	22.342	55.498	28.377	-149.665	-82.435	10.597
1800	22.604	56.796	30.631	-148.731	-76.548	9.177
1900	22.864	58.001	32.897	-147.760	-71.092	8.177
2000	23.100	59.180	35.195	-147.075	-65.491	7.156

Magnesium Dichloride (MgCl₂)

(Liquid) Mol. Wt. = 95.218

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100	17.060	30.949	0.000	-143.779	-134.789	98.798
200	17.088	30.949	0.032	-143.773	-134.733	98.148
300	18.095	31.123	1.796	-143.453	-131.768	97.991
400	18.677	40.228	3.636	-143.108	-128.884	96.332
500	19.090	43.459	5.595	-142.777	-126.072	95.019
600	19.459	46.745	7.569	-142.484	-123.321	93.801
700	20.000	49.745	9.769	-141.695	-120.654	92.959
800	22.000	52.336	11.569	-141.146	-118.056	92.667
900	22.000	54.654	14.485	-142.759	-115.337	92.206
1000	22.000	56.751	16.269	-142.258	-112.621	92.375
1100	22.000	60.426	20.769	-141.340	-107.313	90.040
1200	22.000	62.056	22.969	-171.288	-104.231	16.270
1300	22.000	63.574	25.169	-170.491	-99.669	14.492
1400	22.000	64.994	27.269	-169.696	-94.762	12.943
1500	22.000	67.158	31.769	-168.110	-89.102	11.583
1600	22.000	68.775	33.969	-167.318	-80.920	9.307
1700	22.000	69.903	36.169	-166.530	-76.392	8.347
1800	22.000	70.977	38.369	-165.742	-71.008	7.483
1900	22.000	72.978	42.769	-164.173	-63.040	5.900
2000	22.000	73.914	44.969	-163.391	-58.660	5.341
2100	22.000	74.812	47.169	-162.613	-54.313	4.748
2200	22.000	75.676	49.369	-161.836	-49.995	4.202
2300	22.000	76.506	51.569	-161.065	-45.711	3.700
2400	22.000	77.306	53.769	-160.293	-41.453	3.235
2500	22.000	78.078	55.969	-159.526	-37.222	2.805
2600	22.000	78.824	58.169	-158.764	-33.019	2.405

MAGNESIUM DICHLORIDE (MgCl₂)

(LIQUID)

MOL. WT. = 95.218

Cl₂Mg

S_{298.15} = 30.949 cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^{298.15} = -143.779$ kcal. mole⁻¹
 $\Delta H_m^{298.15} = 10.30 \pm 0.05$ kcal. mole⁻¹
 $\Delta H_v^{298.15} = [37.34]$ kcal. mole⁻¹
 $T_m = 987^\circ\text{K.}$
 $T_b = [1710]^\circ\text{K.}$

Heat of Formation.

$\Delta H_f^{298.15}(l)$ was calculated from $\Delta H_f^{298.15}(c)$ by adding $\Delta H_m^{298.15}$ and the difference between $H_m^{298.15}$ and $H_l^{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A constant $C_p(l) = 22.0$ cal. deg.⁻¹ mole⁻¹ over the temperature range 1006-1428°K. is from the high temperature heat content data of G. E. Moore, J. Am. Chem. Soc. **65**, 1700 (1943). This constant value was assumed to hold from an assumed glass transition of 660°K. to 3000°K. $C_p(l)$ below 660°K. is taken to be that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See MgCl₂(c) table for details.

Vaporization Data.

T_b is calculated as the temperature at which the free energy change of the reaction $\text{MgCl}_2(l) = \text{MgCl}_2(g)$ approaches zero. The difference between $\Delta H_f^{298.15}$ for $\text{MgCl}_2(l)$ and $\text{MgCl}_2(g)$ at T_b is $\Delta H_v^{298.15}$.

Cl₂Mg

Magnesium Dichloride (MgCl₂)

(Ideal Gas) QFW = 95.218

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^c	Log K _p
0	11.000	10.000	10.000	0.000	0.000	10.000
100	11.006	10.006	10.006	0.006	0.006	10.006
200	11.012	10.012	10.012	0.012	0.012	10.012
300	11.018	10.018	10.018	0.018	0.018	10.018
400	11.024	10.024	10.024	0.024	0.024	10.024
500	11.030	10.030	10.030	0.030	0.030	10.030
600	11.036	10.036	10.036	0.036	0.036	10.036
700	11.042	10.042	10.042	0.042	0.042	10.042
800	11.048	10.048	10.048	0.048	0.048	10.048
900	11.054	10.054	10.054	0.054	0.054	10.054
1000	11.060	10.060	10.060	0.060	0.060	10.060
1100	11.066	10.066	10.066	0.066	0.066	10.066
1200	11.072	10.072	10.072	0.072	0.072	10.072
1300	11.078	10.078	10.078	0.078	0.078	10.078
1400	11.084	10.084	10.084	0.084	0.084	10.084
1500	11.090	10.090	10.090	0.090	0.090	10.090
1600	11.096	10.096	10.096	0.096	0.096	10.096
1700	11.102	10.102	10.102	0.102	0.102	10.102
1800	11.108	10.108	10.108	0.108	0.108	10.108
1900	11.114	10.114	10.114	0.114	0.114	10.114
2000	11.120	10.120	10.120	0.120	0.120	10.120
2100	11.126	10.126	10.126	0.126	0.126	10.126
2200	11.132	10.132	10.132	0.132	0.132	10.132
2300	11.138	10.138	10.138	0.138	0.138	10.138
2400	11.144	10.144	10.144	0.144	0.144	10.144
2500	11.150	10.150	10.150	0.150	0.150	10.150
2600	11.156	10.156	10.156	0.156	0.156	10.156
2700	11.162	10.162	10.162	0.162	0.162	10.162
2800	11.168	10.168	10.168	0.168	0.168	10.168
2900	11.174	10.174	10.174	0.174	0.174	10.174
3000	11.180	10.180	10.180	0.180	0.180	10.180
3100	11.186	10.186	10.186	0.186	0.186	10.186
3200	11.192	10.192	10.192	0.192	0.192	10.192
3300	11.198	10.198	10.198	0.198	0.198	10.198
3400	11.204	10.204	10.204	0.204	0.204	10.204
3500	11.210	10.210	10.210	0.210	0.210	10.210
3600	11.216	10.216	10.216	0.216	0.216	10.216
3700	11.222	10.222	10.222	0.222	0.222	10.222
3800	11.228	10.228	10.228	0.228	0.228	10.228
3900	11.234	10.234	10.234	0.234	0.234	10.234
4000	11.240	10.240	10.240	0.240	0.240	10.240
4100	11.246	10.246	10.246	0.246	0.246	10.246
4200	11.252	10.252	10.252	0.252	0.252	10.252
4300	11.258	10.258	10.258	0.258	0.258	10.258
4400	11.264	10.264	10.264	0.264	0.264	10.264
4500	11.270	10.270	10.270	0.270	0.270	10.270
4600	11.276	10.276	10.276	0.276	0.276	10.276
4700	11.282	10.282	10.282	0.282	0.282	10.282
4800	11.288	10.288	10.288	0.288	0.288	10.288
4900	11.294	10.294	10.294	0.294	0.294	10.294
5000	11.300	10.300	10.300	0.300	0.300	10.300
5100	11.306	10.306	10.306	0.306	0.306	10.306
5200	11.312	10.312	10.312	0.312	0.312	10.312
5300	11.318	10.318	10.318	0.318	0.318	10.318
5400	11.324	10.324	10.324	0.324	0.324	10.324
5500	11.330	10.330	10.330	0.330	0.330	10.330
5600	11.336	10.336	10.336	0.336	0.336	10.336
5700	11.342	10.342	10.342	0.342	0.342	10.342
5800	11.348	10.348	10.348	0.348	0.348	10.348
5900	11.354	10.354	10.354	0.354	0.354	10.354
6000	11.360	10.360	10.360	0.360	0.360	10.360

Dec. 31, 1950; Dec. 31, 1951; Dec. 31, 1959

Point Group D_{2h}S_{298.15}° = 66.184 ± 0.5 gibbs/mol

Ground State Quantum Weight = 1

ΔH_f° = -93.82 ± 0.5 kcal/molΔH_f°_{298.15} = -93.80 ± 0.5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	g
590 (1)	80 (2)
900 (2)	160 (4)
1273 (1)	127 (3)

Bond Distance: Mg-Cl = 2.10 Å
Bond Angle: Cl-Mg-Cl = 180°
Rotational Constant: B₀ = 0.05003 cm⁻¹
σ = 2

Heat of Formation

Analysis of vapor pressure data on MgCl₂ is clouded by conflicting evidence for the amount of dimer in the vapor. Berkowitz and Marquart (1) by mass spectrometer studies found about 21 dimer at 820°K and derived ΔH_D = -39.2 kcal/mol and ΔS_D = -29.9 gibbs/mol. Schriber and Clark (2) from gas transpiration data calculated about 30% dimer in the saturated vapor at 1100°K, with ΔH_D = -32.0 kcal/mol and ΔS_D = -18.8 gibbs/mol. Thermodynamic functions for the gaseous monomer adopted here are clearly not compatible with large amounts of dimer and it is assumed for the present that the mass spectrometer results are correct.

Several vapor pressure studies have been published and third law analyses are given below. Berkowitz and Marquart (1) gave a single point while the remaining publications gave only equations but not individual points. Total pressures calculated from the equations were corrected for dimer.

Source	Method	Temperature Range (°K)	ΔH _f ° (kcal/mol)
Berkowitz and Marquart (1)	Mass spectrometer	920	68.10
Schriber and Clark (2)	Boiling Point	1208-1413	59.55-59.68
Hildenbrand et al. (3)	Torsion-effusion	802-985	59.55-59.19
Hildenbrand et al. (4)	Torsion-effusion	800-970	58.53-59.38
Fischer et al. (5)	"Ball" method (total vapor pressures)	1138-1435	59.30-59.56

The selected value for ΔH_f°₂₉₈ is 59.55 kcal/mol which is combined with ΔH_f°₂₉₈ of the crystal to give ΔH_f°₂₉₈(s) = -83.80 kcal/mol.

Heat Capacity and Entropy

White, Mann, and co-workers (6) by matrix infrared spectroscopy determined the molecule to be linear with the asymmetric stretching frequency at 590 cm⁻¹ and the doubly degenerate bending frequency at 88 cm⁻¹. The symmetric stretching frequency was estimated as 273 cm⁻¹. The asymmetric stretching was observed by Buchler and Klemperer (7) at 597 cm⁻¹ and by Randall et al. (8) at 588 cm⁻¹, both by infrared spectroscopy of the vapor at high temperature. Electric deflection experiments by Klemperer and co-workers as summarized by Hayes (9) and the electron diffraction data of Akishin and Spiridonov (10) agree with the linear structure within their error limits of about 20°. The Mg-Cl bond length was determined as 2.18 Å by Akishin and Spiridonov (10).

References

1. J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, **37**, 1853 (1962).
2. E. E. Schriber and H. M. Clark, *J. Phys. Chem.*, **67**, 1259 (1963).
3. D. L. Hildenbrand, W. F. Hall, F. Ju, and N. D. Potter, *J. Chem. Phys.*, **40**, 2882 (1964).
4. D. L. Hildenbrand et al., *Aeronautics Report U-2183*, June, 1965.
5. W. Fischer, T. Patai, and S. Lauter, *Z. anorg. allgem. Chem.*, **333**, 226 (1964).
6. Unpublished work cited by D. L. Hildenbrand, *J. Chem. Phys.*, in press.
7. A. Buchler and W. Klemperer, *J. Chem. Phys.*, **29**, 121 (1958).
8. S. P. Randall, F. T. Greene, and J. L. Margrave, *J. Phys. Chem.*, **63**, 758 (1959).
9. E. F. Hayes, *J. Phys. Chem.*, **70**, 3740 (1966).
10. P. A. Akishin and V. P. Spiridonov, *Kristallografiya*, **2**, 475 (1957).

Molybdenum Dioxychloride (MoO₂Cl₂)
(Ideal Gas) GFW = 198.845

Point Group C_{2v}
S_{298.15} = 80.70 ± 1.30 gibbs/mol
Ground State Quantum Weight = 1
ΔH_{f,0}⁰ = -150.3 ± 3.5 kcal/mol
ΔH_{f,298.15}⁰ = -151.3 ± 3.5 kcal/mol

T, °K	Cp ^a	S ^b	-(G°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	kcal/mol ΔH ^c	Log Kp
0	+0.00	INFINITE		4.398	-150.333	INFINITE
100	12.763	62.512	96.872	3.436	-148.307	324.124
200	17.752	73.084	82.493	-1.862	-151.187	159.102
298	20.368	80.705	80.705	-1.862	-151.300	104.694
300	20.405	80.831	80.705	-0.938	-151.301	104.010
400	22.034	86.942	81.527	2.166	-151.304	132.973
500	23.081	91.979	83.129	4.425	-151.245	176.453
600	23.773	96.253	84.999	6.770	-151.155	230.921
700	24.294	100.015	86.991	9.113	-151.051	286.806
800	24.691	103.215	89.091	11.456	-150.935	344.063
900	24.987	105.875	91.299	13.800	-150.808	402.698
1000	25.177	108.125	92.475	16.075	-150.673	462.626
1100	25.269	110.088	93.621	18.286	-150.530	523.856
1200	25.333	111.738	94.740	20.430	-150.380	586.386
1300	25.379	113.125	95.829	22.512	-150.223	650.212
1400	25.410	114.293	96.883	24.538	-150.060	715.336
1500	25.428	115.269	97.910	26.510	-149.892	781.756
1600	25.436	116.183	98.910	28.430	-149.720	849.466
1700	25.434	117.047	99.883	30.300	-149.545	918.466
1800	25.423	117.869	100.833	32.125	-149.366	988.756
1900	25.404	118.647	101.759	33.910	-149.183	1060.326
2000	25.378	119.383	102.659	35.655	-148.995	1133.176
2100	25.345	120.083	103.533	37.370	-148.802	1207.306
2200	25.306	120.753	104.383	39.055	-148.605	1282.726
2300	25.263	121.393	105.209	40.710	-148.405	1359.436
2400	25.216	121.999	105.999	42.340	-148.202	1437.426
2500	25.166	122.579	106.759	43.945	-148.000	1516.696
2600	25.113	123.129	107.489	45.525	-147.795	1597.226
2700	25.057	123.653	108.189	47.080	-147.588	1678.916
2800	24.998	124.153	108.859	48.610	-147.378	1761.756
2900	24.936	124.629	109.499	50.115	-147.165	1845.746
3000	24.871	125.083	110.113	51.595	-146.948	1930.876
3100	24.803	125.517	110.704	53.050	-146.728	2017.146
3200	24.732	125.933	111.274	54.480	-146.505	2104.546
3300	24.658	126.333	111.823	55.885	-146.278	2193.076
3400	24.581	126.717	112.353	57.265	-146.048	2282.726
3500	24.501	127.087	112.863	58.620	-145.815	2373.496
3600	24.418	127.443	113.353	59.950	-145.578	2465.376
3700	24.332	127.787	113.823	61.255	-145.338	2558.356
3800	24.243	128.117	114.274	62.535	-145.095	2652.426
3900	24.151	128.433	114.704	63.790	-144.848	2747.576
4000	24.056	128.737	115.113	65.020	-144.598	2843.806
4100	23.958	129.029	115.504	66.235	-144.345	2941.116
4200	23.857	129.309	115.874	67.435	-144.088	3039.506
4300	23.753	129.577	116.224	68.620	-143.828	3138.976
4400	23.646	129.833	116.554	69.790	-143.565	3239.526
4500	23.536	130.077	116.869	70.945	-143.298	3341.146
4600	23.423	130.309	117.169	72.085	-143.028	3443.826
4700	23.307	130.529	117.454	73.210	-142.755	3547.556
4800	23.188	130.737	117.724	74.320	-142.478	3652.326
4900	23.066	130.933	117.979	75.415	-142.198	3758.126
5000	22.941	131.117	118.219	76.495	-141.915	3864.946
5100	22.813	131.289	118.444	77.560	-141.628	3972.776
5200	22.683	131.449	118.654	78.610	-141.338	4081.606
5300	22.550	131.597	118.849	79.645	-141.045	4191.526
5400	22.414	131.733	119.029	80.665	-140.748	4302.536
5500	22.276	131.857	119.194	81.670	-140.448	4414.636
5600	22.136	131.969	119.344	82.660	-140.145	4527.826
5700	21.993	132.069	119.479	83.635	-139.838	4642.096
5800	21.847	132.157	119.600	84.595	-139.528	4757.526
5900	21.699	132.233	119.709	85.540	-139.215	4874.106
6000	21.548	132.297	119.804	86.470	-138.900	4991.826

June 30, 1970

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
972 (1)	134 (1)	156 (1)
453 (1)	233 (1)	437 (1)
347 (1)	996 (1)	287 (1)

Bond Distance: Mo-O = 1.75 ± 0.10 Å Mo-Cl = 2.28 ± 0.03 Å
Bond Angle: O-Mo-O = 109.5° Cl-Mo-Cl = 113°
O-Mo-O plane perpendicular to Cl-Mo-Cl plane
Product of Moments of Inertia: I_AI_BI_C = 1.0986 x 10⁻¹¹² g³ cm⁶

Heat of Formation

Graham and Hepler (1) determined calorimetrically ΔH⁰ = -65.3 ± 0.5 kcal/mol for the reaction:
MoO₂Cl₂(c) + 4 NaOH(∞ H₂O) + 2 NaCl(∞ H₂O) + 2 H₂O(l).
Combining this result with the following heat of formation data: ΔH⁰(Na₂MoO₄, ∞ H₂O) = -353.4 ± 0.4 kcal/mol (2);
ΔH⁰(NaCl, ∞ H₂O) = -97.33 ± 0.09 kcal/mol (3); ΔH⁰(NaOH, ∞ H₂O) = -112.46 ± 0.1 kcal/mol (5); ΔH⁰(H₂O, l) = -68.315 kcal/mol (6); we derive ΔH⁰(MoO₂Cl₂, c) = -169.6 ± 1.0 kcal/mol.
Shchukarev et al. (7) measured the heats of solution of MoO₃(c), MoO₂Cl₂(c) and NaCl(c) in NaOH(aq) and derived ΔH⁰ = -45.56 ± 0.5 kcal/mol for the reaction MoO₂Cl₂(c) + 2 NaOH-77 H₂O + MoO₃(c) + 2 NaCl(c) + H₂O(l). Using JANAF auxiliary data (8) we obtain ΔH⁰(MoO₂Cl₂, c) = -172.86 ± 1.0 kcal/mol.
The two investigations differ only in the heat of solution of MoO₂Cl₂(c), both samples were better than 99.9% pure, and multiple determinations on two different samples were employed in each case. We adopt an average of the two values, -171.2 ± 1.7 kcal/mol for ΔH⁰(MoO₂Cl₂, c). Shchukarev et al. (10) reported an equation for the vapor pressure of the solid from which we have calculated a 2nd law ΔH⁰₂₉₈ = 19.9 kcal/mol with an estimated uncertainty of ± 2 kcal/mol, a ΔCp correction of -4.1 gibbs/mol was used (11). Thus, our adopted value is ΔH⁰₂₉₈(MoO₂Cl₂, g) = -151.3 ± 3.5 kcal/mol.

Shchukarev et al. (8) report equilibrium constants for the reaction MoO₂Cl₂(g) + 0.5 O₂(g) ± MoO₃(c) + Cl₂(g). Shchukarev et al. (10) and Hultgren and Brewer (12) reported equilibrium data for the reaction MoO₃(c) + 2 HCl(g) ± MoO₂Cl₂(g) + H₂O(g). Second and third law analyses of these equilibrium data give the following results:

Investigator	No. of Points	ΔH ₂₉₈ ⁰ , kcal/mol	2nd law	3rd law	Drift, gibbs/mol	kcal/mol
Shchukarev et al. (8)	7		-15.6	-30.11 ± 2.0	-15.0	148.0 ± 3.0
Shchukarev et al. (10)	Equation		12.1	13.8 ± 1.0	2.95	150.6 ± 1.2
Hultgren and Brewer (12)	Set I	5	27.2	15.2 ± 1.7	-21.37	149.2 ± 2.0
	Set II	5	26.5	15.4 ± 3.2	-21.75	149.4 ± 3.5

*Third law values
These equilibrium data are in agreement with the adopted heat of formation but are suspect because of the significant drifts and because the range of validity of the equation (10) is estimated.

Heat Capacity and Entropy

The molecular structural data are from the compilation of Sutton (13). Infrared data (14, 15, 16) for vapor phase MoO₂Cl₂ have indicated that the molecule possesses a distorted tetrahedral structure by reason of the similarity of its spectra to that of CrO₂Cl₂. Individual moments of inertia are I_A = 53.397 x 10⁻³⁹, I_B = 63.898 x 10⁻³⁹, and I_C = 32.200 x 10⁻³⁹ g cm². The vibrational frequencies 972, 996, 453, and 437 have been observed in the infrared vapor phase spectra of MoO₂Cl₂ by Baracough and Stals (14). These frequencies were assigned to the symmetric and asymmetric Mo-O and Mo-Cl stretches, respectively. Similar infrared data for these four frequencies have been reported by Iorns and Stafford (15) and Ward and Stafford (16). The rest of the frequencies are from the infrared and Raman studies of crystalline MoO₂Cl₂ by Adams and Churchill (17). Assignments are made by comparison with data reported for CrO₂Cl₂(s) by Miller et al. (18).

References

1. R. L. Graham and L. G. Hepler, J. Phys. Chem., **63**, 723 (1959).
2. JANAF Thermochemical Tables, The Dow Chemical Co. Midland, Michigan, Sept. 30, 1964, and Ref. 4.
3. JANAF Thermochemical Tables, The Dow Chemical Co. Midland, Michigan, Sept. 30, 1964, and Ref. 4.
4. V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.
5. JANAF Thermochemical Tables, The Dow Chemical Co. Midland, Michigan, March 31, 1966.
6. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
7. S. A. Shchukarev, I. V. Vasil'Kova, and B. N. Sharupin, Vestnik Leningrad Univ., **13**, No. 4, Ser. Fiz. Khim. No. 1, 73 (1959).
8. S. A. Shchukarev, I. V. Vasil'Kova, and B. N. Sharupin, Vestnik Leningrad Univ., **13**, No. 4, Ser. Fiz. Khim. No. 1, 87 (1961).
9. Ref. 4 and 5.
10. S. A. Shchukarev, I. V. Vasil'Kova, and B. N. Sharupin, Vestnik Leningrad Univ., **13**, No. 22, Ser. Fiz. Khim. No. 4, 130 (1961).
11. Ref. 5, March 31, 1967.
12. N. Hultgren and L. Brewer, J. Phys. Chem., **60**, 947 (1956).
13. L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions" Special Publication No. 11, The Chemical Society London, 1958.
14. C. G. Baracough and F. E. Stals, J. Chem. Soc., **19**, 791 (1966).
15. T. V. Iorns and F. E. Stafford, J. Amer. Chem. Soc., **88**, 4819 (1966).
16. B. G. Ward and F. E. Stafford, Inorg. Chem., **7**, 2568 (1968).
17. D. M. Adams and R. G. Churchill, J. Chem. Soc., **2310** (1968).
18. F. A. Miller, G. L. Carlson, and W. B. White, Spectrochim. Acta, **15B**, 709 (1959).

Sodium Chloride, Dimeric ((NaCl)₂)
(Ideal Gas) Mol. Wt. = 116.896

T, °K.	C _p	S° - (F° - H ₂₉₈ ⁰)/T	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞
100	13.734	49.381	-134.433	-134.433	205.175
200	13.734	93.590	-134.433	-134.433	147.424
298	13.734	137.757	-134.433	-134.433	96.145
300	18.843	77.873	-135.300	-135.300	96.145
400	18.843	77.873	-135.300	-135.300	96.145
500	18.843	77.873	-135.300	-135.300	96.145
600	18.843	77.873	-135.300	-135.300	96.145
700	18.843	77.873	-135.300	-135.300	96.145
800	18.843	77.873	-135.300	-135.300	96.145
900	18.843	77.873	-135.300	-135.300	96.145
1000	18.843	77.873	-135.300	-135.300	96.145
1100	18.843	77.873	-135.300	-135.300	96.145
1200	18.843	77.873	-135.300	-135.300	96.145
1300	18.843	77.873	-135.300	-135.300	96.145
1400	18.843	77.873	-135.300	-135.300	96.145
1500	18.843	77.873	-135.300	-135.300	96.145
1600	18.843	77.873	-135.300	-135.300	96.145
1700	18.843	77.873	-135.300	-135.300	96.145
1800	18.843	77.873	-135.300	-135.300	96.145
1900	18.843	77.873	-135.300	-135.300	96.145
2000	18.843	77.873	-135.300	-135.300	96.145
2100	18.843	77.873	-135.300	-135.300	96.145
2200	18.843	77.873	-135.300	-135.300	96.145
2300	18.843	77.873	-135.300	-135.300	96.145
2400	18.843	77.873	-135.300	-135.300	96.145
2500	18.843	77.873	-135.300	-135.300	96.145
2600	18.843	77.873	-135.300	-135.300	96.145
2700	18.843	77.873	-135.300	-135.300	96.145
2800	18.843	77.873	-135.300	-135.300	96.145
2900	18.843	77.873	-135.300	-135.300	96.145
3000	18.843	77.873	-135.300	-135.300	96.145
3100	18.843	77.873	-135.300	-135.300	96.145
3200	18.843	77.873	-135.300	-135.300	96.145
3300	18.843	77.873	-135.300	-135.300	96.145
3400	18.843	77.873	-135.300	-135.300	96.145
3500	18.843	77.873	-135.300	-135.300	96.145
3600	18.843	77.873	-135.300	-135.300	96.145
3700	18.843	77.873	-135.300	-135.300	96.145
3800	18.843	77.873	-135.300	-135.300	96.145
3900	18.843	77.873	-135.300	-135.300	96.145
4000	18.843	77.873	-135.300	-135.300	96.145
4100	18.843	77.873	-135.300	-135.300	96.145
4200	18.843	77.873	-135.300	-135.300	96.145
4300	18.843	77.873	-135.300	-135.300	96.145
4400	18.843	77.873	-135.300	-135.300	96.145
4500	18.843	77.873	-135.300	-135.300	96.145
4600	18.843	77.873	-135.300	-135.300	96.145
4700	18.843	77.873	-135.300	-135.300	96.145
4800	18.843	77.873	-135.300	-135.300	96.145
4900	18.843	77.873	-135.300	-135.300	96.145
5000	18.843	77.873	-135.300	-135.300	96.145
5100	18.843	77.873	-135.300	-135.300	96.145
5200	18.843	77.873	-135.300	-135.300	96.145
5300	18.843	77.873	-135.300	-135.300	96.145
5400	18.843	77.873	-135.300	-135.300	96.145
5500	18.843	77.873	-135.300	-135.300	96.145
5600	18.843	77.873	-135.300	-135.300	96.145
5700	18.843	77.873	-135.300	-135.300	96.145
5800	18.843	77.873	-135.300	-135.300	96.145
5900	18.843	77.873	-135.300	-135.300	96.145
6000	18.843	77.873	-135.300	-135.300	96.145

Dec. 31, 1964

SODIUM CHLORIDE, DIMERIC (Na₂Cl₂)

Point Group D_{2h}
S_{298.15} = [77.8] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 1

(IDEAL GAS)

MOL. WT. = 116.896

$$\Delta H_f^0 = -134.4 \pm 2 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = -135.3 \pm 2 \text{ kcal. mole}^{-1}$$

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
[265] (1)	[155] (1)
[159] (1)	[222] (1)
[226] (1)	[260] (1)

Bond Distance: Cl-Na = [2.624] Å

Bond Angle: Cl-Na-Cl = [108.4°]

Product of the Moments of Inertia: I_AI_BI_C = [6.649 X 10⁻¹¹³] g.³ cm.⁶

Heat of Formation.

An analysis is given below of the more extensive measurements relating to the dimer dissociation, (NaCl)₂(g) → 2NaCl(g). The mass spectrometric studies suggest that higher polymeric species may be neglected. Velocity distribution analyses are consistent with this procedure. When reduced to 298.15°K, the observed heats of dissociation of the dimer show a range of more than 7 kcal., reflecting the considerable uncertainty involved in such measurements. A value of ΔH_f^{0 = 48.6 kcal. was selected for the dissociation; combining this with ΔH_f^{0 = 54.9 kcal. mole⁻¹ for sublimation to the monomer leads to ΔH_f^{0 = 61.2 kcal. mole⁻¹ for sublimation to the dimer.}}}

Source	Method	T (Kcal. mole ⁻¹)	ΔH _f ⁰ (Kcal. mole ⁻¹)
1	Molecular weight from vapor pressures	1350	51.0
2	Molecular weight from P-V-T measurements	1337	52.6
3	Double oven effusion with mass spectrometer	1002	52.4
4	Knudsen effusion with mass spectrometer	870	47.4
5	Knudsen effusion with mass spectrometer	930	48.3
6	Velocity distribution analysis	940	45.6
7	Velocity distribution analysis	980	50.9
1)	J. L. Barton, H. Bloom, J. Phys. Chem. 63 , 1765 (1959).		47.8
2)	S. Datz, W. T. Smith, E. H. Taylor, J. Chem. Phys. 34 , 558 (1961).		
3)	P. A. Akishin, L. N. Gorokhov, L. N. Sidorov, Zhur. Fiz. Khim. 33 , 2822 (1959); Vestn. Mosk. Univ. Ser. Mat. Mekh. Astron. Fiz. Khim. 1959 , No. 6, 194 (1959).		
4)	L. N. Gorokhov, Yu. S. Khodsev, P. A. Akishin, Zhur. Neorg. Khim. 3 , 2597 (1958).		
5)	T. A. Milne, H. M. Klein, J. Chem. Phys. 33 , 1628 (1960).		
6)	M. Eisenstadt, V. S. Rao, G. M. Rothberg, J. Chem. Phys. 30 , 804 (1959).		
7)	R. C. Miller, P. Kusch, J. Chem. Phys. 27 , 981 (1957); 25 , 860 (1956).		

Heat Capacity and Entropy.

The structure and vibrational frequencies are those calculated from an ionic model by J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960), **29**, 1386 (1958). Electron diffraction studies by Akishin and Rabinovich, Z. Physik. Chem. (Leipzig) **213**, 111 (1960) gave a similar bond angle (108°) and a slightly shorter bond distance (2.50 Å); however, interpretation of the diffraction pattern was complicated by uncertainty in the monomer-dimer ratio for the vapor. Principal moments of inertia for the Berkowitz structure are I_A = 18.01 X 10⁻³⁹, I_B = 53.31 X 10⁻³⁹ and I_C = 71.32 X 10⁻³⁹ g. cm.².

Cl₂Na₂

Dichlorine Monoxide (Cl_2O)

(Ideal Gas) Mol. wt. = 86.9054

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.484	53.356	73.241	21.436	21.436	INFINITE
200	10.099	59.722	65.026	22.445	22.445	- 49.051
298	11.427	64.019	-	23.763	23.763	- 25.965
300	11.447	64.019	0.021	25.131	25.131	- 18.402
400	12.280	67.508	64.480	26.509	26.509	- 18.307
500	12.777	70.306	65.374	27.882	27.882	- 14.483
600	13.086	72.665	66.397	29.246	29.246	- 10.652
700	13.224	74.441	67.060	30.600	30.600	- 7.144
800	13.324	75.682	67.442	31.958	31.958	- 6.490
900	13.392	76.369	67.763	33.290	33.290	- 6.233
1000	13.432	76.947	68.031	34.626	34.626	- 6.009
1100	13.455	77.415	68.248	35.958	35.958	- 5.814
1200	13.465	77.785	68.418	37.286	37.286	- 5.637
1300	13.468	78.061	68.548	38.609	38.609	- 5.478
1400	13.471	78.248	68.637	39.929	39.929	- 5.334
1500	13.473	78.351	68.691	41.248	41.248	- 5.225
1600	13.473	78.375	68.715	42.564	42.564	- 5.112
1700	13.473	78.375	68.715	43.875	43.875	- 5.016
1800	13.473	78.375	68.715	45.181	45.181	- 4.931
1900	13.473	78.375	68.715	46.481	46.481	- 4.852
2000	13.473	78.375	68.715	47.775	47.775	- 4.782
2100	13.473	78.375	68.715	49.063	49.063	- 4.722
2200	13.473	78.375	68.715	50.345	50.345	- 4.670
2300	13.473	78.375	68.715	51.621	51.621	- 4.625
2400	13.473	78.375	68.715	52.891	52.891	- 4.587
2500	13.473	78.375	68.715	54.155	54.155	- 4.554
2600	13.473	78.375	68.715	55.413	55.413	- 4.525
2700	13.473	78.375	68.715	56.665	56.665	- 4.499
2800	13.473	78.375	68.715	57.911	57.911	- 4.476
2900	13.473	78.375	68.715	59.151	59.151	- 4.455
3000	13.473	78.375	68.715	60.385	60.385	- 4.437
3100	13.473	78.375	68.715	61.613	61.613	- 4.421
3200	13.473	78.375	68.715	62.835	62.835	- 4.406
3300	13.473	78.375	68.715	64.051	64.051	- 4.392
3400	13.473	78.375	68.715	65.261	65.261	- 4.379
3500	13.473	78.375	68.715	66.465	66.465	- 4.367
3600	13.473	78.375	68.715	67.663	67.663	- 4.356
3700	13.473	78.375	68.715	68.855	68.855	- 4.346
3800	13.473	78.375	68.715	69.941	69.941	- 4.337
3900	13.473	78.375	68.715	71.021	71.021	- 4.329
4000	13.473	78.375	68.715	72.095	72.095	- 4.322
4100	13.473	78.375	68.715	73.163	73.163	- 4.316
4200	13.473	78.375	68.715	74.225	74.225	- 4.311
4300	13.473	78.375	68.715	75.281	75.281	- 4.306
4400	13.473	78.375	68.715	76.331	76.331	- 4.302
4500	13.473	78.375	68.715	77.375	77.375	- 4.298
4600	13.473	78.375	68.715	78.413	78.413	- 4.294
4700	13.473	78.375	68.715	79.445	79.445	- 4.290
4800	13.473	78.375	68.715	80.471	80.471	- 4.287
4900	13.473	78.375	68.715	81.491	81.491	- 4.284
5000	13.473	78.375	68.715	82.505	82.505	- 4.281
5100	13.473	78.375	68.715	83.513	83.513	- 4.278
5200	13.473	78.375	68.715	84.515	84.515	- 4.275
5300	13.473	78.375	68.715	85.511	85.511	- 4.272
5400	13.473	78.375	68.715	86.501	86.501	- 4.270
5500	13.473	78.375	68.715	87.485	87.485	- 4.267
5600	13.473	78.375	68.715	88.463	88.463	- 4.265
5700	13.473	78.375	68.715	89.435	89.435	- 4.263
5800	13.473	78.375	68.715	90.401	90.401	- 4.261
5900	13.473	78.375	68.715	91.361	91.361	- 4.259
6000	13.473	78.375	68.715	92.315	92.315	- 4.257

Dec. 31, 1960; Dec. 31, 1965

Dichlorine Monoxide (Cl_2O)

(Ideal Gas) Mol. wt. = 86.9054

Point Group	C _{2v}	ΔH _f °	ΔF _f °	Log K _p
S ^{298.15}	64.019 cal. deg. ⁻¹ mole ⁻¹	21.4	21.4	INFINITE
Ground State Quantum Weight	1	21.0	21.0	- 49.051
		21.0	21.0	- 25.965
		21.0	21.0	- 18.402
		21.0	21.0	- 14.483
		21.0	21.0	- 10.652
		21.0	21.0	- 7.144
		21.0	21.0	- 6.490
		21.0	21.0	- 6.233
		21.0	21.0	- 6.009
		21.0	21.0	- 5.814
		21.0	21.0	- 5.637
		21.0	21.0	- 5.478
		21.0	21.0	- 5.334
		21.0	21.0	- 5.225
		21.0	21.0	- 5.112
		21.0	21.0	- 5.016
		21.0	21.0	- 4.931
		21.0	21.0	- 4.852
		21.0	21.0	- 4.782
		21.0	21.0	- 4.722
		21.0	21.0	- 4.670
		21.0	21.0	- 4.625
		21.0	21.0	- 4.587
		21.0	21.0	- 4.554
		21.0	21.0	- 4.525
		21.0	21.0	- 4.499
		21.0	21.0	- 4.476
		21.0	21.0	- 4.455
		21.0	21.0	- 4.437
		21.0	21.0	- 4.421
		21.0	21.0	- 4.406
		21.0	21.0	- 4.392
		21.0	21.0	- 4.379
		21.0	21.0	- 4.367
		21.0	21.0	- 4.356
		21.0	21.0	- 4.346
		21.0	21.0	- 4.337
		21.0	21.0	- 4.329
		21.0	21.0	- 4.322
		21.0	21.0	- 4.316
		21.0	21.0	- 4.311
		21.0	21.0	- 4.306
		21.0	21.0	- 4.302
		21.0	21.0	- 4.298
		21.0	21.0	- 4.294
		21.0	21.0	- 4.290
		21.0	21.0	- 4.287
		21.0	21.0	- 4.284
		21.0	21.0	- 4.281
		21.0	21.0	- 4.278
		21.0	21.0	- 4.275
		21.0	21.0	- 4.272
		21.0	21.0	- 4.270
		21.0	21.0	- 4.267
		21.0	21.0	- 4.265
		21.0	21.0	- 4.263
		21.0	21.0	- 4.261
		21.0	21.0	- 4.259
		21.0	21.0	- 4.257

V. A. Kustodins, K. P. Mishchenko and I. E. Flis, Zh. Prikl. Khim. 35, 1374 (1962) (Source 1) derived the heat of formation of Cl_2O dissolved in CCl_4 from solution calorimetry at 278, 283, 298 and 308°K. The heat of formation in CCl_4 was interpolated to 285°K. D. M. Yost and R. C. Felt, J. Am. Chem. Soc. 55, 68 (1934) (Source 2) measured the partial vapor pressures of Cl_2O above its CCl_4 solution at 273 and 298°K which yield the heat of solution -6.59 kcal. mole⁻¹ at 285°K. The ΔH_f° 298.15 = 21.0 kcal. mole⁻¹ was calculated from these two values. J. I. Wallace and C. P. Goodeve, Trans. Faraday Soc. 27, 648 (1931) (Source 3) obtained the heat of explosion of $\text{Cl}_2\text{O}(\text{g})$; their data give ΔH_f° 298.15 $\text{Cl}_2\text{O}(\text{g})$ = 21.4 kcal. mole⁻¹ which is in very good agreement with the above. Also F. Günther and K. Wekua, Z. Physik Chem. 154, 153 (1931) (Source 4) measured the heat of explosion; their data give ΔH_f° 298.15 $\text{Cl}_2\text{O}(\text{g})$ = 24.7 kcal. mole⁻¹.

Source	Reaction	ΔH _f °	ΔF _f °	Log K _p
1	$\text{Cl}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{Cl}_2\text{O}(\text{in } \text{CCl}_4)$	285	14.38	—
2	$\text{Cl}_2\text{O}(\text{in } \text{CCl}_4) \rightarrow \text{Cl}_2\text{O}(\text{g})$	285	6.59	21.0
3	$\text{Cl}_2\text{O}(\text{g}) \rightarrow \text{Cl}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$	298	-21.4	21.4
4	$\text{Cl}_2\text{O}(\text{g}) \rightarrow \text{Cl}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$	298	-24.7	24.7

Heat Capacity and Entropy.

The vibrational frequencies were obtained from M. M. Rochkind and G. C. Pimentel, J. Chem. Phys. 42, 1361 (1965). The infrared spectrum of $\text{Cl}_2\text{O}(\text{g})$ has been investigated previously beginning with the work of C. R. Bailey and A. B. Casate, Proc. Roy. Soc. (London) A142, 132 (1933). K. Hedberg, J. Chem. Phys. 19, 508 (1951) proposed stretching frequencies at 688 cm.⁻¹ (ν_1) and 989 cm.⁻¹ (ν_2) but left the bending frequency unknown. Previous evidence concerning the bending mode (ν_2) was shown by Hedberg (loc. cit.) to be spurious. Rochkind and Pimentel (loc. cit.) present infrared studies of Cl_2O gas and condensed phases which reveal the bending frequency and require reassignment of the stretching fundamentals. The bond distance and bond angle were obtained from J. D. Dunitz and K. Hedberg, J. Am. Chem. Soc. 72, 3108 (1950).

The three principal moments of inertia are: $I_A = 2.022 \times 10^{-39}$, $I_B = 2.30808 \times 10^{-39}$, and $I_C = 2.51028 \times 10^{-38}$ g. cm.²

*O. B. B. M. Sutherland and W. B. Penny, Proc. Roy. Soc. (London) A159, 678 (1936).

Titanium Oxide Dichloride (TiOCl₂)
(Ideal Gas) Mol. Wt. = 134.814

T. °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞	∞	∞	∞	∞	∞
100	12.291	60.411	0.000	-130.002	-130.002	INFINITE
200	15.642	70.130	-3.041	-129.491	-129.491	282.989
300	17.197	76.697	0.000	-130.338	-128.608	140.628
400	17.819	76.803	0.032	-130.291	-127.863	97.143
500	18.330	76.899	0.032	-130.291	-127.015	69.195
600	18.761	76.981	0.032	-130.291	-126.158	55.141
700	19.179	77.048	0.032	-130.291	-125.295	45.636
800	19.579	77.103	0.032	-130.291	-124.427	39.845
900	19.956	77.148	0.032	-130.291	-123.547	34.750
1000	20.315	77.185	0.032	-130.291	-122.657	29.784
1100	20.657	77.215	0.032	-130.291	-121.759	24.010
1200	20.984	77.240	0.032	-130.291	-120.851	21.834
1300	21.298	77.260	0.032	-130.291	-119.893	19.984
1400	21.598	77.275	0.032	-130.291	-118.878	18.397
1500	21.884	77.287	0.032	-130.291	-117.815	17.019
1600	22.158	77.296	0.032	-130.291	-116.704	15.812
1700	22.421	77.302	0.032	-130.291	-115.546	14.745
1800	22.673	77.306	0.032	-130.291	-114.342	13.796
1900	22.915	77.308	0.032	-130.291	-113.094	12.945
2000	23.148	77.309	0.032	-130.291	-111.801	12.167
2100	23.373	77.309	0.032	-130.291	-110.463	11.453
2200	23.590	77.308	0.032	-130.291	-109.089	10.793
2300	23.799	77.306	0.032	-130.291	-107.680	10.208
2400	23.999	77.303	0.032	-130.291	-106.236	9.682
2500	24.191	77.300	0.032	-130.291	-104.757	9.215
2600	24.375	77.296	0.032	-130.291	-103.243	8.804
2700	24.551	77.291	0.032	-130.291	-101.694	8.441
2800	24.719	77.285	0.032	-130.291	-100.110	8.124
2900	24.879	77.278	0.032	-130.291	-98.491	7.852
3000	25.031	77.270	0.032	-130.291	-96.836	7.618
3100	25.175	77.261	0.032	-130.291	-95.146	7.419
3200	25.312	77.251	0.032	-130.291	-93.420	7.242
3300	25.442	77.240	0.032	-130.291	-91.658	7.085
3400	25.565	77.229	0.032	-130.291	-89.860	6.946
3500	25.682	77.217	0.032	-130.291	-88.026	6.822
3600	25.793	77.205	0.032	-130.291	-86.156	6.712
3700	25.898	77.192	0.032	-130.291	-84.250	6.614
3800	25.997	77.179	0.032	-130.291	-82.308	6.526
3900	26.091	77.165	0.032	-130.291	-80.330	6.447
4000	26.179	77.151	0.032	-130.291	-78.316	6.375
4100	26.262	77.137	0.032	-130.291	-76.266	6.309
4200	26.340	77.122	0.032	-130.291	-74.180	6.248
4300	26.413	77.107	0.032	-130.291	-72.058	6.191
4400	26.481	77.091	0.032	-130.291	-69.900	6.137
4500	26.544	77.075	0.032	-130.291	-67.706	6.086
4600	26.602	77.058	0.032	-130.291	-65.476	6.037
4700	26.655	77.041	0.032	-130.291	-63.210	5.990
4800	26.703	77.024	0.032	-130.291	-60.908	5.945
4900	26.746	77.007	0.032	-130.291	-58.570	5.902
5000	26.784	76.989	0.032	-130.291	-56.196	5.860
5100	26.817	76.971	0.032	-130.291	-53.786	5.819
5200	26.845	76.953	0.032	-130.291	-51.340	5.779
5300	26.868	76.935	0.032	-130.291	-48.858	5.740
5400	26.886	76.916	0.032	-130.291	-46.340	5.702
5500	26.900	76.897	0.032	-130.291	-43.786	5.665
5600	26.910	76.878	0.032	-130.291	-41.196	5.629
5700	26.916	76.858	0.032	-130.291	-38.570	5.594
5800	26.919	76.838	0.032	-130.291	-35.906	5.560
5900	26.919	76.817	0.032	-130.291	-33.206	5.526
6000	26.916	76.795	0.032	-130.291	-30.470	5.493

Sept. 30, 1963

Cl₂O₇

TITANIUM OXIDE DICHLORIDE (TiOCl₂) (IDEAL GAS) MOL. WT. = 134.814

Point Group [C_{2v}]
ΔH°_f 0 = [-130.0] kcal. mole⁻¹
ΔH°_f 298.15 = [-130.4] kcal. mole⁻¹
S°_{298.15} = [76.697] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

Vibrotional Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[455] (1)	[250] (1)
[849] (1)	[250] (1)
[120] (1)	[180] (1)

Bond Distances: O-Ti = [1.82] Å Ti-Cl = [2.20] Å
Bond Angles: O-Ti-Cl = [120°] ε = 2

Product of Moments of Inertia: I_AI_BI_C = [4.628 X 10⁻¹¹³] g.³ cm.⁶

Heat of Formation.

ΔH°_f 0 was estimated as -130 kcal. mole⁻¹ by J. S. Gordon, Astrocyeteme, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. ΔH°_f 298.15 was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. Principal moments were: I_A = 42.72 X 10⁻³⁹ g. cm.², I_B = 17.88 X 10⁻³⁹ g. cm.², and I_C = 60.60 X 10⁻³⁹ g. cm.²

Cl₂O₇

Tungsten Dioxychloride (WO_2Cl_2)
(Crystal) GFW = 286.7548

T, °K	C_p°	$S^\circ - (C_p^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log Kp
0						
100						
200						
298	24.954	48.000	48.000	.000	-167.500	123.136
300	25.000	48.155	48.000	-.046	-167.471	122.294
400	27.500	55.489	49.011	2.671	-161.733	88.367
500	30.000	62.096	51.002	5.547	-155.742	66.075
600	32.500	67.781	53.333	8.669	-149.909	54.604
700	34.550	72.445	55.211	11.557	-143.738	44.504
800	36.250	76.186	56.711	15.257	-137.226	37.904
900	37.750	81.986	60.522	19.228	-130.801	32.392
1000	38.000	85.953	62.959	22.994	-124.410	28.0

TUNGSTEN DIOXYCHLORIDE (WO_2Cl_2)

(CRYSTAL)

OPW = 286.7548

$\Delta H_f^\circ = \text{Unknown}$

$\Delta H_f^\circ_{298.15} = -186.5 \pm 1.4 \text{ kcal/mol}$

$S^\circ_{298.15} = [48.0] \text{ gibbs/mol}$

Td = 642°K

Heat of Formation.

S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov¹ measured calorimetrically the heats of reaction (1) and (2) at 298°K as -67.3 ± 0.2 and $-13.6 \pm 0.11 \text{ kcal/mol}$, respectively. The reactions are given as follows:

(1) $\text{WO}_2\text{Cl}_2(\text{c}) + 4 \text{ NaOH}(16.3\text{H}_2\text{O}) \rightarrow \text{Na}_2\text{WO}_4(80,000 \text{ H}_2\text{O}) + 2 \text{ NaCl}(40,000 \text{ H}_2\text{O}) + 2 \text{ H}_2\text{O}(1)$

(2) $\text{H}_2\text{WO}_4(\text{c}) + 2 \text{ NaOH}(16.3 \text{ H}_2\text{O}) \rightarrow \text{Na}_2\text{WO}_4(20,000 \text{ H}_2\text{O}) + 2 \text{ H}_2\text{O}(1)$.

Based on these data and the heats of dilution for $\text{NaOH}(\text{aq})^2$ and $\text{Na}_2\text{WO}_4(\text{aq})^3$, we obtain $\Delta H_f^\circ_{298} = -53.77 \pm 1.0 \text{ kcal/mol}$ for $\text{WO}_2\text{Cl}_2(\text{c}) + 2 \text{ OH}^-(\infty \text{ H}_2\text{O}) \rightarrow \text{H}_2\text{WO}_4(\text{c}) + 2 \text{ Cl}^-(\infty \text{ H}_2\text{O})$. This leads to $\Delta H_f^\circ_{298}(\text{WO}_2\text{Cl}_2, \text{c}) = -166.5 \text{ kcal/mol}$ using $\Delta H_f^\circ_{298}(\text{H}_2\text{WO}_4, \text{c}) = -270.5 \pm 0.4 \text{ kcal/mol}$ ⁵.

Heat Capacity and Entropy.

$CP_{300} = 25.0 \text{ gibbs/mol}$ is estimated using Kopp's rule. Heat capacities at higher temperature are estimated from those of $\text{WO}_2(\text{c})$, $\text{WO}_3(\text{c})$, $\text{WOCl}_6(\text{c})$. The entropy, $S^\circ_{298} = 48.0 \text{ eu}$, is calculated from $\Delta S^\circ_{298.6} = 32.27 \pm 1.3 \text{ eu}$ for $\text{WO}_2\text{Cl}_2(\text{c}) \rightarrow \text{WO}_2\text{Cl}_2(\text{g})$. The value of $\Delta S^\circ_{298.6}$ is obtained from the second law analysis of the vapor pressure data given by S. A. Shchukarev and A. V. Suvorov⁴.

Temperature of Decomposition.

Shchukarev and Suvorov⁴ found that $\text{WO}_2\text{Cl}_2(\text{c})$ does not melt but decomposes. The saturated vapor over $\text{WO}_2\text{Cl}_2(\text{c})$ consists mainly of $\text{WOCl}_4(\text{g})$ which will disproportionate to form $\text{WO}_2\text{Cl}_2(\text{g})$ and $\text{WOCl}_6(\text{g})$. The estimated Td is derived by interpolation to one atmosphere in the total pressure of $\text{WOCl}_4(\text{g})$, $\text{WO}_2\text{Cl}_2(\text{g})$ reported by Shchukarev and Suvorov⁴.

References.

1. S. A. Shchukarev, I. V. Vasil'kova and O. I. Novikov, Zh. Neorg. Khim. **3**, 2642 (1958).
2. "Thermal Properties of Aqueous Uni-univalent Electrolytes," V. B. Parker, NBS-RS-NBS2, Natl. Bur. Std., Washington, D.C., Apr. 1965.
3. We have assumed $\Delta H^\circ_{\text{dil}} = 0$ for $\text{Na}_2\text{WO}_4(20,000 \text{ H}_2\text{O}) \rightarrow \text{Na}_2\text{WO}_4(80,000 \text{ H}_2\text{O})$.
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. **15**, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Earlier data reported by Shchukarev et al, Zh. Neorg. Khim. **3**, 2630 (1958); **5**, 1650 (1960), have been revised and they are not used here.
5. JANAF $\text{H}_2\text{WO}_4(\text{c})$ table dated Mar. 31, 1967.

$\text{Cl}_2\text{O}_2\text{W}$

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ₂₉₈)/T	H ^o - H ₂₉₈	ΔH ^o , kcal/mol	ΔG ^o	Log K _p
0	+0.000	INFINITE	-	4.661	-159.703	INFINITE
100	14.105	63.365	-101.387	-3.602	-160.190	344.964
200	18.348	76.692	-86.404	-1.982	-160.432	169.795
298	20.941	84.563	-76.000	-	-160.500	112.069
300	20.974	84.692	84.568	0.39	-160.500	111.344
400	29.334	90.912	85.402	2.204	-160.465	92.114
500	33.287	96.006	91.029	4.489	-160.365	64.584
600	36.222	100.312	95.893	6.951	-160.218	52.006
700	38.465	103.708	99.660	9.581	-159.989	42.551
800	40.246	106.308	102.660	11.716	-159.665	34.376
900	41.688	108.226	104.935	14.197	-159.832	33.472
1000	42.854	110.258	106.163	16.694	-159.710	30.592
1100	43.781	115.252	97.791	19.204	-159.978	26.620
1200	44.521	119.644	97.331	21.729	-159.998	23.778
1300	45.158	123.574	100.611	24.260	-159.411	21.565
1400	45.721	127.155	102.712	26.800	-159.337	19.631
1500	46.272	130.463	104.548	29.345	-159.277	17.973
1600	46.814	133.546	106.027	31.884	-159.232	16.593
1700	47.346	136.433	107.207	34.424	-159.200	15.263
1800	47.868	139.169	108.126	37.004	-159.186	14.106
1900	48.380	141.784	108.836	39.563	-159.187	13.089
2000	48.883	144.300	109.400	42.125	-159.205	12.173
2100	49.376	146.731	110.833	44.689	-159.238	11.345
2200	49.860	149.087	112.142	47.256	-159.282	10.592
2300	50.334	151.368	113.387	49.821	-159.360	9.903
2400	50.798	153.581	114.572	52.389	-159.447	9.272
2500	51.253	155.736	116.709	54.959	-159.553	8.691
2600	51.700	157.838	118.792	57.529	-159.676	8.061
2700	52.138	159.890	120.821	60.101	-159.823	7.390
2800	52.568	161.904	122.797	62.673	-160.004	6.715
2900	52.990	163.881	124.726	65.246	-160.227	6.041
3000	53.404	165.820	126.613	67.820	-160.498	5.361
3100	53.810	167.726	128.459	70.394	-160.820	4.684
3200	54.208	169.600	130.266	72.969	-161.206	4.008
3300	54.598	171.443	132.036	75.545	-161.655	3.328
3400	54.980	173.256	133.770	78.120	-162.247	2.649
3500	55.354	175.038	135.478	80.697	-162.892	2.011
3600	55.721	176.790	137.160	83.273	-163.658	1.436
3700	56.080	178.513	138.817	85.850	-164.500	0.911
3800	56.431	180.207	140.450	88.428	-165.400	0.387
3900	56.775	181.873	142.060	91.005	-166.364	0.000
4000	57.112	183.512	143.648	93.583	-167.390	-0.361
4100	57.441	185.126	145.216	96.162	-168.472	-0.711
4200	57.762	186.716	146.764	98.742	-169.608	-1.056
4300	58.076	188.282	148.293	101.319	-170.800	-1.400
4400	58.383	189.824	149.800	103.894	-172.048	-1.740
4500	58.683	191.342	151.288	106.477	-173.350	-2.077
4600	58.976	192.836	152.756	109.056	-174.702	-2.411
4700	59.262	194.306	154.200	111.635	-176.100	-2.740
4800	59.541	195.752	155.629	114.215	-177.548	-3.065
4900	59.813	197.174	157.043	116.795	-179.048	-3.387
5000	60.079	198.574	158.443	119.375	-180.600	-3.700
5100	60.339	200.000	159.828	121.955	-182.200	-4.000
5200	60.593	201.452	161.197	124.535	-183.850	-4.290
5300	60.842	202.930	162.550	127.115	-185.550	-4.570
5400	61.086	204.434	163.900	129.695	-187.300	-4.840
5500	61.325	205.962	165.284	132.274	-189.100	-5.100
5600	61.559	207.516	166.693	134.857	-190.950	-5.350
5700	61.788	209.096	168.137	137.437	-192.850	-5.590
5800	62.012	210.700	169.610	140.014	-194.800	-5.820
5900	62.231	212.328	171.114	142.589	-196.800	-6.040
6000	62.445	213.980	172.750	145.160	-198.850	-6.250

Sept. 30, 1962; Mar. 31, 1967

TUNGSTEN DIOXYDICHLORIDE (WO₂Cl₂)

(IDEAL GAS)

OPW = 286.7548

Point Group: [C_{2v}]

$$\Delta H_f^{\circ} = -159.7 \pm 8 \text{ kcal/mol}$$

$$\Delta H_f^{\circ} = -160.5 \pm 6 \text{ kcal/mol}$$

$$S_{298,15}^{\circ} = [84.6] \text{ gibbs/mol}$$

$$\text{Ground State Quantum Weight} = 1$$

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}	ω_e, cm^{-1}
984 (1)	(400) (1)	(150) (1)
972 (1)	(300) (1)	(100) (1)
[400] (1)	(300) (1)	(100) (1)

$$\text{Bond Distance: W-Cl} = [2.26] \text{ \AA}$$

$$\text{Bond Angle: Cl-W-Cl} = [113^{\circ}]$$

$$\text{Product of the Moments of Inertia: } I_A I_B I_C = [1.165 \times 10^{-112}] \text{ g}^3 \text{ cm}^6$$

$$\text{W-O} = [1.81] \text{ \AA}$$

$$\text{O-W-O} = [109.47^{\circ}]$$

$$\text{O-W-Cl} = [90^{\circ}]$$

Heat of Formation.

The adopted heat of formation, $\Delta H_f^{\circ}(\text{WO}_2\text{Cl}_2, g) = -160.5 \text{ kcal/mol}$, is obtained from $\Delta H_f^{\circ}(\text{WO}_2\text{Cl}_2, g) = 26.0 \text{ kcal/mol}$ for $\text{WO}_2\text{Cl}_2(c) \rightarrow \text{WO}_2\text{Cl}_2(g)$. The latter is calculated by the third law method from the partial pressures of $\text{WO}_2\text{Cl}_2(g)$ given by S. A. Shekharov and A. V. Suvorov.⁶ Second law analysis gives $\Delta H_f^{\circ}(\text{WO}_2\text{Cl}_2, g) = 24.1 \pm 0.8 \text{ kcal/mol}$ ($\Delta H_f^{\circ}(\text{WO}_2\text{Cl}_2, g) = 26.0 \text{ kcal/mol}$). These reported partial vapor pressures of $\text{WO}_2\text{Cl}_2(g)$ were derived by the optical tonometric method from total pressures over $\text{WO}_2\text{Cl}_2(c)$ considering the species $\text{WOCl}_4(g)$, $\text{WO}_2\text{Cl}_2(g)$ and $\text{WCl}_6(g)$. Since the decomposition of $\text{WO}_2\text{Cl}_2(c)$ was very complicated, we tentatively assign 6 kcal/mol uncertainty to the adopted heat of formation.

Shekharov and Suvorov⁶ have also derived a log K_p equation for the disproportionation process,

$$2 \text{WOCl}_4(g) \rightarrow \text{WO}_2\text{Cl}_2(g) + \text{WCl}_6(g). \text{ Third law analysis gives } \Delta H_f^{\circ}(\text{WO}_2\text{Cl}_2, g) = 10.3 \text{ kcal/mol for the above process. This leads to } \Delta H_f^{\circ}(\text{WO}_2\text{Cl}_2, g) = -145.7 \pm 16 \text{ kcal/mol. The second law } \Delta H_f^{\circ}(\text{WO}_2\text{Cl}_2, g) \text{ is } 11.0 \text{ kcal/mol. The drift in the third law analysis is } 0.3 \text{ eu.}$$

Heat Capacity and Entropy.

The molecular configuration is assumed to be a distorted tetrahedron of C_{2v} symmetry, similar to that of $\text{MoO}_2\text{Cl}_2(g)^1$, and $\text{CrO}_2\text{Cl}_2(g)^2$. The bond distances W-O and W-Cl are estimated to be the same as those in $\text{WO}_3(g)$ and $\text{WCl}_6(g)$, respectively. The bond angles are assumed to be the same as those in $\text{MoO}_2\text{Cl}_2(g)^1$. The three principal moments of inertia are $I_A = 6.419 \times 10^{-38}$, $I_B = 5.342 \times 10^{-38}$ and $I_C = 3.397 \times 10^{-38} \text{ g cm}^2$.

The vibrational frequencies, 984 cm⁻¹ and 972 cm⁻¹, were observed in the infrared spectra by C. O. Barreclough and J. Stala.³ They tentatively assigned these two as the asymmetric and symmetric W-O stretching frequencies. The rest of the frequencies are estimated by comparison with those observed in the infrared and Raman spectra for $\text{CrO}_2\text{Cl}_2(g)^4,5$. They are not listed in point group order.

References.

1. L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.
2. K. J. Palmer, J. Am. Chem. Soc. 60, 2360 (1938).
3. C. O. Barreclough and J. Stala, Aust. J. Chem. 19, 741 (1966).
4. H. Stammreich, K. Kawai and Y. Tazawa, Spectrochim. Acta 1959, 438 (1959).
5. F. A. Millor, O. L. Carlson and W. B. White, Spectrochim. Acta 1959, 709 (1959).
6. S. A. Shekharov and A. V. Suvorov, Vestnik Leningrad. Univ. 18, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).

Earlier data reported by Shukerov et al., Zh. Neorg. Khim. 3, 2630 (1958); 5, 1650 (1960), have been revised and they are not used here.

Lead Dichloride (PbCl₂)

INTERIM TABLE

(Crystal) Mol. Wt. = 278.12

T, °K	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	.000	INFINITE	-	86.412	-	INFINITE
100	13.810	18.887	4.049	86.723	-	161.000
200	15.620	25.597	1.805	86.866	-	66.323
298	17.483	32.500	.000	86.866	75.386	55.237
300	17.500	32.608	.032	86.196	75.319	54.867
400	18.490	37.777	1.631	85.679	71.740	39.195
500	19.491	42.010	3.730	85.506	66.248	28.930
600	20.480	45.491	5.729	85.066	64.635	23.615
700	21.480	48.883	7.702	85.216	61.313	19.142
800	22.360	51.814	9.626	85.127	57.866	15.606
900	23.160	54.894	12.299	84.455	54.498	13.233
1000	23.960	56.976	14.655	83.699	51.210	11.191
1100	24.760	59.297	17.091	82.659	48.001	9.536
1200	25.560	61.486	19.607	81.934	44.871	8.172
1300	26.360	63.563	22.203	80.926	41.623	7.031
1400	27.160	65.546	24.879	79.639	38.687	6.065
1500	27.960	67.447	27.635	78.673	35.968	5.240
1600	28.760	69.277	30.471	77.432	33.162	4.529
1700	29.560	71.045	33.387	76.114	30.432	3.912
1800	30.360	72.757	36.383	74.723	27.788	3.374
1900	31.160	74.420	39.459	73.257	25.219	2.901
2000	31.960	76.038	42.615	71.719	22.730	2.484
2100	32.760	77.617	45.851	70.112	20.316	2.123
2200	33.560	79.159	49.167	68.434	17.984	1.825
2300	34.360	80.669	52.563	66.692	15.738	1.580
2400	35.160	82.148	56.039	64.899	13.578	1.383
2500	35.960	83.600	59.595	63.057	11.500	1.236

Lead Dichloride (PbCl₂) (Crystal)

Mol. Wt. = 278.12
 $\Delta H_f^{298.15} = -86.20 \pm 0.07$ kcal. mole⁻¹
 $S^{298.15} = 32.5 \pm 0.5$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^{298.15} = 45.59 \pm 0.70$ kcal. mole⁻¹
 $T_m = 769^\circ K$
 $\Delta H_m = 5.70$ kcal. mole⁻¹

Heat of Formation. Recalculated from the data reported by E. J. Salstrom, J. Am. Chem. Soc. 55, 2426 (1933) and A. Wachten, J. Am. Chem. Soc. 54, 2271 (1932).

Heat Capacity, Entropy and Melting Data. C_p (15.8° to 205.5°K.) reported by W. Nemst, Ann. Physik, 35, 395 (1911) and adjusted so that S_{298.15} is equal to the value reported by K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592 (1961). C_p above 298.15°K. obtained from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) and joined smoothly to the low temperature heat capacity curve by graphical extrapolation. T_m and ΔH_m obtained from M. Blanc and O. Petit, Compt. rend. 249, 1305 (1959).

Heat of Sublimation. Calculated from vapor pressure data of E. D. Eastman and L. H. Duachak, U. S. Bur. Mines Tech. Paper 225 (1919), C. G. Naier, U. S. Bur. Mines Tech. Paper 360, 28 (1925), H. V. Wartenberg and O. Bogase, Z. Elektrochem. 29, 384 (1922), and M. Jahn-Held and K. Jellinek, Z. Elektrochem. 43, 191 (1937), which are in good agreement. Vapor pressure was also measured by F. Volmer, Physik. Z. 30, 580 (1929), J. L. Barton and H. Bloom, J. Phys. Chem. 60, 1413 (1956), B. Gredner and K. Jellinek, Z. Physik. Chem. A165, 97 (1933), and K. Mwa, M. Sato and M. Yosiyama, J. Faculty Sci. Hokkaido Imp. Univ. Ser. III, 2, 17 (1940).

INTERIM TABLE

March 31, 1962

T. °K.	C _p	S° -(F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H°-H° ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _f
0							
100							
200							
298	17.485	36.336	36.336	.000	- 81.488	- 72.413	53.076
300	17.500	36.336	36.336	.032	- 81.483	- 72.357	52.710
400	18.444	38.444	38.444	1.932	- 81.066	- 66.362	37.896
500	19.490	40.385	40.385	3.730	- 80.793	- 66.453	29.045
600	24.900	52.178	41.987	6.114	- 79.968	- 63.653	23.184
700	24.900	56.016	43.724	9.602	- 78.328	- 60.606	18.497
800	24.900	58.841	45.453	13.584	- 76.457	- 55.501	13.477
900	24.900	62.274	47.140	17.074	- 74.567	- 52.999	11.582
1000	24.900	64.897	48.623	18.564	- 76.673	- 50.566	10.050
1100	24.900	67.270	50.394	21.024	- 72.573	- 46.523	7.789
1200	24.900	69.430	51.972	24.034	- 73.071	- 43.810	6.639
1300	24.900	71.275	53.479	26.524	- 73.071	- 41.685	6.073
1400	24.900	72.925	55.077	28.524	- 72.176	- 39.623	5.412
1500	24.900	74.593	56.669	31.014	- 71.268	- 37.613	4.835
1600	24.900	76.600	57.216	33.904	- 69.519	- 33.754	3.882
1700	24.900	78.110	58.401	36.484	- 68.647	- 31.894	3.485
1800	24.900	80.879	60.526	40.974	- 110.230	- 28.526	2.969
1900	24.900	82.156	61.669	43.464	- 109.278	- 28.659	2.989
2000	24.900	83.371	62.674	45.954	- 107.481	- 17.045	1.552
2100	24.900	84.530	63.641	50.934	- 106.560	- 13.299	1.163
2200	24.900	85.647	64.474	53.424	- 105.701	- 9.585	.806
2300	24.900	87.713	65.343	55.914	- 104.665	- 5.904	.478
2400	24.900	88.689	67.183	58.404	- 103.584	- 1.568	.103
2500	24.900	89.659	67.988	60.552	- 102.493	- 4.963	.362
2600	24.900	91.603	68.525	63.384			
2700	24.900	92.252	70.294	65.874			
2800	24.900						
2900	24.900						
3000	24.900						

Lead Dichloride (PbCl₂) (Liquid)

Mol. Wt. = 278.12

 ΔH_f° 298.15 = [-81.49] kcal. mole⁻¹ $S_{298.15}^\circ$ = [39.336] cal. deg.⁻¹ mole⁻¹ T_m = 768°K ΔH_m° = 5.70 kcal. mole⁻¹ T_b = 1226°K ΔH_v° = 26.61 ± 0.70 kcal. mole⁻¹Heat of Formation. Calculated from that of the crystal.Heat Capacity, Entropy and Melting Data. C_p reported by M.Bizouard and P. Pauly, Compt. rend. 252, 511 (1961). T_m and ΔH_m°

obtained from M. Blanc and G. Petit, Compt. rend. 248, 1305 (1959).

A glass transition temperature of 520°K. is assumed.

Vaporization Phenomena. T_b and ΔH_v° calculated from ΔH_g° 298.15 and functions for condensed and gaseous states.

Lead Dichloride (PbCl₂)

(Ideal Gas) Mol. Wt. = 278.12

INTERIM TABLE

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _f
0	11.084	0.000	INFINITE	-	3.486	-40.218	-40.218	INFINITE
100	11.084	63.059	84.677	-2.502	-	-41.304	-41.304	96.267
200	12.821	71.390	77.839	-1.200	-	-40.510	-42.162	46.070
298	13.370	76.630	76.630	-1.000	-	-40.610	-42.953	31.484
300	13.377	76.713	76.630	-0.925	-	-40.612	-42.947	31.300
400	13.599	80.596	77.158	-1.375	-	-40.744	-43.733	23.893
500	13.708	83.643	78.161	-2.741	-	-40.904	-44.463	19.434
600	13.769	86.148	78.990	-4.115	-	-41.089	-45.156	16.447
800	13.816	90.276	81.825	-5.874	-	-42.436	-45.028	14.245
900	13.847	91.749	82.571	-6.260	-	-42.903	-46.495	11.285
1000	13.859	93.208	83.563	-9.645	-	-43.118	-46.861	10.241
1100	13.868	94.530	84.501	-11.031	-	-43.328	-47.226	9.382
1200	13.875	95.726	85.379	-12.408	-	-43.522	-47.589	8.693
1300	13.880	96.897	86.209	-13.782	-	-43.702	-47.946	8.126
1400	13.884	97.976	87.023	-15.154	-	-43.933	-48.213	7.526
1500	13.888	98.934	87.779	-16.583	-	-44.134	-48.510	7.060
1600	13.890	99.731	88.498	-17.972	-	-44.340	-48.766	6.665
1700	13.893	100.573	89.186	-19.361	-	-44.549	-49.066	6.307
1800	13.895	101.316	90.466	-20.750	-	-44.754	-49.374	5.970
2000	13.898	102.831	91.066	-23.530	-	-45.213	-49.809	5.443
2100	13.899	103.509	91.643	-24.920	-	-45.920	-48.482	5.045
2200	13.901	104.178	92.730	-26.310	-	-46.704	-46.704	4.529
2300	13.901	104.776	93.245	-27.700	-	-47.574	-44.574	3.999
2400	13.902	105.365	93.245	-29.090	-	-48.407	-42.618	3.469
2500	13.902	105.933	94.741	-30.480	-	-49.296	-40.916	3.577
2600	13.903	106.478	94.220	-31.870	-	-49.667	-39.002	3.278
2700	13.904	107.003	94.694	-33.261	-	-49.130	-37.079	3.001
2800	13.904	107.509	94.694	-34.651	-	-48.728	-35.203	2.803
2900	13.905	107.996	94.568	-36.041	-	-49.057	-33.202	2.605
3000	13.905	108.468	94.991	-37.432	-	-49.057	-31.246	2.276
3100	13.905	108.924	94.400	-38.822	-	-49.406	-29.282	2.064
3200	13.906	109.365	94.799	-40.213	-	-49.773	-27.305	1.895
3300	13.906	110.208	94.583	-41.604	-	-50.152	-25.312	1.698
3400	13.906	110.611	94.930	-42.994	-	-50.552	-23.312	1.498
3500	13.907	110.611	94.930	-44.385	-	-50.962	-21.302	1.330
3600	13.907	111.003	94.268	-45.776	-	-51.382	-19.274	1.170
3700	13.907	111.384	94.637	-47.166	-	-51.813	-17.238	1.018
3800	13.907	111.758	94.939	-48.556	-	-52.250	-15.199	0.874
3900	13.907	112.116	95.209	-49.946	-	-52.693	-13.159	0.734
4000	13.908	112.468	95.434	-51.338	-	-53.143	-11.100	0.604
4100	13.908	112.812	95.951	-52.729	-	-54.595	-8.978	0.479
4200	13.908	113.147	100.565	-54.120	-	-55.500	-6.784	0.356
4300	13.908	113.474	100.565	-55.510	-	-56.402	-4.582	0.232
4400	13.908	113.794	100.662	-56.902	-	-57.302	-2.361	0.132
4500	13.908	114.107	101.153	-58.292	-	-58.202	-0.140	0.026
4600	13.908	114.412	101.438	-59.683	-	-59.683	1.598	0.076
4700	13.908	114.717	101.697	-61.074	-	-61.074	3.762	0.174
4800	13.909	115.011	101.939	-62.465	-	-62.465	5.926	0.272
4900	13.909	115.291	102.259	-63.856	-	-63.856	8.084	0.360
5000	13.909	115.572	102.523	-65.247	-	-65.247	10.235	0.447
5100	13.909	115.847	102.781	-66.638	-	-66.638	12.420	0.532
5200	13.909	116.118	103.035	-68.028	-	-68.028	14.613	0.614
5300	13.909	116.389	103.289	-69.419	-	-69.419	16.806	0.696
5400	13.909	116.642	103.529	-70.810	-	-70.810	19.010	0.773
5500	13.909	116.898	103.770	-72.201	-	-72.201	21.234	0.844
5600	13.909	117.148	104.007	-73.592	-	-73.592	23.456	0.915
5700	13.909	117.395	104.240	-74.983	-	-74.983	25.681	0.985
5800	13.909	117.635	104.469	-76.374	-	-76.374	27.906	1.055
5900	13.909	117.874	104.694	-77.765	-	-77.765	30.127	1.117
6000	13.909	118.108	104.915	-79.156	-	-79.156	32.416	1.181

Hersch 31, 1962

Cl₂PbCl₂PbLead Dichloride (PbCl₂)

(Ideal Gas)

Mol. Wt. = 278.12

ΔH°_f 298.15 = -40.61 ± 0.70 kcal. mole⁻¹S°_{298.15} = [76.530]Point group C_{2v}

Vibrational Levels and Multiplicities

ω₂, cm.⁻¹

[240] (1)

[70] (1)

[300] (1)

Pb-Cl distance = 2.46 ± 0.02 Å Cl-Pb-Cl angle = 95° σ = 2

I_A = 24.223 X 10⁻³⁹ g. cm.² I_B = 39.741 X 10⁻³⁹ g. cm.²I_C = I_A + I_B = 62.970 X 10⁻³⁹ g. cm.²Heat of Formation. calculated from ΔH°_f 298.15 for PbCl₂(c) and ΔH°_s 298.15.

Heat Capacity and Entropy. Molecular dimensions obtained from L. E. Sutton (ed.), "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.

Vibrational frequencies estimated by comparison with the vibrational frequencies for the mercury dihalides.

Point Group C_{2v} $\Delta H_f^\circ = -39.34 \pm 1.0$ kcal/mol $S_{298.15}^\circ = 67.36 \pm 0.5$ gibbs/mol $\Delta H_f^\circ = -39.3 \pm 1.0$ kcal/molSilicon Dichloride (SiCl₂)
(Ideal Gas) GFW = 98.992

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	9.000	55.000	INF	0.000	39.343	30.343	1.671
100	11.000	62.695	66.440	1.153	39.257	41.205	0.927
200	11.103	67.360	67.360	1.000	42.154	42.154	30.900
298	12.269	67.360	67.360	1.023	42.172	42.172	30.722
300	12.284	67.436	67.436	1.285	39.301	42.172	30.722
400	12.693	71.063	67.956	2.352	39.376	43.043	23.539
500	13.424	73.919	68.794	3.879	39.466	44.043	19.251
600	13.420	76.408	69.666	5.925	39.570	44.949	16.373
700	13.543	78.487	70.953	8.274	39.684	45.836	14.311
800	13.624	80.301	72.011	10.633	39.811	46.708	12.760
900	13.684	81.910	72.996	13.066	39.946	47.568	11.549
1000	13.726	83.334	73.965	15.580	40.093	48.410	10.578
1100	13.757	84.664	74.897	17.645	40.253	49.223	9.760
1200	13.781	85.862	75.762	19.220	40.421	50.031	9.112
1300	13.800	86.966	76.581	21.399	40.599	50.825	8.554
1400	13.815	87.969	77.360	23.680	40.787	51.604	8.056
1500	13.827	88.942	78.101	26.162	40.986	52.370	7.636
1600	13.837	89.895	78.807	28.845	41.196	53.122	7.256
1700	13.845	90.824	79.480	31.629	41.409	53.854	6.911
1800	13.852	91.666	80.124	34.514	41.635	54.568	6.595
1900	13.856	92.435	80.741	37.500	41.871	55.264	6.306
2000	13.858	93.126	81.333	40.687	42.119	55.942	6.041
2100	13.858	93.742	81.901	44.072	42.378	56.602	5.795
2200	13.857	94.286	82.448	47.655	42.648	57.244	5.565
2300	13.854	94.764	82.974	51.436	42.929	57.868	5.348
2400	13.849	95.176	83.482	55.414	43.221	58.474	5.143
2500	13.842	95.521	83.969	59.589	43.525	59.064	4.950
2600	13.833	95.800	84.440	63.962	43.841	59.638	4.767
2700	13.822	96.060	84.895	68.535	44.168	60.194	4.594
2800	13.809	96.300	85.340	73.308	44.506	60.732	4.431
2900	13.793	96.520	85.595	78.281	44.854	61.252	4.278
3000	13.776	96.720	85.830	83.462	45.212	61.754	4.134
3100	13.757	96.900	86.040	88.845	45.580	62.238	4.000
3200	13.736	97.060	86.220	94.430	45.958	62.704	3.875
3300	13.712	97.200	86.380	100.215	46.346	63.152	3.758
3400	13.686	97.320	86.520	106.200	46.744	63.582	3.647
3500	13.658	97.420	86.640	112.385	47.152	64.000	3.540
3600	13.628	97.500	86.740	118.768	47.570	64.400	3.437
3700	13.596	97.560	86.820	125.350	48.000	64.784	3.336
3800	13.562	97.600	86.880	132.135	48.440	65.152	3.236
3900	13.526	97.620	86.920	139.120	48.890	65.504	3.136
4000	13.488	97.620	86.940	146.305	49.350	65.840	3.036
4100	13.448	97.600	86.940	153.690	49.820	66.160	2.936
4200	13.406	97.560	86.920	161.275	50.300	66.472	2.836
4300	13.362	97.500	86.880	169.060	50.790	66.776	2.736
4400	13.316	97.420	86.820	177.045	51.290	67.072	2.636
4500	13.268	97.320	86.740	185.230	51.800	67.360	2.536
4600	13.218	97.200	86.640	193.615	52.320	67.640	2.436
4700	13.166	97.060	86.520	202.200	52.850	67.912	2.336
4800	13.112	96.900	86.380	211.085	53.390	68.176	2.236
4900	13.056	96.720	86.220	220.270	53.940	68.432	2.136
5000	13.000	96.520	86.040	229.755	54.500	68.680	2.036
5100	12.942	96.300	85.830	239.540	55.070	68.920	1.936
5200	12.882	96.060	85.595	249.625	55.650	69.152	1.836
5300	12.820	95.800	85.340	260.010	56.240	69.376	1.736
5400	12.756	95.520	85.060	270.695	56.840	69.592	1.636
5500	12.690	95.220	84.760	281.680	57.450	69.792	1.536
5600	12.622	94.900	84.440	292.965	58.070	69.984	1.436
5700	12.552	94.560	84.100	304.550	58.700	70.168	1.336
5800	12.480	94.200	83.740	316.435	59.340	70.344	1.236
5900	12.406	93.820	83.360	328.620	60.000	70.512	1.136
6000	12.330	93.420	82.960	341.105	60.670	70.672	1.036

Dec. 31, 1950; Dec. 31, 1969

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	(1)	[28300]	(1)
[23000]	(3)	[29950]	(1)

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	g_i
513 (1)	(1)
1300 (1)	(1)
502 (1)	(1)

Bond Distance: Si-Cl = [2.04] Å

Bond Angle: Cl-Si-Cl = [106°]

Product of the Moments of Inertia: $I_A I_B I_C = (5.709 \times 10^{-114})$ g³ cm⁶

o = 2

Heat of Formation

The adopted value is derived from $\Delta H_f^\circ = 78.5 \pm 2$ kcal/mol at 298.15 K for the reaction $\text{Si(c)} + \text{SiCl}_4(\text{g}) \rightarrow 2 \text{SiCl}_2(\text{g})$. JANAF analyses of equilibrium data for this reaction are summarized below. Three sets of data (1, 2, 3) yield average values of ΔH_f° (3rd law) which agree within 0.5 kcal/mol and values of ΔS_f° (2nd law) which are in reasonable agreement with the JANAF functions. Two of the equilibrium studies used flow techniques while the third used a static technique. A median value of ΔH_f° is adopted. Its uncertainty is estimated by assuming that the JANAF entropy for $\text{SiCl}_2(\text{g})$ may be too low by 0.7 gibbs/mol at 1400 K. The adopted value corresponds to ΔH_f° atom = 203.0 kcal/mol and an average bond energy of 101.5 kcal/mol.

Two other flow studies (3, 4) yield large entropy errors, suggesting that there are temperature-dependent errors in Kp. The reported equilibrium constants are reasonable at the lower temperatures but deviate progressively at the higher temperatures. In contrast, the static study of Ishino (5) gave Kp values which differ by a factor of five from the adopted ones. These data yield a consistent entropy but ΔH_f° (3rd law) is lower by 5 kcal/mol.

Source

Source	Date	Method	Input	Range T, °K	Entropy Test ^a 6, gibbs/mol	ΔH_f° , kcal/mol 2nd Law	3rd Law
Schäfer (1)	1967	Flow	Equation	1273-1473	1.6 ± 1	80.6 ± 1	78.35
Teichmann (2)	1966	Flow	Equation	1223-1573	1.7 ± 0.8	80.8 ± 1.1	78.49
Chechenev (3)	1965	Flow	Data	1473-1573	36 ± 6	132 ± 9	76.4
Antipin (4)	1954	Flow	Data	1273-1573	26 ± 3	114 ± 4	75.4
Ishino (5)	1965	Static	Data	1448-1573	-2.1 ± 1.4	70.2 ± 2.1	73.4
Schäfer (6)	1953	Static	Equation	1400-1593	0.6 ± 0.9	79.8 ± 1.4	78.84

^a ΔS_f° (2nd law) - ΔS_f° (JANAF functions); where equations are used as input, the uncertainties are those given by the original authors.

Heat Capacity and Entropy

The point group is assumed to be the same as that of CF_2 and SiF_2 . The Si-Cl bond length and Cl-Si-Cl bond angle are estimated to be intermediate between those in HSiCl_3 and H_2SiCl_2 . Comparisons with CF_2 , SiF_2 , H_2O , and H_2SiF_2 confirm that the estimated angle is reasonable. Further confirmation of the structure comes from analysis of isotopic splittings in the infrared spectra of matrix-isolated SiCl_2 . Milligan and Jacox (7) deduced angles of 90 to 120° from alternative assignments for the two stretching vibrations. Observations on argon matrices gave 502 and 513 cm⁻¹ for these vibrations, but it was not possible to decide which is the symmetric mode. Principal moments of inertia are $I_A = 31.25 \times 10^{-38}$, $I_B = 5.035 \times 10^{-38}$, and $I_C = 36.29 \times 10^{-38}$ g² cm².

Milligan and Jacox (7) also observed an unstructured absorption in the ultraviolet spectrum. This is the region in which gas-phase emission studies (8) showed features tentatively ascribed to SiCl_2^+ . Vibrational spacings of about 250 and 540 cm⁻¹ were associated (8) with the ground state; however, this analysis should be reviewed in the light of the matrix spectra. Meanwhile, we estimate that the bending mode should be similar to that in H_2SiCl_2 , probably 190 ± 40 cm⁻¹.

The ground state is assumed to be 1A_1 , as suggested by Hückel-molecular-orbital calculations (9). Singlet excited states (8, 10) are included near 28000 and 30000 cm⁻¹, but the values are placed in brackets to emphasize the uncertainty in the analysis. Also tentatively adopted is the suggestion by Hastie et al. (10) that the continuous spectrum near 23000 cm⁻¹ is due to a triplet excited state.

References

1. H. Schäfer, H. Brudersack and B. Morcher, *Z. Anorg. Allg. Chem.* **352**, 122 (1967).
2. R. Schumann and E. Wolf, *ibid.*, **357**, 145 (1966).
3. V. K. Teichmann and L. A. Fomochuk, *Izv. Vsesoyuzh. Nauchn. Tsentr. Akad. Nauk SSSR*, **1966**, 100.
4. P. F. Antipin and V. V. Sargayev, *Russ. J. Appl. Chem. (English trans.)* **27**, 737 (1954).
5. T. Ishino, A. Matsumoto and S. Yamagishi, *Kogyo Kagaku Zasshi* **68**, 262 (1965).
6. H. Schäfer and J. Nickl, *Z. Anorg. Allg. Chem.* **274**, 250 (1953).
7. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **43**, 1338 (1965).
8. J. M. Asundi, M. Karim and R. Samuel, *Proc. Phys. Soc.*, **50**, 561 (1968).
9. J. M. Asundi, M. Karim and R. Samuel, *Proc. Chem. Soc.*, **1968**, 100.
10. J. M. Hastie, R. H. Hauge and V. L. Margrave, *J. Mol. Spectrosc.* **29**, 152 (1969).



GFW = 118.806

(CRYSTAL)

TITANIUM DICHLORIDE (TiCl_2)

Titanium Dichloride (TiCl_2)

(Crystal) GFW = 118.806

$\Delta H_f^\circ = -123.0 \pm 4.0$ kcal/mol

$S_{298.15}^\circ = 20.88 \pm 1.0$ gibbs/mol

$T_s = [1581.5]^\circ\text{K}$

$\Delta H_s^\circ = [59.4]$ kcal/mol

Heat of Formation

The heat of formation of $\text{TiCl}_2(\text{c})$ has been measured calorimetrically. The chosen value of ΔH_f° is the average of two such determinations. Values of ΔH_f° are also calculated from the heats of reaction for the processes (A) $2\text{TiCl}_3(\text{c}) = \text{TiCl}_2(\text{c}) + \text{TiCl}_4(\text{g})$, (B) $3\text{TiCl}_3(\text{c}) = 2\text{TiCl}_2(\text{c}) + \text{TiCl}_4(\text{g})$, and (C) $2\text{TiCl}_3(\text{c}) = \text{TiCl}_4(\text{g}) + \text{TiCl}_2(\text{c})$. These heats of reaction are combined with auxiliary JANAF values for the heats of formation of $\text{TiCl}_3(\text{c})$, $\text{TiCl}_4(\text{g})$, $\text{TiCl}_3(\text{c})$ and $\text{TiCl}_2(\text{c})$. The following table summarizes the data used to calculate ΔH_f° .

Source	Reac.	Method	No. Pts.	Range $T^\circ\text{K}$	ΔH_f° Second Law	ΔH_f° Third Law	Drift eu	ΔH_f° kcal/mol
Clifton and MacLeod (1)		Calorimetric						
Krievie et al. (2)	A	Calorimetric	11	615-732	35.0 $\pm$ 1.4	38.9	4.2 $\pm$ 2.1	-123.7
Farber and Darnell (3)	A	Effusion	27**	593-720	35.5 $\pm$ 0.8	39.6	6.1 $\pm$ 1.3	-123.0
Sanderson and MacLeod (4)	A	Knudsen	13***	679-821	38.5 $\pm$ 0.5	35.9	-3.4 $\pm$ 0.7	-126.7
Sanderson and MacLeod (4)	A	Static	13	790-893	94.4 $\pm$ 1.9	112.6	21.4 $\pm$ 2.7	-123.1
Farber and Darnell (5)	B	Effusion	11	790-893	51.5 $\pm$ 1.4	63.0	13.6 $\pm$ 1.7	-122.7
Farber and Darnell (5)	C	Effusion	11	815-974	38.5 $\pm$ 0.5	35.7	-3.3 $\pm$ 0.5	-126.9
Hartman and Rinds (6)	A	Effusion	20	807-928	37.5 $\pm$ 0.5	36.0	-1.9 $\pm$ 0.6	-126.9
Skinner and Ruehrwein (7)	A	Manometric	5					
*Calculated values based on third law ΔH_f° 298.15°								
**Four points rejected due to failure of a statistical test.								
***Two points rejected due to failure of a statistical test.								

Heat Capacity and Entropy

The heat capacity of $\text{TiCl}_2(\text{c})$ has been measured by Kim and Stout (8) over the range 6° to 300°K. They calculated the adopted value of S_{298}° from their measurements based on $S_{298}^\circ = 0.017$ eu. The heat capacity above 300°K is estimated by graphical extrapolation. The large uncertainty on S_{298}° is due to the possibility of sizeable electronic contributions to the heat capacity below 6°K which would account for the rather low value of S_{298}° reported by Kim and Stout (8).

Heat of Sublimation

The heat of sublimation is calculated from the heats of formation of $\text{TiCl}_2(\text{c})$ and $\text{TiCl}_2(\text{g})$. The temperature of sublimation is taken as the point at which $\Delta G^\circ = 0$ for the process $\text{TiCl}_2(\text{c}) = \text{TiCl}_2(\text{g})$. These values are hypothetical since TiCl_2 would be decomposed to $\text{TiCl}_3(\text{g})$ and $\text{TiCl}_4(\text{g})$ below this temperature.

References

1. D. G. Clifton and G. E. MacLeod, J. Phys. Chem. **60**, 311 (1956).
2. W. F. Krievie, S. P. Vango and D. M. Mason, J. Chem. Phys. **25**, 519 (1956).
3. M. Farber and A. J. Darnell, J. Phys. Chem. **59**, 156 (1955).
4. B. S. Sanderson and G. E. MacLeod, J. Phys. Chem. **60**, 316 (1956).
5. M. Farber and A. J. Darnell, J. Chem. Phys. **25**, 526 (1956).
6. H. Hartman and G. Rinds, Z. Physik, Chem. **11**, 213 (1957).
7. G. B. Skinner and R. A. Ruehrwein, J. Phys. Chem. **59**, 113 (1955).
8. S. Kim and J. W. Stout, private communication, University of Chicago, 1967.

T, °K	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f° kcal/mol	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	-	-123.033	-	INFINITE
100	9.000	4.000	22.367	3.179	-123.033	-123.033	250.919
200	14.700	14.602	22.367	1.589	-123.017	-115.292	250.919
298	16.600	20.876	20.876	0.000	-123.200	-111.552	61.623
300	16.706	20.879	20.876	0.031	-123.195	-111.279	61.066
400	17.541	25.902	21.542	1.744	-122.930	-107.346	56.651
500	18.700	29.637	22.626	3.536	-122.637	-103.483	45.232
600	18.732	33.270	24.293	5.387	-122.321	-99.662	36.309
700	19.184	36.192	25.768	7.282	-121.990	-95.935	29.652
800	19.636	38.783	27.254	9.223	-121.645	-92.237	25.198
900	20.088	41.122	28.667	11.210	-121.284	-88.561	21.510
1000	20.540	43.262	30.021	13.241	-120.911	-84.969	18.570
1100	20.992	45.240	31.315	15.318	-120.520	-81.392	16.171
1200	21.444	47.066	32.554	17.439	-120.051	-77.815	14.172
1300	21.896	48.821	33.739	19.606	-120.500	-74.235	12.440
1400	22.348	50.460	34.875	21.819	-119.920	-70.698	11.036
1500	22.800	52.017	35.966	24.076	-119.314	-67.203	9.791
1600	23.252	53.503	37.016	26.379	-118.602	-63.768	8.708
1700	23.704	54.926	38.028	28.726	-117.807	-60.334	7.756
1800	24.156	56.294	39.005	31.119	-117.350	-56.961	6.916
1900	24.608	57.612	39.950	33.558	-116.650	-53.628	6.168
2000	25.060	58.886	40.865	36.041	-120.380	-53.172	5.462



Titanium Dichloride (TiCl₂)

(Ideal Gas) GFW = 118.806

Point Group [D_{2h}] $\Delta H_f^\circ = -56.8 \pm 3$ kcal/mol $S_{298.15}^\circ = [66.5 \pm 3.0]$ gibbs/mol $\Delta H_f^\circ_{298.15} = -56.7 \pm 3$ kcal/mol

Ground State Quantum Weight = 3

T, °K	C _p ^o	gibbs/mol S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0	0.000	0.000	INFINITE	3.237	56.591	56.591	INFINITE
100	9.629	53.355	77.684	56.631	56.631	56.631	125.145
200	12.686	61.266	67.759	56.673	56.673	56.673	63.236
298	13.743	66.500	66.500	56.700	56.700	56.700	42.648
300	13.756	66.595	66.500	56.701	56.701	56.701	42.592
400	14.216	70.614	67.046	56.747	56.747	56.747	32.262
500	14.452	73.614	68.091	56.811	56.811	56.811	26.056
600	14.595	76.462	69.271	56.894	56.894	56.894	21.917
700	14.668	79.179	70.484	56.985	56.985	56.985	18.727
800	14.686	81.782	71.725	57.083	57.083	57.083	16.134
900	14.763	84.316	73.074	57.173	57.173	57.173	14.091
1000	14.803	86.774	74.534	57.255	57.255	57.255	12.559
1100	14.842	89.166	76.000	57.329	57.329	57.329	11.455
1200	14.879	91.500	77.466	57.396	57.396	57.396	10.604
1300	14.913	93.782	78.922	57.456	57.456	57.456	9.967
1400	14.947	96.019	80.377	57.509	57.509	57.509	9.497
1500	15.068	98.216	81.832	57.556	57.556	57.556	9.133
1600	15.146	100.382	83.287	57.597	57.597	57.597	8.842
1700	15.232	102.516	84.742	57.633	57.633	57.633	8.602
1800	15.324	104.619	86.197	57.664	57.664	57.664	8.402
1900	15.419	106.692	87.652	57.691	57.691	57.691	8.239
2000	15.516	108.734	89.107	57.714	57.714	57.714	8.104
2100	15.613	110.746	90.562	57.733	57.733	57.733	8.000
2200	15.709	112.728	92.017	57.748	57.748	57.748	7.922
2300	15.804	114.681	93.472	57.759	57.759	57.759	7.866
2400	15.893	116.605	94.927	57.766	57.766	57.766	7.828
2500	15.980	118.500	96.382	57.769	57.769	57.769	7.804
2600	16.062	120.366	97.837	57.768	57.768	57.768	7.792
2700	16.139	122.201	99.292	57.763	57.763	57.763	7.790
2800	16.212	124.006	100.747	57.754	57.754	57.754	7.796
2900	16.282	125.781	102.202	57.741	57.741	57.741	7.809
3000	16.346	127.526	103.657	57.724	57.724	57.724	7.828
3100	16.407	129.241	105.112	57.703	57.703	57.703	7.852
3200	16.464	130.926	106.567	57.678	57.678	57.678	7.881
3300	16.517	132.581	108.022	57.649	57.649	57.649	7.914
3400	16.567	134.206	109.477	57.616	57.616	57.616	7.950
3500	16.615	135.801	110.932	57.579	57.579	57.579	8.000
3600	16.660	137.366	112.387	57.538	57.538	57.538	8.060
3700	16.702	138.901	113.842	57.493	57.493	57.493	8.130
3800	16.741	140.406	115.297	57.444	57.444	57.444	8.210
3900	16.778	141.881	116.752	57.391	57.391	57.391	8.290
4000	16.812	143.326	118.207	57.334	57.334	57.334	8.380
4100	16.857	144.741	119.662	57.273	57.273	57.273	8.480
4200	16.897	146.126	121.117	57.208	57.208	57.208	8.590
4300	16.937	147.481	122.572	57.139	57.139	57.139	8.710
4400	16.976	148.806	124.027	57.066	57.066	57.066	8.840
4500	16.992	150.101	125.482	56.989	56.989	56.989	8.980
4600	17.023	151.366	126.937	56.908	56.908	56.908	9.130
4700	17.052	152.601	128.392	56.823	56.823	56.823	9.290
4800	17.082	153.806	129.847	56.734	56.734	56.734	9.460
4900	17.110	155.001	131.302	56.640	56.640	56.640	9.640
5000	17.137	156.166	132.757	56.541	56.541	56.541	9.830
5100	17.163	157.301	134.212	56.437	56.437	56.437	10.030
5200	17.189	158.406	135.667	56.329	56.329	56.329	10.240
5300	17.212	159.481	137.122	56.216	56.216	56.216	10.460
5400	17.235	160.526	138.577	56.099	56.099	56.099	10.690
5500	17.256	161.541	139.932	55.978	55.978	55.978	10.930
5600	17.276	162.526	141.287	55.853	55.853	55.853	11.180
5700	17.296	163.481	142.642	55.724	55.724	55.724	11.440
5800	17.313	164.406	143.997	55.591	55.591	55.591	11.710
5900	17.330	165.301	145.352	55.454	55.454	55.454	11.990
6000	17.345	166.166	146.707	55.313	55.313	55.313	12.280

Dec. 31, 1960; Mar. 31, 1984; June 30, 1988; Dec. 31, 1988

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[3]
[7000]	[6]
[17000]	[8]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	g_i
[279] (1)	[1]
[196] (2)	[2]
[439] (1)	[1]

Bond Distance: Ti-Cl = [2.3] Å

Bond Angle: Cl-Ti-Cl = [180°]

Rotational Constant: B₀ = [0.0449] cm⁻¹

o = 2

Heat of Formation

Gross and Levi (1) have measured the equilibrium $2\text{TiCl}_3(\text{g}) + \text{Ti}(\text{c}) \rightarrow 3\text{TiCl}_2(\text{g})$ at 1723°K and obtain $\Delta G_{1723}^\circ = 21.7$ kcal/mol from four measurements. This yields $\Delta H_{298}^\circ(\text{TiCl}_2, \text{g}) = -56.7 \pm 3$ kcal/mol. They discuss the measurements of Farber and Darnall (2), on the vapor pressure of $\text{TiCl}_2(\text{c})$, and show that the results are probably in error due to disproportionation of $\text{TiCl}_3(\text{g})$ on condensation. In the work of Skinner and Rushwain (3) on the reaction $2\text{NaCl}(\text{g}) + \text{Ti}(\text{c}) = 2\text{Na}(\text{g}) + \text{TiCl}_2(\text{g})$, Gross and Levi indicate that the basic assumption, of conversion to TiCl_2 only, is erroneous. In the third law analysis of both these data sets significant drifts are obtained which tends to confirm the above arguments.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $\text{TiCl}_2(\text{c})$ reported by Benzinger and Rundle (4). The vibrational frequencies are estimated from a valence force field model.

The electronic levels are assumed to correspond to the inverted states of $\text{NiCl}_2(\text{g})$ (5). This linear configuration is adopted, since experimental evidence indicates that other transition metal dihalides are linear (6, 7, 8, 9).

References

1. P. Gross and D. L. Levi, 168 Cong. Intern. Chim. Pure et Appl. 628, (1958).
2. M. Farber and A. J. Darnall, J. Chem. Phys. 25, 526 (1956).
3. G. B. Skinner and R. A. Rushwain, J. Phys. Chem. 59, 113 (1955).
4. N. C. Benzinger and R. E. Rundle, Acta Cryst. 1, 274 (1949).
5. C. W. DeLoock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966).
6. R. A. Barg and O. Sinanoglu, J. Chem. Phys. 32, 1082 (1960).
7. J. T. Hougen, G. E. Leroy, and T. C. James, J. Chem. Phys. 31, 1670 (1959).
8. G. E. Leroy, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. 35, 2879 (1962).
9. A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. 40, 3471 (1964).

Tungsten Dichloride (WCl₂)

GF_W = 254.756

(Crystal)

T, °K	CP°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	18.600	31.200	31.200	0.000	- 61.500	- 52.587	38.547
300	18.610	31.315	31.200	-0.34	- 61.492	- 52.532	38.269
400	19.133	36.740	31.937	1.922	- 61.023	- 49.616	27.109
500	19.656	41.065	33.344	3.861	- 60.538	- 46.819	20.465
600	20.179	44.696	34.941	5.853	- 60.026	- 44.123	16.072
700	20.702	48.327	36.818	7.845	- 59.494	- 41.426	12.681
800	21.225	51.958	38.695	9.837	- 58.904	- 38.989	10.051
900	21.750	55.589	40.572	11.829	- 58.287	- 36.534	8.072
1000	22.273	59.220	42.449	13.821	- 57.634	- 34.153	7.464
1100	22.796	62.851	44.320	15.813	- 56.942	- 31.839	6.326
1200	23.319	66.482	46.191	17.805	- 56.211	- 29.588	5.409
1300	23.842	70.113	48.062	19.797	- 55.441	- 27.390	4.688
1400	24.365	73.744	49.943	21.789	- 54.632	- 25.244	3.945
1500	24.888	77.375	51.824	23.781	- 53.783	- 23.205	3.381
1600	25.411	81.006	53.705	25.773	- 52.895	- 21.196	2.995
1700	25.934	84.637	55.586	27.765	- 51.968	- 19.248	2.706
1800	26.457	88.268	57.467	29.757	- 51.001	- 17.345	2.406
1900	26.980	91.899	59.348	31.749	- 49.994	- 15.502	1.783
2000	27.503	95.530	61.229	33.741	- 48.950	- 13.712	1.498

TUNGSTEN DICHLORIDE (WCl₂)

(CRYSTAL)

GF_W = 254.756

Cl₂W

ΔHf° = Unknown

ΔHf°_{298.15} = -61.5 ± 3 kcal/mol

S°_{298.15} = [31.2] gibbs/mol

Td = 862°K

Heat of Formation.

The heat of formation, ΔHf°₂₉₈ (WCl₂, c) = -61.5 ± 3 kcal/mol, is derived from the heat of combustion, ΔHc° = -140 ± 3 kcal/mol for WCl₂(c) + 3/2 O₂(g) → WO₃(c) + Cl₂(g), reported by S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kovs, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zhur. Neorg. Khim. 5, 1650 (1960). The value of ΔHc° was determined calorimetrically, but no further information about the combustion process was given in the paper.

Heat Capacity and Entropy.

CP°₂₉₈ = 6.2 gibbs/g-atom and CP°₉₀₀ = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. Between 298° and 900°, which is near the decomposition temperature, the heat capacity is obtained by linear interpolation.

The entropy, S°₂₉₈ = 31.2 eu, is estimated by the method of W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, 1952. S. A. Shchukarev et al., loc. cit., have estimated ΔS° = -30 eu for W(c) + Cl₂(g) = WCl₂(c) which leads to S°₂₉₈ (WCl₂, c) = 31.1 eu, using JANAP auxiliary data.

Temperature of Decomposition.

The decomposition temperature is obtained by extrapolation to one atmosphere total pressure of a log P versus 1/T plot of the decomposition pressure data reported by S. A. Shchukarev, G. I. Novikov, and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 10, Ser. Fiz. i Khim., No. 2, 78 (1959). Decomposition pressure data for Cl:W ratios less than two suggest that the decomposition reaction is not simple.

Point Group [D_{∞h}]
S_{298.15} = [74] gibbs/mol
Ground State Quantum Weight = [5]
ΔH_f⁰ = [-3 ± 25] kcal/mol
ΔH_{298.15}⁰ = [-3 ± 25] kcal/mol

Electronic Levels and Quantum Weights

ε _i cm ⁻¹	g _i
0	[5]
[5600]	[10]
[8900]	[10]

Vibrational Frequencies and Degeneracies

ω _i cm ⁻¹	
[360]	(1)
[60]	(2)
[423]	(1)

$$\sigma = [2]$$

Bond Distance: W-Cl = [2.26] Å

Bond Angle: Cl-W-Cl = [180]°

Rotational Constant: B₀ = [0.04655] cm⁻¹

Heat of Formation.

The value of ΔH_f⁰₂₉₈(WCl₂,g) = -3 ± 25 kcal/mol is calculated from the heat of formation of the crystal plus the heat of sublimation, ΔH_s₂₉₈ = 58.5 ± 25 kcal/mol. The latter is estimated from the heats of sublimation of TiCl₂, CrCl₂, MnCl₂, FeCl₂, CoCl₂, NiCl₂ given by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).

The uncertainty covers the difference between the heats of sublimation among the above compounds and also the possible error in transference from the first row transition metal chlorides to tungsten dichloride.

S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Beev, Zh. Neorg. Khim. 5, 1650 (1960), have also estimated the heat of sublimation as 102 kcal/mol.

Heat Capacity and Entropy.

The molecular configuration of WCl₂(g) is assumed to be linear. The bond distance is estimated to be the same as that in WCl₆(g). The ground state configuration (⁵Σ_g⁺), the low lying electronic levels and their quantum weights are assumed to be the same as those for CrCl₂(g), observed by C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966). The vibrational frequencies are calculated from a valence force field model. The stretching force constant, K₁, is estimated to be the same as that of HgCl₂(g), 2.7 millidynes/Å. The bending force constant is assumed to be one hundredth of the stretching force constant. The moment of inertia is I = 6.013 x 10⁻³⁸ g cm².

Sept. 30, 1962; Dec. 31, 1966



GFW = 162.126

(CRYSTAL)

ZIRCONIUM DICHLORIDE (ZrCl_2)

Zirconium Dichloride (ZrCl_2)

(Crystal) GFW = 162.126

$\Delta H_f^\circ = \text{Unknown}$

$\Delta H_{298.15}^\circ = [-103.0 \pm 10] \text{ kcal/mol}$

$\Delta H_m^\circ = [6.4 \pm 3] \text{ kcal/mol}$

$\Delta H_{298.15}^\circ = [58.5 \pm 10] \text{ kcal/mol}$

$S_{298.15}^\circ = [26.3 \pm 3] \text{ gibbs/mol}$

$T_m = [1000]^\circ\text{K}$

Heat of Formation

The value of $\Delta H_f^\circ(\text{ZrCl}_2, c) = -103.0 \text{ kcal/mol}$ is calculated from the estimated $\Delta H_{298}^\circ = 58.5 \text{ kcal/mol}$ for $\text{ZrCl}_2(c) + \text{ZrCl}_2(g)$, using $\Delta H_{298}^\circ(\text{ZrCl}_2, g) = -44.5 \text{ kcal/mol}$ (1). The estimated ΔH_{298}° is obtained as an average of the heats of sublimation at 298°K for TiCl_2 , VCl_2 , CrCl_2 , FeCl_2 , CoCl_2 , NiCl_2 given by L. Brewer, G. R. Somayajulu and E. Brackett (2).

Heat Capacity and Entropy

The heat capacities of $\text{ZrCl}_2(c)$ are estimated based on the assumption that $\text{Cp}(\text{ZrCl}_2, c) = 1/2[\text{Cp}(\text{ZrCl}_4, c) + \text{Cp}(\text{Zr}, c)]$. The entropy, S_{298}° , is also estimated in a manner similar to that of the heat capacity.

Melting Data

The melting point was estimated to be 1000°K by L. Brewer (3) and the heat of melting was also estimated by A. Glassner (4).

References

1. JANAF $\text{ZrCl}_2(g)$ table dated Dec. 31, 1969.
2. L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).
3. L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., McGraw-Hill Book Company, New York, 1949.
4. A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500°K ," ANL Report 5750, Argonne National Laboratory.

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	17.350	26.300	26.300	0.000	-103.000	-92.176	67.567
300	17.378	26.407	26.300	0.032	-102.994	-92.109	67.101
400	18.168	31.521	26.992	1.612	-102.667	-88.529	48.370
500	18.700	35.634	28.323	3.656	-102.327	-85.034	37.168
600	19.130	39.082	29.836	5.548	-101.962	-81.408	29.726
700	19.550	41.975	31.475	7.475	-101.562	-77.726	20.468
800	19.688	44.692	32.878	9.491	-101.122	-74.022	14.686
900	20.206	47.052	34.324	11.455	-100.630	-71.646	17.399
1000	20.536	49.159	35.706	13.493	-100.575	-68.414	14.952
1100	20.720	51.165	37.023	15.556	-100.226	-65.215	12.957
1200	20.900	53.078	38.278	17.648	-99.741	-62.041	10.981
1300	21.080	54.656	39.474	19.737	-99.237	-58.787	9.683
1400	21.180	56.222	40.615	21.650	-99.733	-55.617	8.682
1500	21.250	57.686	41.705	23.971	-99.234	-52.463	7.687
1600	21.300	59.059	42.747	26.009	-98.742	-49.383	6.745
1700	21.350	60.522	43.745	27.954	-98.251	-46.371	5.854
1800	21.400	61.573	44.702	30.169	-97.760	-43.271	5.254
1900	21.450	62.732	45.620	32.511	-97.311	-40.254	4.630
2000	21.500	63.833	46.504	34.659	-96.850	-37.264	4.072



ZIRCONIUM DICHLORIDE (ZrCl₂) (LIQUID) GFW = 162.126

$$\Delta H_f^{\circ} = [-98.372] \text{ kcal/mol}$$

$$S_{298.15}^{\circ} = [29.278] \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} = [-98.372] \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = [6.4 \pm 3] \text{ kcal/mol}$$

$$T_m = [1000]^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = [6.4 \pm 3] \text{ kcal/mol}$$

$$\Delta H_v^{\circ} = [45.0] \text{ kcal/mol}$$

$$T_b = [1565.3]^{\circ}\text{K}$$

$$\Delta H_v^{\circ} = [45.0] \text{ kcal/mol}$$

Heat of Formation

The $\Delta H_f^{\circ}(\text{ZrCl}_2, l)$ is calculated from $\Delta H_f^{\circ}(\text{ZrCl}_2, c)$ by adding ΔH_m° and the difference between $H_{1000} - H_{298}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacities are assumed to be constant at 7.25 gibbs/g-atom. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

The melting point was estimated to be 1000°K by L. Brewer (1), and the heat of melting was also estimated by A. Glasner (2).

Vaporization Data

T_b is the temperature at which the Gibbs energy change approaches zero for the process $\text{ZrCl}_2(l) \rightarrow \text{ZrCl}_2(g)$. The difference between ΔH_f° for $\text{ZrCl}_2(l)$ and $\text{ZrCl}_2(g)$ at T_b is ΔH_v° .

References

1. L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., McGraw-Hill Book Company, New York, 1949.
2. A. Glasner, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500°K," ANL Report 5750, Argonne National Laboratory.

Zirconium Dichloride (ZrCl₂)

(Liquid) GFW = 162.126

T, °K	C _p ^a	$-\frac{G^{\circ}-H_{298}^{\circ}}{T}$	$\frac{H^{\circ}-H_{298}^{\circ}}{T}$	$\frac{\Delta H_f^{\circ}}{T}$	ΔG_f°	Log K _p
100						
200						
250	21.750	29.278	29.278	.000	- 88.436	64.025
300	21.750	29.413	29.278	.040	- 88.378	64.361
400	21.750	35.670	30.132	2.215	- 85.157	46.528
500	21.750	40.523	31.743	4.390	- 82.116	35.893
600	21.750	44.489	33.546	6.565	- 79.206	28.851
700	21.750	47.881	35.325	8.740	- 76.398	23.853
800	21.750	50.746	37.102	10.915	- 73.673	20.126
900	21.750	53.307	38.763	13.090	- 71.015	17.245
1000	21.750	55.599	40.334	15.265	- 68.414	14.952
1100	21.750	57.472	41.817	17.440	- 65.860	13.085
1200	21.750	59.564	43.218	19.615	- 63.298	11.528
1300	21.750	61.305	44.544	21.790	- 60.750	10.213
1400	21.750	62.917	45.799	23.965	- 58.247	9.093
1500	21.750	64.418	46.991	26.140	- 55.785	8.128
1600	21.750	65.422	48.125	28.315	- 53.359	7.289
1700	21.750	67.140	49.205	30.490	- 50.965	6.552
1800	21.750	68.383	50.236	32.665	- 48.605	5.901
1900	21.750	69.559	51.222	34.840	- 46.270	5.322
2000	21.750	70.675	52.167	37.015	- 43.963	4.808

June 30, 1962; Dec. 31, 1969

GFV = 162.126

(IDEAL GAS)

ZIRCONIUM DICHLORIDE (ZrCl₂)Point Group = [D_{2h}] $\Delta H_f^\circ = -44.4 \pm 5 \text{ kcal/mol}$ $S_{298.15}^\circ = [69.9 \pm 3] \text{ gibbs/mol}$ $\Delta H_f^\circ_{298.15} = -44.5 \pm 5 \text{ kcal/mol}$

Ground State Quantum Weight = [3]

Zirconium Dichloride (ZrCl₂)

(Ideal Gas) GFV = 162.126

T, °K	Cp°	$S^\circ - (C_p^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	Log Kp
0	10.690	56.359	2.450	-44.389	9.81116
100	12.856	64.565	1.132	-45.951	50.213
200	13.785	69.696	1.000	-44.500	34.213
300	13.796	69.681	1.026	-44.500	34.012
400	14.231	70.017	1.843	-44.500	22.903
500	14.457	71.219	2.665	-44.618	21.032
600	14.587	72.668	4.318	-44.712	17.779
700	14.668	82.123	7.865	-44.833	15.449
800	14.724	84.085	7.022	-44.983	13.697
900	14.765	85.360	7.176	-45.168	12.416
1000	14.803	86.360	7.176	-45.384	11.230
1100	14.841	86.792	78.169	-45.596	10.327
1200	14.885	90.066	13.172	-46.706	9.560
1300	14.937	91.279	80.000	-46.811	8.905
1400	14.987	92.425	14.663	-46.940	8.347
1500	15.067	93.425	17.663	-47.042	7.853
1600	15.146	94.400	19.173	-47.168	7.425
1700	15.232	95.321	20.692	-47.296	7.045
1800	15.323	96.194	22.250	-47.429	6.707
1900	15.419	97.018	23.847	-47.566	6.405
2000	15.516	97.818	25.304	-47.705	6.129
2100	15.613	98.578	26.660	-47.847	5.881
2200	15.709	99.306	28.046	-47.996	5.636
2300	15.803	100.007	30.092	-48.155	5.407
2400	15.893	100.682	31.175	-48.325	5.192
2500	15.980	101.332	32.059	-48.506	5.002
2600	16.062	101.960	32.882	-48.692	4.822
2700	16.140	102.568	33.639	-48.884	4.656
2800	16.215	103.156	34.310	-49.082	4.500
2900	16.287	103.726	34.916	-49.285	4.352
3000	16.346	104.279	35.458	-49.492	4.220
3100	16.403	104.816	36.034	-49.704	4.093
3200	16.457	105.338	36.644	-49.921	3.974
3300	16.507	105.843	37.187	-50.143	3.862
3400	16.554	106.332	37.764	-50.370	3.756
3500	16.614	106.820	38.274	-50.602	3.656
3600	16.660	107.289	38.816	-50.840	3.561
3700	16.702	107.746	39.389	-51.084	3.472
3800	16.741	108.187	39.991	-51.334	3.387
3900	16.783	108.627	40.621	-51.589	3.306
4000	16.821	109.053	41.277	-51.848	3.229
4100	16.857	109.469	41.965	-52.112	3.156
4200	16.892	109.875	42.684	-52.381	3.084
4300	16.924	110.273	43.434	-52.655	3.012
4400	16.954	110.660	44.214	-52.934	2.940
4500	16.992	111.044	45.026	-53.218	2.869
4600	17.023	111.418	45.869	-53.506	2.799
4700	17.053	111.784	46.744	-53.798	2.729
4800	17.083	112.146	47.651	-54.094	2.659
4900	17.110	112.506	48.589	-54.394	2.589
5000	17.137	112.842	49.557	-54.698	2.519
5100	17.163	113.182	50.555	-55.006	2.449
5200	17.188	113.515	51.584	-55.318	2.379
5300	17.213	113.843	52.644	-55.634	2.309
5400	17.235	114.166	53.734	-55.954	2.239
5500	17.256	114.481	54.854	-56.278	2.169
5600	17.276	114.792	55.994	-56.606	2.099
5700	17.295	115.098	57.164	-56.938	2.029
5800	17.313	115.399	58.364	-57.274	1.959
5900	17.330	115.695	59.594	-57.614	1.889
6000	17.345	115.987	60.854	-57.958	1.819

June 30, 1962; Dec. 31, 1969

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}
[346] (1)
[92] (2)
[461] (1)

Bond Distance: Zr-Cl = [2.3] Å

Bond Angle: Cl-Zr-Cl = [180°]

Rotational Constant: $B_0 = [0.0494] \text{ cm}^{-1}$ $\sigma = [2]$

Heat of Formation

Potter (1) investigated mass spectrometrically the gaseous equilibria among ZrCl , ZrCl_2 , ZrCl_3 and ZrCl_4 . Ion intensities were measured 2.5 eV above the ionization threshold. Using the reported equilibrium constants for the reaction $\text{ZrCl}_4(g) + \text{ZrCl}_2(g) \rightleftharpoons \text{ZrCl}_3(g)$ in the temperature range 1873-2110°K, second and third law analyses give the heat of reaction at 298°K as -15.6 and -17.7 kcal/mol, respectively. The third law drift is 8.9 ± 3.7 eu. Based on the third law heat of reaction and $\Delta H_f^\circ(\text{ZrCl}_4, g) = -207.77 \text{ kcal/mol}$ (2) and $\Delta H_f^\circ(\text{ZrCl}_3, g) = -125.3 \text{ kcal/mol}$ (3), we obtain $\Delta H_f^\circ(\text{ZrCl}_2, g) = -44.5 \text{ kcal/mol}$ which is adopted in the tabulation.

Ferber et al. (4) also studied mass spectrometrically the reaction (a) $\text{Zr}(c) + \text{ZrCl}_4(g) \rightleftharpoons \text{ZrCl}_3(g)$ and the reaction (b) $\text{Zr}(c) + \text{ZrCl}_2(g) \rightleftharpoons \text{ZrCl}(g)$. They reported second law heats of reaction as $\Delta H_{298}^\circ = 28.6 \pm 1.6 \text{ kcal/mol}$ for reaction (a); and $-141.1 \pm 2.2 \text{ kcal/mol}$ for reaction (b). Third law analysis of the equilibrium constants which were calculated from their ion intensities of run 3 (the only available values) gives $\Delta H_f^\circ(\text{ZrCl}_2, g) = -43.4 \text{ kcal/mol}$. See JANAF $\text{ZrCl}_3(g)$ table (3) for details.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that other transition metal dichlorides are linear (5, 6, 7, 8, 9, 10) even though some fluorides are bent (11). The bond distance is assumed to be the same as that of $\text{ZrCl}_4(g)$. The electronic levels and quantum weights are estimated to be the same as those of $\text{TiCl}_2(g)$ (12).

The vibrational frequencies are calculated from a valence force field model. The stretching force constant is estimated to be 2.5 millidyne/Å and the bending force constant 0.05 millidyne/Å. The moment of inertia is $52.217 \times 10^{-39} \text{ g cm}^2$.

References

1. N. D. Potter, Aeronutronic Div., Philco-Ford, Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. JANAF $\text{ZrCl}_4(g)$ table dated Dec. 31, 1969.
3. JANAF $\text{ZrCl}_3(g)$ table dated Dec. 31, 1969.
4. M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRPL-TR-67-244, Contract F04611-67-C-0010, Nov. 1967.
5. R. A. Berg and G. Sinnaglu, J. Chem. Phys. **32**, 1082 (1960).
6. J. T. Houghen, G. E. Leroi and T. C. James, J. Chem. Phys. **34**, 1870 (1961).
7. G. E. Leroi, T. C. James, J. T. Houghen and W. Klemperer, J. Chem. Phys. **35**, 2879 (1962).
8. A. Buchler, J. L. Strauffer and W. Klemperer, J. Chem. Phys. **40**, 3471 (1964).
9. M. E. Jacox and D. E. Milligan, J. Chem. Phys. **51**, 4143 (1969).
10. K. R. Thompson and K. D. Carlson, J. Chem. Phys. **49**, 4379 (1968).
11. J. W. Hastie, R. H. Hauge and J. L. Margrave, J. Chem. Phys. **51**, 2648 (1969).
12. JANAF $\text{TiCl}_2(g)$ table dated Dec. 31, 1968.

T, °K.	C _p	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	ΔH_f°	ΔF°	Log K _p
0	∞.000	INFINITE	- 6.865	- 61.789	-	INFINITE
100	21.780	102.631	- 6.865	- 61.789	-	1.570
200	21.780	102.631	- 6.865	- 61.789	-	67.307
298	20.773	102.631	- 6.865	- 61.789	-	61.489
300	20.795	102.815	- 6.865	- 61.800	-	61.488
400	30.621	111.515	- 6.865	- 61.810	-	33.539
500	31.028	118.397	- 6.865	- 61.853	-	28.761
600	31.256	124.076	- 6.865	- 61.940	-	22.273
700	31.396	128.905	- 6.865	- 62.059	-	16.047
800	31.488	133.104	- 6.865	- 62.215	-	10.623
900	31.552	136.817	- 6.865	- 62.399	-	6.664
1000	31.598	140.144	- 6.865	- 62.616	-	3.224
1100	31.632	143.157	- 6.865	- 62.858	-	0.024
1200	31.657	145.910	- 6.865	- 63.131	-	10.625
1300	31.678	148.445	- 6.865	- 63.430	-	10.038
1400	31.694	150.803	- 6.865	- 63.750	-	8.227
1500	31.707	152.980	- 6.865	- 64.091	-	6.175
1600	31.717	155.027	- 6.865	- 64.453	-	4.056
1700	31.726	156.950	- 6.865	- 64.834	-	2.061
1800	31.733	158.764	- 6.865	- 65.232	-	0.286
1900	31.740	160.480	- 6.865	- 65.646	-	- 1.283
2000	31.745	162.108	- 6.865	- 66.074	-	- 2.953
2100	31.750	163.657	- 6.865	- 66.516	-	- 4.722
2200	31.754	165.134	- 6.865	- 66.972	-	- 6.586
2300	31.757	166.546	- 6.865	- 67.442	-	- 8.539
2400	31.760	167.897	- 6.865	- 67.926	-	- 10.574
2500	31.763	169.194	- 6.865	- 68.424	-	- 12.686
2600	31.765	170.440	- 6.865	- 68.936	-	- 14.866
2700	31.767	171.638	- 6.865	- 69.461	-	- 17.114
2800	31.769	172.794	- 6.865	- 69.999	-	- 19.430
2900	31.771	173.909	- 6.865	- 70.550	-	- 21.814
3000	31.773	174.986	- 6.865	- 71.114	-	- 24.266
3100	31.774	176.028	- 6.865	- 71.691	-	- 26.784
3200	31.775	177.036	- 6.865	- 72.280	-	- 29.366
3300	31.776	178.014	- 6.865	- 72.880	-	- 31.999
3400	31.777	178.963	- 6.865	- 73.491	-	- 34.672
3500	31.778	179.884	- 6.865	- 74.114	-	- 37.384
3600	31.779	180.779	- 6.865	- 74.749	-	- 40.134
3700	31.780	181.650	- 6.865	- 75.396	-	- 42.922
3800	31.781	182.497	- 6.865	- 76.054	-	- 45.748
3900	31.782	183.323	- 6.865	- 76.724	-	- 48.611
4000	31.782	184.128	- 6.865	- 77.404	-	- 51.511
4100	31.783	184.912	- 6.865	- 78.094	-	- 54.444
4200	31.783	185.678	- 6.865	- 78.794	-	- 57.410
4300	31.784	186.426	- 6.865	- 79.504	-	- 60.408
4400	31.784	187.157	- 6.865	- 80.224	-	- 63.436
4500	31.785	187.871	- 6.865	- 80.954	-	- 66.494
4600	31.785	188.570	- 6.865	- 81.694	-	- 69.582
4700	31.786	189.253	- 6.865	- 82.444	-	- 72.700
4800	31.786	189.923	- 6.865	- 83.204	-	- 75.848
4900	31.787	190.578	- 6.865	- 83.974	-	- 79.026
5000	31.787	191.220	- 6.865	- 84.754	-	- 82.234
5100	31.787	191.850	- 6.865	- 85.544	-	- 85.472
5200	31.787	192.467	- 6.865	- 86.344	-	- 88.740
5300	31.788	193.072	- 6.865	- 87.154	-	- 92.038
5400	31.788	193.667	- 6.865	- 87.974	-	- 95.366
5500	31.788	194.250	- 6.865	- 88.804	-	- 98.724
5600	31.788	194.823	- 6.865	- 89.644	-	- 102.112
5700	31.789	195.385	- 6.865	- 90.494	-	- 105.530
5800	31.789	195.938	- 6.865	- 91.354	-	- 108.978
5900	31.789	196.481	- 6.865	- 92.224	-	- 112.456
6000	31.789	197.016	- 6.865	- 93.104	-	- 115.964

Mar. 31, 1966

Point Group D_{3h}S_{298.15} = [102.63] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

ΔH_f⁰ = -61.8 ± 0.5 kcal. mole⁻¹ΔH_f⁰ 298.15 = -61.8 ± 0.5 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[100](1)	350 (2)
[150](1)	[300](2)
[250](1)	[60](2)
[200](1)	[80](2)

Bond Distance: Cu-Cl = 2.16 Å

Bond Angles: Cl-Cu-Cl = 150°

Product of the Moments of Inertia: I_AI_BI_C = 2.02847 × 10⁻¹¹ g.³ cm.⁶

Cu-Cl-Cu = 90°

σ = 6

Heat of Formation.

The heat of sublimation was determined by second and third law analysis of the following vapor pressure data. D. W. Fages, Doctoral Thesis, Ohio State University (1955), measured both vapor pressure by torsion effusion and vapor density in the range 533-644°K. and found only trimer present. The 2nd and 3rd law analyses gave ΔH_f⁰ 298 = 37.37 ± 0.04 and 37.24 ± 0.02 kcal. mole⁻¹ with a drift of -0.25 ± 0.07 cal. deg.⁻¹ mole⁻¹. R. A. J. Shelton, Trans. Faraday Soc. 57, 2113 (1961) using Knudsen effusion in the range 547-657°K. obtained ΔH_f⁰ 298 = 40.35 ± 1.4 and 37.42 ± 0.4 kcal. mole⁻¹ with a drift of -4.9 cal. deg.⁻¹ mole⁻¹. P. I. Fedorov and M. N. Shakhov, Izv. Vsesoyuzn. Nauchn. Issled. 1 Khim. Tekhnol. 4, 550 (1961), using transport methods obtained vapor pressures over the liquid from 751-1057°K. Using 2nd and 3rd law analysis these gave ΔH_f⁰ 298 = 38.6 ± 1.0 and 39.27 ± 0.5 kcal. mole⁻¹.

L. Brewer and N. L. Lofgren, J. Am. Chem. Soc. 72, 3038 (1950) obtained equilibrium constants for the reaction 3Cu(c) + 3HCl(g) → Cu₃Cl₃(g) + 1.5 H₂(g). Second and third law analysis of these constants gave ΔH_r⁰ 298 = 3.9 ± 0.6 and 4.39 ± 0.3 kcal. mole⁻¹ which leads to ΔH_f⁰ = -61.8 ± 0.5 kcal. mole⁻¹. This was the value adopted since it is dependent only on HCl(g) and does not involve three times the uncertainty of CuCl(c) as do the sublimation experiments, which yield values in good agreement but of larger uncertainty.

Heat Capacity and Entropy.

The structure of the trimer has been investigated by C-H. Wong and V. Schomaker, J. Phys. Chem. 61, 358 (1957). They conclude that the molecule is planar with D_{3h} symmetry and a Cu-Cl bond length of 2.16 Å. They also state that a very large amplitude of the asymmetric in-plane bending appears plausible from the diffraction pattern. The infra-red spectrum has been investigated by W. Klumper, S. A. Rice and R. S. Berry, J. Am. Chem. Soc. 79, 1810 (1957). They observed one strong absorption with a maximum at 350 cm.⁻¹ they attribute this to bond stretching motion of type E'. They also suggest that the broad absorption may involve another mode of approximately equal frequency.

In order to estimate the remaining frequencies we assumed that the other infra-red active E' mode would be close to the observed 350 cm.⁻¹ and this was estimated as 300 cm.⁻¹. The in-plane bending is the third E' mode and since this has a very large amplitude it was estimated as 60 cm.⁻¹. By analogy with other D_{3h} rings the A₂' mode was assumed to be in the same region as the E' stretches and was taken to be 250 cm.⁻¹. The 2A₁' stretches were estimated as 100 and 150 cm.⁻¹, while the out of plane A₂' was taken as 200 cm.⁻¹ and the E'' as 80 cm.⁻¹. These values gave calculated entropies in excellent agreement with the equilibrium data and thus support the estimates.

The individual moments of inertia were I_A=I_B = 100.472 × 10⁻³⁹ g.² cm.², I_C = 200.944 × 10⁻³⁹ g.² cm.²

Cl₃Cu₃

Trichlorofluorosilane (FSiCl₃)
(Ideal Gas) Mol. Wt. = 153.461

INTERIM TABLE

T, °K.	C _p ^o	cal. mole ⁻¹ deg ⁻¹	S ^o	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
100	13.147	61.090	INFINITE	0.592	-200.480	-200.480	INFINITE	
200	19.443	72.211	87.416	3.432	-200.986	-200.986	194.197	831.136
298	21.530	80.595	86.595	3.926	-201.043	-201.043	195.354	213.462
300	21.545	80.628	86.595	3.940	-201.000	-201.000	195.354	213.462
400	21.671	80.855	87.164	2.924	-200.900	-200.900	192.512	140.238
500	21.871	82.086	88.439	4.625	-200.785	-200.785	186.910	81.694
600	24.398	96.491	96.758	7.040	-200.662	-200.662	184.146	67.072
700	24.743	100.279	96.711	9.498	-200.538	-200.538	181.404	56.634
800	24.980	103.600	96.619	11.985	-200.414	-200.414	178.679	48.811
900	25.127	106.580	96.484	14.500	-200.290	-200.290	175.978	42.667
1000	25.272	109.208	92.195	17.013	-200.162	-200.162	173.291	37.667
1100	25.366	111.622	93.853	19.545	-200.075	-200.075	170.587	33.691
1200	25.418	113.832	95.428	22.085	-199.972	-199.972	167.909	30.579
1300	25.485	115.761	96.923	24.632	-199.873	-199.873	165.241	27.776
1400	25.527	117.525	98.498	27.140	-199.740	-199.740	162.587	25.301
1500	25.577	119.152	100.000	29.740	-199.601	-199.601	159.930	23.301
1600	25.608	121.177	100.990	32.299	-199.601	-199.601	157.280	21.482
1700	25.633	122.730	102.223	34.891	-211.621	-211.621	154.526	19.865
1800	25.653	124.000	103.691	37.520	-211.621	-211.621	151.776	18.305
1900	25.673	125.583	104.535	39.992	-211.300	-211.300	147.827	16.805
2000	25.688	126.901	105.620	42.560	-211.261	-211.261	144.465	15.768
2100	25.702	128.154	106.664	45.130	-211.166	-211.166	141.150	14.689
2200	25.713	129.350	107.668	47.701	-211.032	-211.032	137.820	13.690
2300	25.723	130.527	108.638	50.265	-210.821	-210.821	134.493	12.749
2400	25.733	131.683	109.570	52.821	-210.621	-210.621	131.166	11.868
2500	25.741	132.839	110.471	55.419	-210.706	-210.706	127.856	11.177
2600	25.748	133.869	111.344	57.993	-210.602	-210.602	124.546	10.469
2700	25.754	134.821	112.188	60.566	-210.501	-210.501	121.237	9.813
2800	25.759	135.727	113.006	63.144	-210.402	-210.402	117.933	9.205
2900	25.764	136.596	113.798	65.720	-210.306	-210.306	114.635	8.639
3000	25.769	137.335	114.569	68.297	-210.213	-210.213	111.336	8.111
3100	25.773	138.180	115.317	70.874	-210.122	-210.122	108.040	7.616
3200	25.777	138.998	116.045	73.452	-210.034	-210.034	104.747	7.154
3300	25.780	139.791	116.752	76.029	-209.950	-209.950	101.459	6.719
3400	25.783	140.559	117.438	78.606	-209.868	-209.868	98.176	6.304
3500	25.786	141.309	118.113	81.186	-209.786	-209.786	94.890	5.925
3600	25.789	142.035	118.767	83.765	-209.706	-209.706	91.603	5.532
3700	25.791	142.742	119.405	86.344	-209.628	-209.628	88.316	5.133
3800	25.793	143.431	120.027	88.923	-209.550	-209.550	85.029	4.734
3900	25.796	144.100	120.637	91.503	-209.474	-209.474	81.742	4.335
4000	25.798	144.753	121.232	94.082	-209.400	-209.400	78.456	3.936
4100	25.799	145.390	121.814	96.662	-209.325	-209.325	75.170	3.537
4200	25.801	146.011	122.382	99.242	-209.250	-209.250	71.884	3.138
4300	25.803	146.615	122.939	101.822	-209.174	-209.174	68.598	2.739
4400	25.805	147.212	123.488	104.402	-209.100	-209.100	65.312	2.340
4500	25.805	147.792	124.018	106.983	-209.025	-209.025	62.026	1.941
4600	25.807	148.359	124.541	109.564	-208.950	-208.950	58.740	1.542
4700	25.808	148.914	125.053	112.144	-208.875	-208.875	55.454	1.143
4800	25.809	149.456	125.556	114.725	-208.800	-208.800	52.168	0.744
4900	25.811	149.989	126.053	117.306	-208.725	-208.725	48.882	0.345
5000	25.811	150.511	126.533	119.887	-208.650	-208.650	45.596	-0.054
5100	25.812	151.022	127.008	122.468	-208.575	-208.575	42.310	-0.455
5200	25.813	151.523	127.475	125.050	-208.500	-208.500	39.024	-0.856
5300	25.813	152.019	127.934	127.631	-208.425	-208.425	35.738	-1.257
5400	25.815	152.512	128.388	130.212	-208.350	-208.350	32.452	-1.658
5500	25.815	152.971	128.827	132.793	-208.275	-208.275	29.166	-2.059
5600	25.816	153.436	129.262	135.375	-208.200	-208.200	25.880	-2.460
5700	25.816	153.893	129.690	137.957	-208.125	-208.125	22.594	-2.861
5800	25.816	154.348	130.111	140.538	-208.050	-208.050	19.308	-3.262
5900	25.816	154.783	130.534	143.120	-207.975	-207.975	16.022	-3.663
6000	25.816	155.217	130.934	145.702	-207.900	-207.900	12.736	-4.064

December 31, 1960.



MOL. WT. = 153.461

(IDEAL GAS)

TRICHLOROFUROSILANE (FSiCl₃)

Point Group C_{3v}

ΔH_f^o 298.15 = [-201 ± 15] kcal mole⁻¹

S^o 298.15 = [80.3 ± 4] cal deg⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω_i cm⁻¹

[995] (1)

[350] (1)

[500] (2)

[770] (2)

[700] (2)

σ = 3

Product of the Moments of Inertia: I_AI_BI_C = [147,900 × 10⁻¹¹⁷] g³ cm⁶

All data from C. B. Henderson and R. S. Scheffer, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.



T, °K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.000	INFINITE	-	4.710	-95.804	-	INFINITE
100	13.923	13.127	52.182	-3.946	-96.194	-90.862	197.057
200	20.607	25.303	36.055	-2.150	-95.802	-85.055	92.940
298	23.100	34.019	34.019	0.000	-95.460	-78.824	56.510
300	23.150	34.162	34.020	0.043	-95.451	-79.727	56.078
400	25.500	41.141	34.055	2.475	-94.890	-74.567	40.739
500	28.650	47.131	36.800	5.165	-94.154	-69.564	30.405
600	30.700	51.532	46.970	8.047	-93.306	-64.726	23.575
700	31.750	54.755	54.755	11.047	-92.358	-60.026	18.154
800	31.800	56.188	63.445	14.179	-91.277	-56.076	13.754
900	31.900	56.924	69.645	17.351	-90.015	-51.026	12.300
1000	32.000	56.921	74.744	20.547	-88.618	-46.669	10.109
1100	32.000	56.793	79.793	23.747	-87.038	-42.363	8.416
1200	32.000	56.614	84.614	26.947	-85.277	-38.542	7.066
1300	32.000	56.387	89.387	30.147	-83.427	-35.142	5.766
1400	32.000	56.114	94.114	33.347	-81.472	-32.641	4.658
1500	32.000	55.793	98.793	36.547	-79.417	-30.140	3.761

ΔH_f^o 0 = -95.80 ± 0.20 kcal. mole⁻¹
ΔH_f^o 298.15 = -95.46 ± 0.20 kcal. mole⁻¹
ΔH_m^o = 10.30 kcal. mole⁻¹
ΔH_g^o (to dimer) = 34.52 kcal. mole⁻¹

S_{298.15} = 34.019 cal. deg.⁻¹ mole⁻¹
T_m = 577°K.

Heat of Formation.

The enthalpy change, ΔH_f^o 298.15 = -24.49 ± 0.07 kcal. mole⁻¹, for the reaction Fe() + 3(HCl-12.731 H₂O)(l) + 1/2(H₂O-12.580 H₂O)(l) = FeCl₃(c) + H₂(g) + 45.483 H₂O(l) was determined by M. P. Koehler and J. P. Coughlin, J. Phys. Chem. **63**, 605 (1959). This leads to ΔH_f^o 298.15 = -95.46 ± 0.20 kcal. mole⁻¹ for FeCl₃(c), using ΔH_f^o 298.15 = -38.9 ± 0.05 and -45.68 ± 0.01 kcal. mole⁻¹ for hydrochloric acid and hydrogen peroxide solution, respectively, obtained from F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, National Bureau of Standards Circular 500, 1952. From ΔH_f^o 298.15 = -38.0 ± 0.2 kcal. mole⁻¹ for the reaction FeCl₃(c) = Fe⁺⁺⁺(aq.) reported by J. C. M. Li and N. W. Gregory, J. Am. Chem. Soc. **74**, 4670 (1952), the value of ΔH_f^o 298.15 (FeCl₃, c) was calculated as -93.26 ± 0.2 kcal. mole⁻¹. The former ΔH_f^o 298.15 value is adopted.

The equilibrium pressures of the reaction 2 FeCl₂(c) + Cl₂(g) = 2FeCl₃(c), in the temperature range of 435.7-482.2°K., were measured by H. Schäfer and E. Oehler, Z. anorg. allgem. Chem. **271**, 206 (1953). Using the reported partial pressures for Cl₂(g), the enthalpy change (ΔH_f^o 298.15) of the reaction was evaluated as -27.43 ± 0.44 and -27.21 kcal. mole⁻¹ by the second and third law methods, respectively. Based on the third law value for ΔH_f^o 298.15, the value of ΔH_f^o 298.15(FeCl₃, c) was derived to be -95.36 ± 0.12 kcal. mole⁻¹ which is in good agreement with the adopted value.

Heat Capacity and Entropy.

The low temperature (51-298.15°K.) heat capacities and high temperature (339.6-560.9°K.) heat content of FeCl₃(c) were determined by S. S. Todd and J. P. Coughlin, J. Am. Chem. Soc. **73**, 4184 (1951). The low temperature C_p and the derived high temperature C_p were plotted. The two C_p curves were joined smoothly at 298°K. The C_p values above 560.9°K. were obtained by graphical extrapolation. The value of S_{298.15} was derived from the low temperature data reported by S. S. Todd and J. P. Coughlin, loc. cit., using S₅₁ = 6.29 cal. deg.⁻¹ mole⁻¹. The value of S_{298.15} was selected to make the second and third law values of ΔH_f^o, derived from the equilibrium data reported by H. Schäfer and E. Oehler, loc. cit., in good agreement. The difference in S_{298.15} between the selected value, 6.29, and the reported value, 4.50 cal. deg.⁻¹ mole⁻¹, by S. S. Todd and J. P. Coughlin, loc. cit., is assumed to be the magnetic entropy remaining at 51°K. which was unaccounted for in the report.

Melting Data.

T_m and ΔH_m^o were obtained from S. S. Todd and J. P. Coughlin, loc. cit.

Heat of Sublimation.

The difference between ΔH_f^o 298.15 for Fe₂Cl₆(g) and 2FeCl₃(c) is the heat of sublimation at 298.15°K. The former is obtained by the second and third law analyses of related equilibrium data. See Fe₂Cl₆(g) table for details.

Iron Trichloride (FeCl₃)
(Liquid) Mol. Wt. = 162.206



T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0						
100						
200						
298	32.000	47.955	47.955	.000	- 86.713	- 75.232
300	32.000	48.153	47.956	.059	- 86.687	- 75.161
400	32.000	57.211	49.211	3.259	- 85.358	- 71.522
500	32.000	67.299	59.299	6.459	- 83.118	- 68.612
600	32.000	70.334	54.235	9.659	- 82.946	- 65.138
700	32.000	75.266	56.896	12.859	- 81.852	- 62.257
800	32.000	79.539	59.465	16.059	- 80.849	- 59.529
900	32.000	83.309	61.969	19.259	- 79.960	- 56.918
1000	32.000	86.600	64.221	22.459	- 79.258	- 54.399
1100	32.000	89.730	66.403	25.659	- 78.779	- 51.931
1200	32.000	92.514	68.465	28.859	- 78.092	- 49.526
1300	32.000	95.076	70.415	32.059	- 77.068	- 47.188
1400	32.000	97.447	72.262	35.259	- 76.063	- 44.926
1500	32.000	99.695	74.015	38.459	- 75.075	- 42.758

IRON TRICHLORIDE (FeCl₃) (LIQUID) MOL. WT. = 162.206

S_{298.15} = 47.955 cal. deg.⁻¹ mole⁻¹
 ΔH_f^o 298.15 = -86.713 kcal. mole⁻¹
 ΔH_m^o = 10.30 kcal. mole⁻¹
 ΔH_f^o (to dimer) = 10.46 kcal. mole⁻¹
 T_m = 577°K.
 T_b = 605°K.

Heat of Formation.

The value of ΔH_f^o 298.15 (FeCl₃, l) was obtained from ΔH_f^o 298.15 (FeCl₃, c) by adding ΔH_m^o and the difference between H_m^o - H_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity for FeCl₃(l) was taken from S. S. Todd and J. P. Coughlin, J. Am. Chem. Soc. 73, 4184 (1951) and assumed as constant between 298.15° and 1500°K. The entropy (S_{298.15}) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and ΔH_m^o were reported by S. S. Todd and J. P. Coughlin, loc. cit.

Vaporization Data.

The boiling point (T_b) is determined as the temperature at which the free energy change (ΔG_p^o) of the reaction 2FeCl₃(l) = Fe₂Cl₆(g) approaches zero. The corresponding enthalpy change at T_b is the heat of vaporization (ΔH_v^o).



T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(H°-H° ₂₉₈)/T	cal. mole ⁻¹	H°-H° ₂₉₈	ΔH _f ⁰	Log K _p
0	+0.000	INFINITE	INFINITE	-4.353	-60.487	-60.487	INFINITE	
100	13.511	64.295	97.744	-3.345	-60.633	-60.138	131.425	
200	17.298	75.058	84.910	-2.470	-60.562	-59.666	65.197	
298	18.572	82.244	82.244	-0.000	-60.500	-59.242	43.242	
300	18.586	82.358	82.243	-0.034	-60.499	-59.234	43.150	
400	19.117	87.787	82.980	1.923	-60.487	-58.817	32.134	
500	19.379	92.084	84.186	3.849	-60.510	-58.397	25.524	
600	19.576	95.632	85.973	5.705	-60.598	-57.948	21.114	
700	19.616	98.649	87.742	7.752	-60.746	-57.519	17.957	
800	19.675	101.272	89.126	9.717	-60.978	-57.044	15.563	
900	19.716	103.592	90.407	11.687	-61.320	-56.532	13.727	
1000	19.746	105.671	92.011	13.660	-61.865	-55.976	12.233	
1100	19.767	107.554	93.340	15.636	-62.589	-55.348	10.996	
1200	19.784	109.275	94.497	17.613	-63.421	-54.673	9.957	
1300	19.797	110.859	95.788	19.592	-64.322	-53.960	9.071	
1400	19.807	112.326	97.018	21.573	-65.336	-53.230	8.309	
1500	19.816	113.693	97.991	23.554	-66.453	-52.487	7.647	
1600	19.823	114.972	99.013	25.536	-67.681	-51.727	7.055	
1700	19.828	116.174	99.987	27.518	-69.015	-50.943	6.549	
1800	19.833	117.308	100.918	29.501	-70.457	-50.133	6.087	
1900	19.837	118.380	101.809	31.485	-71.999	-49.311	5.649	
2000	19.841	119.398	102.664	33.469	-73.643	-48.456	5.251	
2100	19.844	120.365	103.484	35.453	-75.387	-47.574	4.888	
2200	19.846	121.289	104.272	37.437	-77.231	-46.672	4.557	
2300	19.848	122.171	105.031	39.422	-79.175	-45.759	4.252	
2400	19.850	123.016	105.763	41.407	-81.218	-44.834	3.971	
2500	19.852	123.827	106.470	43.392	-83.359	-43.897	3.710	
2600	19.854	124.605	107.152	45.376	-85.596	-42.944	3.468	
2700	19.855	125.355	107.813	47.361	-87.931	-41.974	3.243	
2800	19.856	126.077	108.452	49.349	-90.364	-40.988	3.031	
2900	19.857	126.773	109.073	51.334	-92.895	-39.987	2.834	
3000	19.858	127.447	109.673	53.320	-95.522	-38.974	2.648	
3100	19.859	128.098	110.257	55.305	-98.245	-37.947	2.473	
3200	19.860	128.728	110.825	57.289	-101.064	-36.899	2.309	
3300	19.861	129.339	111.376	59.278	-103.978	-35.834	2.157	
3400	19.862	129.932	111.914	61.264	-106.986	-34.753	2.015	
3500	19.862	130.508	112.437	63.250	-109.999	-33.657	1.879	
3600	19.863	131.068	112.944	65.236	-113.017	-32.547	1.753	
3700	19.863	131.612	113.444	67.221	-116.039	-31.423	1.633	
3800	19.864	132.142	113.929	69.209	-119.064	-30.286	1.519	
3900	19.864	132.658	114.402	71.195	-122.092	-29.137	1.410	
4000	19.865	133.161	114.865	73.182	-125.122	-27.974	1.306	
4100	19.865	133.651	115.317	75.168	-128.155	-26.798	1.206	
4200	19.865	134.130	115.760	77.155	-131.191	-25.609	1.110	
4300	19.866	134.597	116.192	79.141	-134.229	-24.407	1.018	
4400	19.866	135.054	116.616	81.128	-137.269	-23.193	0.930	
4500	19.866	135.500	117.030	83.115	-140.311	-21.966	0.846	
4600	19.867	135.937	117.437	85.101	-143.355	-20.727	0.766	
4700	19.867	136.364	117.835	87.088	-146.404	-19.475	0.689	
4800	19.867	136.782	118.225	89.075	-149.457	-18.210	0.615	
4900	19.867	137.192	118.608	91.061	-152.514	-16.933	0.544	
5000	19.867	137.594	118.984	93.048	-155.574	-15.645	0.475	
5100	19.868	137.987	119.355	95.035	-158.637	-14.347	0.409	
5200	19.868	138.373	119.719	97.022	-161.703	-13.039	0.345	
5300	19.868	138.751	120.070	99.008	-164.771	-11.722	0.283	
5400	19.868	139.123	120.420	100.995	-167.840	-10.397	0.223	
5500	19.868	139.487	120.763	102.982	-170.910	-9.063	0.165	
5600	19.869	139.845	121.101	104.969	-173.981	-7.719	0.110	
5700	19.869	140.197	121.431	106.956	-177.053	-6.366	0.057	
5800	19.869	140.547	121.759	108.943	-180.126	-5.004	0.006	
5900	19.869	140.892	122.080	110.930	-183.200	-3.633	0.000	
6000	19.869	141.216	122.397	112.916	-186.274	-2.253	0.000	

June 30, 1985

IRON TRICHLORIDE (FeCl₃) (IDEAL GAS) MOL. WT. = 162.208

Point Group [D_{3h}]
S_{298.15} = [82.243] cal. deg⁻¹ mole⁻¹
Ground State Quantum Weight = [6]
ΔH_f⁰ = -80.5 ± 1.2 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -80.5 ± 1.2 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
[350] (1)
[180] (1)
[130] (2)
[130] (2)

Bond Distance: Fe-Cl = [2.17] Å
Bond Angle: Cl-Fe-Cl = [120]°
Product of the Moments of Inertia: I_AI_BI_C = [1.43769 × 10⁻¹¹²] g.³ cm.⁶
σ⁻ = [8]

Heat of Formation.

The equilibrium pressures for the reaction Fe₂Cl₆(g) = 2FeCl₃(g) were determined by Kangro and Bernstorff¹ and Schiffer², respectively. Using their vapor pressure data the corresponding values of ΔH_f⁰ 298.15 for that reaction were evaluated by both the second and third law methods. Based on the third law values for ΔH_f⁰ 298.15, the heat of formation (ΔH_f⁰ 298.15) for FeCl₃(g) were derived. The results obtained are presented as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	ΔH _f ⁰ 298.15 kcal. mole ⁻¹
Kangro and Bernstorff ¹	760.2-1014.2	34.99 ± 0.44	35.73	-60.34 ± 0.30
Schiffer ²	673.2-1073.2	34.81 ± 0.02	34.93	-60.74 ± 0.20

¹ W. Kangro and H. Bernstorff, Z. anorg. allgem. Chem. **253**, 318 (1950).
² H. Schiffer, Z. anorg. allgem. Chem. **259**, 53 (1949).

The adopted value of ΔH_f⁰ 298.15(FeCl₃ g) is -80.5 ± 1.2 kcal. mole⁻¹.

Heat Capacity and Entropy.

The molecular structure was assumed to be the same as that of AlCl₃(g) due to the similarities in structure between Fe₂Cl₆(g) and Al₂Cl₆(g). The Fe-Cl bond distance was estimated by comparison with those for Fe₂Cl₆(g) reported by E. Z. Zasorin, N. G. Rambidi and P. A. Akishin, Zh. Strukt. Khim., **4**, 910 (1963) and O. Heasel and H. Viorvöll, Acta Chem. Scand., **1**, 149 (1947). Both the ground state quantum weight and vibrational frequencies were estimated so that the second and third law values of ΔH_f⁰ 298.15, derived from the vapor pressure data, for the reaction Fe₂Cl₆(g) = 2FeCl₃(g) are in reasonable agreement. The three principal moments of inertia are: I_A=1.415794 × 10⁻³⁸ and I_C = 8.31588 × 10⁻³⁸ g. cm.²

Cl₃Fe

Trichlorosilane (HSiCl₃)

(Ideal Gas) Mol. Wt. = 135.469

INTERIM TABLE

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H ^o - H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	141.416	0.000	0.000	-110.800	-110.800	141.416
100	11.149	59.271	2.959	-110.800	-109.230	-109.230	28.711
200	15.113	64.274	7.436	-111.336	-106.936	-106.936	116.848
298	16.041	74.892	14.892	-112.000	-104.524	-104.524	76.614
300	16.084	75.004	14.892	-112.005	-104.527	-104.527	76.108
400	17.909	80.965	18.965	-112.303	-103.477	-103.477	43.428
500	21.233	85.095	17.073	-112.306	-99.359	-99.359	35.244
600	22.099	89.047	14.747	-112.363	-96.763	-96.763	29.397
700	22.737	92.504	11.423	-112.380	-94.162	-94.162	25.012
800	23.200	95.433	8.915	-112.383	-91.560	-91.560	21.675
900	23.620	97.833	6.598	-112.383	-88.958	-88.958	18.675
1000	23.934	100.838	4.598	-112.383	-86.357	-86.357	16.675
1100	24.190	103.132	3.690	-112.208	-83.761	-83.761	14.685
1200	24.401	104.946	3.046	-112.133	-81.199	-81.199	12.708
1300	24.576	106.416	2.616	-112.058	-78.658	-78.658	10.738
1400	24.722	107.633	2.324	-111.969	-76.058	-76.058	9.689
1500	24.845	108.643	2.124	-111.883	-73.496	-73.496	8.689
1600	24.950	109.498	2.000	-111.797	-70.938	-70.938	7.777
1700	25.039	110.165	1.942	-111.704	-68.377	-68.377	6.937
1800	25.113	110.685	1.942	-111.611	-65.816	-65.816	6.167
1900	25.176	111.085	1.985	-111.518	-63.255	-63.255	5.467
2000	25.241	111.452	1.985	-111.425	-60.694	-60.694	4.827
2100	25.297	111.785	1.985	-111.332	-58.133	-58.133	4.247
2200	25.337	112.085	1.985	-111.239	-55.572	-55.572	3.727
2300	25.376	112.352	1.985	-111.146	-53.011	-53.011	3.267
2400	25.413	112.585	1.985	-111.053	-50.450	-50.450	2.867
2500	25.441	112.785	1.985	-110.960	-47.889	-47.889	2.527
2600	25.471	124.407	10.129	-110.867	-45.328	-45.328	2.247
2700	25.496	124.407	10.129	-110.774	-42.767	-42.767	2.027
2800	25.519	124.407	10.129	-110.681	-40.206	-40.206	1.867
2900	25.541	124.407	10.129	-110.588	-37.645	-37.645	1.767
3000	25.557	124.407	10.129	-110.495	-35.084	-35.084	1.687
3100	25.574	124.407	10.129	-110.402	-32.523	-32.523	1.627
3200	25.590	124.407	10.129	-110.309	-30.000	-30.000	1.587
3300	25.617	124.407	10.129	-110.216	-27.477	-27.477	1.557
3400	25.629	124.407	10.129	-110.123	-24.954	-24.954	1.537
3500	25.640	124.407	10.129	-110.030	-22.431	-22.431	1.527
3600	25.650	124.407	10.129	-109.937	-19.908	-19.908	1.527
3700	25.658	124.407	10.129	-109.844	-17.385	-17.385	1.537
3800	25.663	124.407	10.129	-109.751	-14.862	-14.862	1.557
3900	25.668	124.407	10.129	-109.658	-12.339	-12.339	1.587
4000	25.676	124.407	10.129	-109.565	-9.816	-9.816	1.627
4100	25.683	124.407	10.129	-109.472	-7.293	-7.293	1.677
4200	25.690	124.407	10.129	-109.379	-4.770	-4.770	1.737
4300	25.696	124.407	10.129	-109.286	-2.247	-2.247	1.807
4400	25.701	124.407	10.129	-109.193	0.276	0.276	1.887
4500	25.707	124.407	10.129	-109.100	2.799	2.799	1.977
4600	25.714	124.407	10.129	-109.007	5.322	5.322	2.077
4700	25.719	124.407	10.129	-108.914	7.845	7.845	2.187
4800	25.724	124.407	10.129	-108.821	10.368	10.368	2.307
4900	25.728	124.407	10.129	-108.728	12.891	12.891	2.437
5000	25.732	124.407	10.129	-108.635	15.414	15.414	2.577
5100	25.736	124.407	10.129	-108.542	17.937	17.937	2.727
5200	25.740	124.407	10.129	-108.449	20.460	20.460	2.887
5300	25.744	124.407	10.129	-108.356	22.983	22.983	3.057
5400	25.748	124.407	10.129	-108.263	25.506	25.506	3.237
5500	25.750	124.407	10.129	-108.170	28.029	28.029	3.427
5600	25.753	124.407	10.129	-108.077	30.552	30.552	3.627
5700	25.756	124.407	10.129	-107.984	33.075	33.075	3.837
5800	25.759	124.407	10.129	-107.891	35.598	35.598	4.057
5900	25.761	124.407	10.129	-107.798	38.121	38.121	4.287
6000	25.763	124.407	10.129	-107.705	40.644	40.644	4.527

December 31, 1960.

Trichlorosilane (HSiCl₃)

(Ideal Gas)

Mol. Wt. = 135.469

ΔH_f^o 298.15 = -119.6 kcal. mole⁻¹

S_{298.15} = 74.924 cal. deg.⁻¹ mole⁻¹

Point Group C_{3v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

cm.⁻¹

2274 (1) 810 (2)

497 (1) 600 (2)

250 (1) 179 (2)

Si-H dist. = 1.48

all angles = [109° 28']

Si-Cl dist. = 2.02

Product of Moments of Inertia: I_AI_BI_C = 75.642 X 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation. ΔH_f^o 298.15 was calculated from heats of reaction reported by E. Wolf, Z. Anorg. u. Allgem. Chem. 313, 228 (1961) for the equation

SiHCl₃(g) + 5NaOH(c) = Na₂SiO₃(c) + 3NaCl(c) + 2H₂O(l)

Heat Capacity and Entropy. Molecular constants were found in Janz and Mikawa, Bull. Chem. Soc. Japan 34, 1495 (1961). Vibrational frequencies can also be found in Henderson and Schaeffer, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data," January, 1960.

Cl₃HSi

Cl₃HSi

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° (F°-H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.000	INFINITE	-4.873	-238.400	-238.400	INFINITE
100	13.559	59.795	98.842	-438.840	-237.515	519.004
200	20.141	71.324	82.331	-439.539	-235.912	257.780
298	24.380	80.223	0.000	-240.134	-234.000	171.219
300	24.441	80.374	0.045	-240.144	-233.963	170.434
400	28.593	93.196	2.668	-243.425	-231.811	100.231
500	28.462	93.959	5.408	-243.425	-228.321	100.231
600	29.376	99.255	8.301	-243.972	-226.446	82.479
700	29.969	103.831	87.731	-244.420	-223.491	69.774
800	30.372	107.861	114.289	-244.807	-220.476	60.229
900	30.653	111.423	140.852	-245.149	-217.413	52.443
1000	30.855	114.697	167.418	-245.497	-214.311	46.835
1100	31.021	117.646	194.991	-245.812	-211.177	41.925
1200	31.142	120.351	222.512	-246.117	-208.017	37.683
1300	31.223	122.848	250.000	-246.409	-204.830	34.013
1400	31.273	125.156	277.459	-246.686	-201.630	30.823
1500	31.313	127.338	304.892	-246.966	-198.431	28.004
1600	31.424	129.354	332.314	-247.232	-195.142	26.654
1700	31.466	131.250	359.726	-247.486	-191.784	24.154
1800	31.501	133.060	387.129	-247.728	-188.459	21.659
1900	31.531	134.796	414.524	-247.958	-185.169	19.169
2000	31.556	136.482	441.912	-248.176	-181.901	17.362
2100	31.578	137.992	469.294	-248.383	-178.659	15.533
2200	31.598	139.362	496.671	-248.580	-175.441	13.871
2300	31.614	140.797	524.044	-248.768	-172.249	12.355
2400	31.628	142.197	551.412	-248.948	-169.083	10.883
2500	31.642	143.564	578.776	-249.119	-165.943	9.459
2600	31.654	144.897	606.139	-249.282	-162.828	8.081
2700	31.664	146.197	633.502	-249.438	-159.738	6.749
2800	31.672	147.464	660.865	-249.586	-156.673	5.463
2900	31.679	148.699	688.228	-249.728	-153.633	4.221
3000	31.689	149.907	715.592	-249.864	-150.617	3.023
3100	31.696	150.247	742.955	-249.994	-147.625	1.869
3200	31.702	151.253	770.318	-250.118	-144.657	0.751
3300	31.708	152.259	797.681	-250.238	-141.713	-0.421
3400	31.713	153.265	825.044	-250.354	-138.793	-1.639
3500	31.717	154.265	852.407	-250.466	-135.896	-2.903
3600	31.722	154.988	879.770	-250.574	-133.023	-4.219
3700	31.726	155.857	907.133	-250.678	-130.173	-5.583
3800	31.730	156.770	934.496	-250.778	-127.346	-6.995
3900	31.733	157.726	961.859	-250.874	-124.541	-8.455
4000	31.736	158.731	989.222	-250.966	-121.759	-9.963
4100	31.739	159.785	1016.585	-251.054	-118.999	-11.519
4200	31.741	159.880	1043.948	-251.138	-116.261	-13.123
4300	31.744	160.027	1071.311	-251.218	-113.545	-14.775
4400	31.746	160.226	1098.674	-251.294	-110.851	-16.475
4500	31.748	162.470	1126.037	-251.366	-108.181	-18.219
4600	31.751	162.768	1153.400	-251.434	-105.535	-19.999
4700	31.752	163.451	1180.763	-251.498	-102.913	-21.813
4800	31.754	164.119	1208.126	-251.558	-100.313	-23.661
4900	31.756	164.782	1235.489	-251.614	-97.733	-25.543
5000	31.758	165.445	1262.852	-251.666	-95.173	-27.459
5100	31.759	166.044	1290.215	-251.714	-92.633	-29.403
5200	31.760	166.661	1317.578	-251.758	-90.113	-31.375
5300	31.761	167.266	1344.941	-251.798	-87.613	-33.375
5400	31.762	167.861	1372.304	-251.834	-85.133	-35.399
5500	31.764	168.443	1399.667	-251.866	-82.673	-37.447
5600	31.765	169.015	1427.030	-251.894	-80.233	-39.519
5700	31.767	169.577	1454.393	-251.918	-77.813	-41.613
5800	31.768	170.130	1481.756	-251.938	-75.413	-43.727
5900	31.769	170.673	1509.119	-251.954	-73.033	-45.859
6000	31.769	171.207	1536.482	-251.966	-70.673	-48.007

June 30, 1962

Lithium Chloride, Trimeric (LiCl)₃ (Ideal Gas)

Mol. Wt. = 127.19

ΔH_f^o 298.15 = -240.134 + 5 kcal. mole⁻¹S_{298.15}^o = 180.223 cal. deg.⁻¹ mole⁻¹298.15 = 180.223 cal. deg.⁻¹ mole⁻¹Point Group = D_{3h}

Vibrational Levels and Multiplicities

 ω_e , cm.⁻¹
[650] {6}
[220] {6}Bond distances and angles
Li-Cl distance = [2.2] Å
Li-Cl-Li angle [120°]
Plane cyclic structure σ = 6Moment of Inertia I_AI_BI_C = 2.675 × 10⁻¹¹² g.³ cm.⁶

Heat of Formation. The heat of sublimation at 298° was chosen so as to give the correct ratio of monomer, dimer and trimer at 870°K. The value used was 52.6 kcal. mole⁻¹, which compares very well with the value 53.6 kcal. mole⁻¹ obtained from a third law analysis of the data of An. N. Nesmeyanov and L. A. Sazonov, Zhur. Neorg. Khim. 4, 231 (1960) in conjunction with the relative concentrations of monomer, dimer, and trimer at 870°K from the work of R. C. Millar and P. Kusch, J. Chem. Phys. 25, 860 (1950).

Heat Capacity and Entropy. The postulated structure, bond lengths and frequencies were all taken from D. L. Hildenbrand, A. M. Saul P. R. Basford, S. E. Stephenson, L. Larson and A. Uyehara, Aeronautics Research Quarterly Report on Contract NORD 17890 Report C-898 (1960).

Phosphoryl Chloride (POCl₃)

(Ideal Gas) Mol. Wt. = 153.346

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	-	-	-	-	-	INFINITE
100	11.939	40.063	43.273	-128.714	-128.714	120.114	120.114	276.026
200	17.430	70.215	79.544	-126.304	-126.304	123.194	123.194	276.026
300	21.296	97.767	106.831	-125.545	-125.545	123.194	123.194	276.026
400	24.235	124.893	134.110	-124.831	-124.831	123.194	123.194	276.026
500	26.407	149.011	157.767	-124.031	-124.031	123.194	123.194	276.026
600	28.079	169.202	177.767	-123.146	-123.146	123.194	123.194	276.026
700	29.412	185.523	194.407	-122.146	-122.146	123.194	123.194	276.026
800	30.562	199.006	208.121	-121.071	-121.071	123.194	123.194	276.026
900	31.573	210.013	219.092	-120.000	-120.000	123.194	123.194	276.026
1000	32.478	219.092	228.146	-119.000	-119.000	123.194	123.194	276.026
1100	33.296	226.407	235.854	-118.000	-118.000	123.194	123.194	276.026
1200	34.047	232.407	242.407	-117.000	-117.000	123.194	123.194	276.026
1300	34.743	237.407	248.000	-116.000	-116.000	123.194	123.194	276.026
1400	35.396	241.854	252.854	-115.000	-115.000	123.194	123.194	276.026
1500	35.996	245.854	257.000	-114.000	-114.000	123.194	123.194	276.026
1600	36.547	249.407	260.500	-113.000	-113.000	123.194	123.194	276.026
1700	37.047	252.500	263.500	-112.000	-112.000	123.194	123.194	276.026
1800	37.496	255.146	266.146	-111.000	-111.000	123.194	123.194	276.026
1900	37.896	257.407	268.407	-110.000	-110.000	123.194	123.194	276.026
2000	38.247	259.407	270.407	-109.000	-109.000	123.194	123.194	276.026
2100	38.547	261.146	272.146	-108.000	-108.000	123.194	123.194	276.026
2200	38.796	262.500	273.500	-107.000	-107.000	123.194	123.194	276.026
2300	39.000	263.500	274.500	-106.000	-106.000	123.194	123.194	276.026
2400	39.164	264.202	275.202	-105.000	-105.000	123.194	123.194	276.026
2500	39.296	264.702	275.702	-104.000	-104.000	123.194	123.194	276.026
2600	39.396	265.000	276.000	-103.000	-103.000	123.194	123.194	276.026
2700	39.464	265.146	276.146	-102.000	-102.000	123.194	123.194	276.026
2800	39.500	265.202	276.202	-101.000	-101.000	123.194	123.194	276.026
2900	39.514	265.250	276.250	-100.000	-100.000	123.194	123.194	276.026
3000	39.514	265.250	276.250	-100.000	-100.000	123.194	123.194	276.026
3100	39.500	265.202	276.202	-100.000	-100.000	123.194	123.194	276.026
3200	39.464	265.146	276.146	-100.000	-100.000	123.194	123.194	276.026
3300	39.400	265.000	276.000	-100.000	-100.000	123.194	123.194	276.026
3400	39.314	264.702	275.702	-100.000	-100.000	123.194	123.194	276.026
3500	39.200	264.202	275.202	-100.000	-100.000	123.194	123.194	276.026
3600	39.064	263.500	274.500	-100.000	-100.000	123.194	123.194	276.026
3700	38.900	262.500	273.500	-100.000	-100.000	123.194	123.194	276.026
3800	38.714	261.146	272.146	-100.000	-100.000	123.194	123.194	276.026
3900	38.500	259.407	270.407	-100.000	-100.000	123.194	123.194	276.026
4000	38.250	257.407	268.407	-100.000	-100.000	123.194	123.194	276.026
4100	37.964	255.146	266.146	-100.000	-100.000	123.194	123.194	276.026
4200	37.647	252.500	263.500	-100.000	-100.000	123.194	123.194	276.026
4300	37.296	249.407	260.500	-100.000	-100.000	123.194	123.194	276.026
4400	36.914	245.854	257.000	-100.000	-100.000	123.194	123.194	276.026
4500	36.500	241.854	253.000	-100.000	-100.000	123.194	123.194	276.026
4600	36.050	237.407	248.000	-100.000	-100.000	123.194	123.194	276.026
4700	35.564	232.407	242.407	-100.000	-100.000	123.194	123.194	276.026
4800	35.047	226.854	236.354	-100.000	-100.000	123.194	123.194	276.026
4900	34.496	220.702	230.000	-100.000	-100.000	123.194	123.194	276.026
5000	33.914	214.000	223.146	-100.000	-100.000	123.194	123.194	276.026
5100	33.296	206.702	215.854	-100.000	-100.000	123.194	123.194	276.026
5200	32.647	198.854	208.000	-100.000	-100.000	123.194	123.194	276.026
5300	31.964	190.407	199.500	-100.000	-100.000	123.194	123.194	276.026
5400	31.247	181.407	190.407	-100.000	-100.000	123.194	123.194	276.026
5500	30.496	171.854	180.854	-100.000	-100.000	123.194	123.194	276.026
5600	29.714	161.702	170.702	-100.000	-100.000	123.194	123.194	276.026
5700	28.896	151.000	160.000	-100.000	-100.000	123.194	123.194	276.026
5800	28.047	139.702	148.702	-100.000	-100.000	123.194	123.194	276.026
5900	27.164	127.854	136.854	-100.000	-100.000	123.194	123.194	276.026
6000	26.247	115.407	124.407	-100.000	-100.000	123.194	123.194	276.026

June 30, 1962



MOL. WT. = 153.346

(IDEAL GAS)

PHOSPHORYL CHLORIDE (POCl₃)

ΔH_f^o 298.15 = -129.6 ± 0.4 kcal. mole⁻¹
S_{298.15}^o = 77.77 cal. deg.⁻¹ mole⁻¹

ΔH_f^o 0 = -128.7 ± 0.4 kcal. mole⁻¹
Point group C_{3v}

Vibrational Levels and Multiplicities

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
1290 (1)	486 (1)	337 (1)
581 (2)	267 (2)	193 (2)

P-O distance = 1.99 ± 0.02 Å
P-Cl distance = 1.45 ± 0.03 Å
I_A = 422.3 X 10⁻⁴⁰ g. cm.²
I_B = 419.2 X 10⁻⁴⁰ g. cm.²
I_C = 576.7 X 10⁻⁴⁰ g. cm.²
σ = 3

Heat of Formation.

The ΔH_f^o 298.15 for POCl₃(g) was derived from the ΔH_f^o 298.15 of POCl₃(l) and the ΔH_v^o 298.15 of the POCl₃(l) was calculated from the heat of hydrolysis observed by T. Charnley and H. A. Skinner, J. Chem. Soc., 450, (1953) for the reaction:



The auxiliary thermochemical data, on the heats of formation of water and aqueous solutions of HCl and of H₃PO₄, were taken from the National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Circular 500, and were adjusted for consistency with JANAF tables. The heat of vaporization was measured and corrected to 298.15°K by J. B. Ott and W. F. Glauque, J. Am. Chem. Soc., 82, 1308 (1960). A correction was made for the change in phosphorus reference state [white (α) → red (v)].

Heat Capacity and Entropy.

The molecular constants are from the microwave spectral data of Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys., 20, 164 (1952). In order to determine the structure Williams et al. (loc. cit.) assumed the P-Cl distance equal to 1.99 Å. This was the smallest value allowed (2.02 ± 0.03 Å) by the electron diffraction work of L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc., 60, 1836 (1938).

Ott and Glauque (loc. cit.) have given the moments of inertia obtained from a weighted average of the isotopic species. I_A ≠ I_B due to isotopic loss of asymmetry. The S_{298.15} calculated from calorimetric data by Ott and Glauque (loc. cit.) was 77.75 cal. deg.⁻¹ mole⁻¹ and the S_{298.15} calculated from the spectral data was 77.77 cal. deg.⁻¹ mole⁻¹.



Point Group C_{3v}

$$\Delta H_f^\circ = -64.5 \pm 1.3 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 74.47 \pm 0.10 \text{ gibbs/mol}$$

$$\Delta H_f^{298.15} = -64.8 \pm 1.3 \text{ kcal/mol}$$

Ground State Quantum Weight = 1

Phosphorus Trichloride (PCl₃)

GFW = 137.3328

(Ideal Gas)

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o)/T	H ^o -H ^o 298	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	-0.000	INFINITE	3.008	-	-64.455	-	INFINITE
100	11.106	59.007	88.146	-2.914	-64.656	-63.675	19.161
200	15.045	68.027	75.976	-1.590	-64.779	-62.614	68.421
298	17.108	74.467	-	-	-64.800	-61.545	45.114
300	17.135	74.473	-	-	-64.800	-61.525	44.821
400	18.173	79.661	75.154	1.403	-64.807	-60.432	33.019
500	18.731	83.782	76.480	3.651	-64.809	-59.338	25.936
600	19.057	87.228	77.992	5.541	-64.823	-58.243	21.215
700	19.263	90.192	79.528	7.086	-64.856	-57.148	17.941
800	19.447	92.655	81.058	8.527	-64.885	-56.053	15.172
900	19.607	94.613	82.582	9.861	-64.911	-54.958	12.906
1000	19.756	97.015	83.823	11.327	-64.987	-55.395	12.106
1100	19.618	98.980	85.117	15.250	-64.814	-52.484	10.420
1200	19.556	100.689	86.345	17.214	-64.643	-49.509	9.017
1300	19.714	102.728	86.616	21.151	-64.304	-43.679	7.819
1400	19.734	105.085	89.669	23.124	-64.136	-40.763	5.942
1500	19.751	106.359	90.673	25.098	-63.971	-37.899	5.177
1600	19.764	107.557	91.631	26.074	-63.807	-35.022	4.502
1700	19.768	108.689	92.546	27.000	-63.643	-32.146	3.917
1800	19.766	109.756	93.425	31.029	-63.481	-29.270	3.370
1900	19.764	110.771	94.266	33.008	-63.327	-26.455	2.891
2000	19.801	111.737	95.077	34.988	-63.169	-23.615	2.458
2100	19.807	112.655	95.855	36.968	-63.017	-20.763	2.065
2200	19.807	113.529	96.600	38.900	-62.865	-17.911	1.711
2300	19.818	114.363	97.328	40.931	-62.717	-15.138	1.379
2400	19.822	115.192	98.027	42.913	-62.572	-12.324	1.077
2500	19.826	115.969	98.702	44.895	-62.431	-9.518	.800
2600	19.829	116.718	99.355	46.878	-62.293	-6.717	.584
2700	19.835	117.435	100.000	48.861	-62.158	-3.916	.421
2800	19.835	118.135	100.628	50.844	-62.028	-1.159	.282
2900	19.837	118.807	101.198	52.828	-61.903	.582	.181
3000	19.839	119.458	101.776	54.811	-61.782	1.443	.113
3100	19.841	120.088	102.339	56.795	-61.666	2.321	.073
3200	19.843	120.691	102.889	58.778	-61.554	3.217	.049
3300	19.845	121.291	103.419	60.764	-61.445	4.123	.032
3400	19.846	121.866	103.938	62.749	-61.342	5.039	.021
3500	19.848	122.425	104.443	64.733	-61.243	5.967	.013
3600	19.849	122.969	104.937	66.716	-61.148	6.914	.008
3700	19.850	123.500	105.418	68.698	-61.056	7.879	.005
3800	19.851	124.018	105.888	70.683	-60.969	8.862	.003
3900	19.852	124.516	106.348	72.673	-60.887	9.864	.002
4000	19.853	125.007	106.797	74.659	-60.806	10.884	.001
4100	19.854	125.485	107.236	76.644	-60.731	11.914	.001
4200	19.854	125.950	107.664	78.628	-60.659	12.954	.000
4300	19.856	126.409	108.087	80.615	-60.586	14.004	.000
4400	19.856	126.855	108.499	82.600	-60.519	15.064	.000
4500	19.857	127.291	108.903	84.586	-60.451	16.134	.000
4600	19.858	127.718	109.299	86.572	-60.387	17.214	.000
4700	19.859	128.136	109.688	88.558	-60.326	18.304	.000
4800	19.859	128.546	110.068	90.543	-60.268	19.404	.000
4900	19.859	128.947	110.441	92.529	-60.203	20.514	.000
5000	19.859	129.340	110.808	94.515	-60.144	21.634	.000
5100	19.860	129.726	111.168	96.501	-60.085	22.764	.000
5200	19.860	130.107	111.519	98.486	-60.029	23.904	.000
5300	19.861	130.475	111.869	100.471	-59.972	25.054	.000
5400	19.861	130.840	112.211	102.460	-59.915	26.214	.000
5500	19.862	131.198	112.547	104.446	-59.859	27.384	.000
5600	19.862	131.549	112.877	106.432	-59.805	28.564	.000
5700	19.862	131.895	113.207	108.418	-59.753	29.754	.000
5800	19.863	132.234	113.524	110.404	-59.695	30.954	.000
5900	19.863	132.568	113.836	112.391	-59.642	32.164	.000
6000	19.863	132.895	114.143	114.377	-59.591	33.384	.000

Data: 31, 1960; Sept. 30, 1962; June 30, 1970

Vibrational Frequencies and Degeneracies

ω_e, cm⁻¹ω_e, cm⁻¹

510 (1)

507 (2)

259 (1)

187 (2)

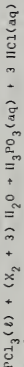
Bond Distance: P-Cl = 2.039 ± 0.0014 Å

Bond Angle: Cl-P-Cl = 100.27 ± 0.09°

Product of Moments of Inertia: I_AI_BI_C = 6.0517 × 10⁻¹¹³ g³ cm⁶ σ = 3

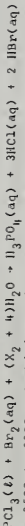
Heat of Formation

Neale and Williams (1) measured the heat of hydrolysis of liquid phosphorus trichloride and reported a ΔH_P = -67.5 ± 0.3 kcal/mol for the following reaction:



with X₂ in range 4500 to 7500. Combining this result with heat of formation data for aqueous H₃PO₃, -223.4 kcal/mol (2, 5, 16), H₂O (2), and aqueous HCl (2) we derive ΔH^o(PCl₃, ℓ) = -76.7 kcal/mol. Chamley and Skinner (3) made an independent investigation of the hydrolysis of liquid phosphorus trichloride and obtained enthalpy data in very good agreement with Neale and Williams' results. Their results lead to ΔH^o(PCl₃, ℓ) = -76.5 kcal/mol when combined with heat of formation data (2, 5, 16).

Neale and Williams (4) also investigated the hydrolysis of liquid phosphorus trichloride in aqueous bromine solution with the formation of phosphoric acid rather than phosphorous acid which results when hydrolysis occurs in water. They reported a ΔH_P = -137.9 kcal/mol for the following reaction:



with X₂ in range 3500 to 6300. Combining this result with the following heat of formation data:

$$\Delta H_f^\circ(\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}) = -308.4 \pm 0.5 \text{ kcal/mol (5)}$$

$$\Delta H_f^\circ(\text{Br}_2(\text{aq})) = -0.2 \text{ kcal/mol (6)}$$

$$\text{HCl}(\text{aq}) \text{ and } \text{HBr}(\text{aq}) (2)$$

along with dilution data for H₃PO₄(aq) (2), we derive ΔH^o_f(PCl₃, ℓ) = -77.0 kcal/mol

The heat of formation from white phosphorus, of gaseous PCl₃, ΔH^o(PCl₃, g) = -69.0 ± 1.1 kcal/mol, is calculated from the heat of formation of the liquid, ΔH^o(PCl₃, ℓ) = -76.7 ± 1.0 kcal/mol, an average value of the three results given above, and the heat of vaporization of PCl₃. The heat of vaporization of the liquid, ΔH^o_{vap} = 7.7 ± 0.1 kcal/mol, is determined from a second law analysis of the combined vapor pressure data of Niselson and Saryakov (7) and Regnault (8). The smoothed vapor pressure data of Regnault as reported by Stull (9) were used. Converting to the Pred, V standard state with a ΔH^o_{trans} = 4.2 ± 0.2 kcal/mol (10), we derive ΔH^o_f(PCl₃, g) = -64.8 ± 1.3 kcal/mol.

An independent value for the heat of formation can be obtained from the work of Dusa and Mykytiuk (12) on the reaction 1.5CaF₂ + PCl₃(g) → 1.5CaCl₂ + PF₃(g). The authors report ΔH₃₀₀ = -2.97 kcal. From a reexamination of their technique we believe that this heat evolution is likely to be too small, perhaps by 100%. The analytical results indicate that the reaction is 93% complete or better; thus, we can use this with JANAF entropies to calculate ΔH^o₂₉₈ ≤ -3.55 kcal. Finch et al. (19) have reported ΔH^o(CaF₂, c) - ΔH^o(CaCl₂, c) = -100.87 ± 0.02 kcal/mol; thus, we obtain ΔH^o_f(PCl₃, g) = -70.1 ± 2.0 kcal/mol from ΔH^o₂₉₈(PF₃, g) = -724.9 ± 0.9 kcal/mol. This value is not adopted because of the lack of calorimeter calibration, but it offers an attractive possibility for further study.

Heat Capacity and Entropy

The molecular structure and bond length given above for PCl₃ are from the electron diffraction studies of Hedberg and Iwasaki (11). The adopted values are in good agreement within experimental error with the following structural data reported by Kialuk and Townes (12) from microwave studies: r_{P-Cl} = 2.043 ± 0.003 Å, the angle Cl-P-Cl = 100°6' ± 20'. The vibrational frequencies are from the recent infrared and Raman studies of Frankins and Miller (13) and are in excellent agreement with those of Miller et al. (14) and Davis and Oetjen (15). Individual moments of inertia calculated from the electron diffraction data are: I_A = I_B = 32.393 × 10⁻³⁹ g cm², and I_C = 57.673 × 10⁻³⁹ g cm².

References

1. E. Neale and L. T. D. Williams, *J. Chem. Soc.*, 1952, 4535.
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. T. Chamley and H. A. Skinner, *J. Chem. Soc.*, 1953, 450.
4. E. Neale and L. T. D. Williams, *J. Chem. Soc.*, 1954, 2156.
5. C. H. Wu, H. M. Bickel, and L. G. Hepler, *J. Chem. Phys.*, 33, 2582 (1960).
6. C. H. Wu, H. M. Bickel, and L. G. Hepler, *J. Chem. Phys.*, 33, 2582 (1960).
7. L. A. Niselson and G. V. Saryakov, *Russ. J. Inorg. Chem. (English Transl.)*, 5, 548 (1960).
8. L. V. Regnault, *Mém. Paris*, 26, 333 (1862).
9. D. R. Stull, *Ind. Eng. Chem.*, 33, 517 (1947).
10. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Mich., June 30, 1961.
11. K. Hedberg and C. Iwasaki, *J. Chem. Phys.*, 36, 589 (1962).
12. K. Kialuk and C. Townes, *J. Chem. Phys.*, 31, 1235 (1959).
13. S. G. Frankins and F. A. Miller, *Spectrochim. Acta*, 21, 1235 (1965).
14. A. Miller, E. Niecke, K. Krebs, and G. Glomier, *Z. Naturforsch.*, 23b, 588 (1968).
15. P. W. Davis and R. A. Oetjen, *J. Mol. Spectroscopy*, 2, 253 (1958).
16. A. Finch, P. J. Gardner, K. S. Hussain and K. K. Sen Gupta, *Chem. Commun.*, 872 (1968).
17. H. C. Dusa and D. P. Mykytiuk, *J. Chem. Eng. Data*, 9, 505 (1964).
18. A. Finch, P. J. Gardner and C. J. Steadman, *Can. J. Chem.*, 46, 3447 (1968).

Thiophosphoryl Chloride (PSCl₃)
(Ideal Gas) Mol. Wt. = 169.412

INTERIM TABLE

T. °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
100	12.000	12.000	1.541	-	86.135	-	86.135	IMF INITE
200	15.573	21.573	1.980	-	84.295	-	84.295	82.109
298	21.474	40.604	2.400	-	83.100	-	83.100	60.911
300	21.513	40.737	2.410	-	83.076	-	83.076	60.518
400	25.039	60.739	3.040	-	82.802	-	82.802	50.518
500	27.943	82.412	3.519	-	82.676	-	82.676	40.518
600	29.469	96.827	3.871	-	82.615	-	82.615	35.113
700	30.407	100.626	4.078	-	82.500	-	82.500	28.699
800	30.936	103.455	4.195	-	82.424	-	82.424	24.095
900	31.196	105.513	4.251	-	82.341	-	82.341	22.434
1000	31.313	106.974	4.285	-	82.250	-	82.250	18.727
1100	31.391	107.886	4.305	-	82.150	-	82.150	15.761
1200	31.431	108.259	4.316	-	82.043	-	82.043	13.357
1300	31.441	108.594	4.319	-	81.930	-	81.930	11.350
1400	31.431	108.894	4.316	-	81.811	-	81.811	9.657
1500	31.401	109.159	4.310	-	81.686	-	81.686	8.209
1600	31.356	109.393	4.302	-	81.556	-	81.556	6.956
1700	31.297	109.596	4.291	-	81.421	-	81.421	5.865
1800	31.225	109.768	4.277	-	81.281	-	81.281	4.904
1900	31.141	109.910	4.261	-	81.136	-	81.136	4.052
2000	31.046	110.024	4.243	-	80.986	-	80.986	3.260
2100	30.941	110.110	4.224	-	80.831	-	80.831	2.506
2200	30.826	110.178	4.204	-	80.671	-	80.671	1.992
2300	30.701	110.228	4.183	-	80.506	-	80.506	1.433
2400	30.566	110.260	4.161	-	80.336	-	80.336	0.923
2500	30.421	110.274	4.138	-	80.161	-	80.161	0.366
2600	30.266	110.274	4.114	-	79.981	-	79.981	0.031
2700	30.101	110.259	4.089	-	79.796	-	79.796	0.363
2800	29.926	110.228	4.063	-	79.606	-	79.606	0.726
2900	29.741	110.181	4.036	-	79.411	-	79.411	1.063
3000	29.546	110.128	4.008	-	79.211	-	79.211	1.375
3100	29.341	110.060	3.979	-	79.006	-	79.006	1.666
3200	29.126	109.978	3.949	-	78.796	-	78.796	1.936
3300	28.901	109.881	3.918	-	78.581	-	78.581	2.192
3400	28.666	109.770	3.886	-	78.361	-	78.361	2.431
3500	28.421	109.645	3.853	-	78.136	-	78.136	2.655
3600	28.166	109.506	3.819	-	77.906	-	77.906	2.865
3700	27.901	109.353	3.784	-	77.671	-	77.671	3.064
3800	27.626	109.186	3.748	-	77.431	-	77.431	3.251
3900	27.341	109.006	3.711	-	77.186	-	77.186	3.428
4000	27.046	108.811	3.673	-	76.936	-	76.936	3.596
4100	26.741	108.601	3.634	-	76.681	-	76.681	3.755
4200	26.426	108.376	3.594	-	76.421	-	76.421	3.906
4300	26.101	108.136	3.553	-	76.156	-	76.156	4.049
4400	25.766	107.881	3.511	-	75.886	-	75.886	4.186
4500	25.421	107.611	3.468	-	75.611	-	75.611	4.316
4600	25.066	107.326	3.424	-	75.331	-	75.331	4.440
4700	24.701	107.026	3.379	-	75.046	-	75.046	4.558
4800	24.326	106.711	3.332	-	74.756	-	74.756	4.672
4900	23.941	106.381	3.284	-	74.461	-	74.461	4.780
5000	23.546	106.036	3.235	-	74.161	-	74.161	4.884
5100	23.141	105.676	3.186	-	73.856	-	73.856	4.984
5200	22.726	105.301	3.136	-	73.546	-	73.546	5.079
5300	22.301	104.911	3.085	-	73.231	-	73.231	5.171
5400	21.866	104.506	3.034	-	72.911	-	72.911	5.258
5500	21.421	104.081	2.982	-	72.586	-	72.586	5.343
5600	20.966	103.641	2.929	-	72.256	-	72.256	5.424
5700	20.501	103.186	2.875	-	71.921	-	71.921	5.502
5800	20.026	102.711	2.820	-	71.581	-	71.581	5.578
5900	19.541	102.226	2.764	-	71.236	-	71.236	5.651
6000	19.046	101.731	2.707	-	70.886	-	70.886	5.720

Dec. 31, 1960; Sept. 30, 1962

Thiophosphoryl Chloride (PSCl₃) (Ideal Gas)

Mol. Wt. = 169.412

ΔH°_f 298.15 = [-86.8] kcal. mole⁻¹

S°_{298.15} = 80.60 cal. deg.⁻¹ mole⁻¹

Point Group C_{3v}

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
169 (2)	[247] (2)	247 (1)
431 (1)	540 (2)	751 (1)

Bond distance P-S = 1.65 ± 0.02 Å P-Cl = 2.02 ± 0.01 Å σ = 3
Cl-P-Cl angle = 100.5° ± 1° I_AI_BI_C = 2.0690 × 10⁻¹¹² g.³ cm.⁶

Heat of Formation. ΔH°_f 298 was estimated by C. B. Henderson and R. S. Scheffé, Atlantic Research Corporation, Alexandria, Virginia, "Survey of Thermochemical Data," January 1960. Henderson and Scheffé (loc. cit.) use white(α) phosphorus as a reference state. Their estimated ΔH°_f 298 was adjusted to the Red (V) phosphorus reference state [see white(α) phosphorus sheet.]

Heat Capacity and Entropy. J. S. Zimek and E. A. Plotrowski, J. Chem. Phys. 34, 1087 (1961) have chosen the most probable values for the wave numbers from the infrared spectral data of G. Cilento, D. A. Ramsey, and R. N. Jones, J. Am. Chem. Soc. 71, 2753 (1949), and the Raman spectral data of A. Simon and O. Schulze, Naturwissenschaften 25, 669 (1937); V. N. Matthe, Nature 139, 469 (1936); H. Gerding and R. Hestrick, Rec. trav. chim. 61, 842 (1942); and M. Delvaule and F. Francota, Compt. Rend. 220, 817 (1945). Zimek and Plotrowski (loc. cit.) found their normal coordinate treatments gave the listed wave numbers as fundamentals and lent support for the 247 cm.⁻¹ band missing from the Raman spectral data. The structure (bond distances and angles) was determined from microwave data by Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys. 20, 164 (1952).

Silicon Trichloride (SiCl₃)

(Ideal Gas) GFW = 134.445

Point Group C_{3v} $\Delta H_f^\circ = -85.7 \pm 10 \text{ kcal/mol}$ $S_{298.15}^\circ = 76.17 \pm 1.5 \text{ gibbs/mol}$ $\Delta H_f^\circ = -85.7 \pm 10 \text{ kcal/mol}$

Ground State Quantum Weight = 12

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	11.922	60.745	3.807	95.747	95.747	INF.NITE
100	11.922	60.745	2.000	95.940	95.158	207.967
200	14.916	69.798	1.573	95.991	94.346	103.096
298	16.931	76.168	1.000	96.000	93.536	68.568
300	16.934	76.272	0.931	96.000	93.521	68.130
400	18.953	85.407	1.622	95.997	92.455	50.440
500	19.975	88.836	2.000	95.985	91.869	40.158
600	19.975	88.836	2.000	95.976	91.008	33.164
700	19.200	91.779	1.910	95.968	90.227	28.170
800	19.350	94.353	1.825	95.960	89.466	24.525
900	19.446	96.693	1.750	95.951	88.766	21.811
1000	19.533	98.857	1.681	95.941	88.127	19.181
1100	19.590	100.857	1.622	95.930	87.549	16.724
1200	19.634	102.664	1.573	95.918	87.027	14.404
1300	19.669	104.337	1.531	95.905	86.551	12.218
1400	19.700	105.895	1.494	95.891	86.118	10.158
1500	19.719	107.368	1.462	95.876	85.724	8.218
1600	19.737	108.768	1.433	95.860	85.368	6.388
1700	19.752	109.126	1.407	95.843	85.041	4.658
1800	19.765	109.455	1.383	95.825	84.743	3.028
1900	19.776	109.758	1.360	95.806	84.474	1.508
2000	19.785	110.038	1.338	95.786	84.234	0.000
2100	19.793	110.304	1.317	95.765	84.023	-1.482
2200	19.800	110.555	1.297	95.743	83.841	-2.964
2300	19.806	110.792	1.277	95.720	83.688	-4.446
2400	19.811	111.015	1.257	95.696	83.564	-5.928
2500	19.816	111.225	1.237	95.671	83.469	-7.410
2600	19.820	111.424	1.217	95.645	83.394	-8.892
2700	19.824	111.612	1.197	95.618	83.338	-10.374
2800	19.827	111.790	1.177	95.590	83.299	-11.856
2900	19.830	111.958	1.157	95.561	83.276	-13.338
3000	19.833	120.372	107.790	92.745	81.381	4.469
3100	19.835	121.022	103.368	94.778	81.121	5.970
3200	19.838	121.652	103.929	96.712	80.884	7.472
3300	19.840	122.262	104.476	98.646	80.660	8.974
3400	19.842	122.852	105.012	100.580	80.446	10.476
3500	19.843	123.430	105.526	102.514	80.242	11.978
3600	19.845	123.989	106.031	104.448	80.048	13.480
3700	19.846	124.532	106.523	106.382	79.864	14.982
3800	19.848	125.062	107.004	108.316	79.690	16.484
3900	19.849	125.578	107.476	110.250	79.526	17.986
4000	19.850	126.080	107.933	112.184	79.372	19.488
4100	19.851	126.570	108.382	114.118	79.228	20.990
4200	19.852	127.048	108.820	116.052	79.094	22.492
4300	19.853	127.516	109.250	117.986	78.969	24.000
4400	19.854	127.974	109.668	119.919	78.854	25.502
4500	19.854	128.418	110.082	121.853	78.749	27.004
4600	19.854	128.855	110.485	123.787	78.654	28.506
4700	19.854	129.282	110.880	125.721	78.569	30.008
4800	19.854	129.698	111.268	127.655	78.494	31.510
4900	19.854	130.105	111.650	129.589	78.429	33.012
5000	19.854	130.510	112.022	131.523	78.374	34.514
5100	19.854	130.903	112.386	133.457	78.329	36.016
5200	19.854	131.289	112.748	135.391	78.294	37.518
5300	19.854	131.667	113.101	137.325	78.269	39.020
5400	19.854	132.038	113.448	139.259	78.244	40.522
5500	19.854	132.403	113.790	141.193	78.229	42.024
5600	19.861	132.761	114.126	143.127	78.214	43.526
5700	19.861	133.112	114.458	145.061	78.209	45.028
5800	19.861	133.458	114.785	147.000	78.204	46.530
5900	19.861	133.800	115.108	148.934	78.209	48.032
6000	19.862	134.131	115.418	150.868	78.214	49.534

Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
470 (1)	582 (2)
[240] (1)	[175] (2)

Bond Distance: Si-Cl = [2.02] Å

Bond Angle: Cl-Si-Cl = 110.9°

Product of the Moments of Inertia: $I_A I_B I_C = [7.5469 \times 10^{-113}] \text{ g cm}^6$ $\sigma = 3$

Heat of Formation

The adopted value is derived from an average bond energy of $\Delta H_{\text{atom}}^\circ/3 = 96 \pm 3 \text{ kcal/mol}$. This value is estimated by comparison of average bond energies for M_n where M = C or Si, X = F or Cl, and n = 2, 3 or 4. These comparisons suggest that the average bond energy for SiCl_3 should be bracketed by those for SiCl_4 and SiCl_2 , i.e. 94.3 and 101.5 kcal/mol, respectively. Alternative estimates from linear plots of $\Delta H_f^\circ(\text{SiCl}_n)$ versus ΔH_f° for SiF_4 , CCl_4 , and CF_4 yield -96, -96, and -96 kcal/mol for ΔH_f° of SiCl_3 at 298.15°K. These agree with the adopted value of -86 ± 10 kcal/mol, which corresponds to $\Delta H_{\text{atom}}^\circ = 288 \pm 10 \text{ kcal/mol}$.

Kerr et al. (1) reported relative rates for several reactions of SiCl_3 , but the authors state that no absolute activation energies are known for reactions of this radical. This precludes derivation of thermochemical values from the kinetic studies. Recently, however, Vurzel et al. (2) reported studies of the decomposition of SiCl_4 by adiabatic compression. Rate constants, as reported in Chemical Abstracts, led to an activation energy of $88 \pm 5 \text{ kcal/mol}$ for $\text{SiCl}_4 \rightarrow \text{SiCl}_3 + \text{Cl}$. This activation energy for recombination should be very close to zero, so $\Delta H_f^\circ = 88 \pm 5$ compared with the adopted result of 86 ± 10 at room temperature. Steele et al. (3) derived an average value of $\Delta H_f^\circ(\text{SiCl}_3) = 93 \pm 4 \text{ kcal/mol}$ from an interpretation of electron impact studies on several molecules. Using $\Delta H_f^\circ(\text{Cl}_3\text{SiH}, g) = -122.6 \text{ kcal/mol}$ (3), we calculate $\Delta H_f^\circ(\text{SiCl}_3) = -82 \text{ kcal/mol}$ and estimate the uncertainty as about 10 kcal/mol.

Heat Capacity and Entropy

Jacob and Milligan (5) studied the formation of SiCl_3 by photolysis of HSiCl_3 trapped in matrices of argon, nitrogen and CO. The two stretching fundamentals were assigned from the infrared spectra. Isotopic splittings were found to be consistent with an angle of $72 \pm 5^\circ$ between the threefold axis and each of the Si-Cl bonds. This yields a bond angle of 110.9° which is similar to that of HSiCl_3 . Non-planarity of SiCl_3 is consistent with the electron-spin-resonance studies of Poinc (6).

We adopt the results of Jacob (5) and estimate the bond length and two bending vibrations by analogy with HSiCl_3 . Similar analogies are reliable for SiF_3 and CF_3 . The ground state quantum weight is taken as two, but excited electronic levels are neglected. Jacob (5) observed unstructured absorptions corresponding to excitation energies of 30000-34500 cm⁻¹ and 41000-46000 cm⁻¹. Principal moments of inertia are $I_A = 65.18 \times 10^{-39}$ and $I_B = I_C = 34.03 \times 10^{-39} \text{ g cm}^2$.

References

1. J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson and J. C. Young, J. Chem. Soc. A1968, 510.
2. W. C. Steele, L. D. Nichols and F. G. A. Stone, J. Amer. Chem. Soc. 84, 4441 (1962).
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. F. B. Vurzel, L. S. Polak and V. S. Shchepachev, Kinet. Katal. 7 (6), 1068 (1966); Chem. Abst. 57, 59296 (1967).
5. M. E. Jacob and D. E. Milligan, J. Chem. Phys. 48, 3130 (1968).
6. J. Poinc, Mol. Cryst. 3 (1), 117-44 (1967); Chem. Abst. 68, 64560 (1968).



Titanium Trichloride (TiCl_3)

(Crystal) GFW = 154.259

T, °K	Cp°	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	∞	∞	INFINITE	- 5.000	- 173.057	- 173.057	INFINITE
100	13.011	16.600	54.440	- 4.384	- 173.619	- 167.710	366.529
200	20.261	25.626	35.636	- 2.562	- 173.384	- 161.869	176.660
298	23.722	33.401	∞	∞	- 172.500	- 156.442	116.875
300	23.730	33.245	33.401	- 0.83	- 172.491	- 156.383	113.496
400	23.652	46.284	34.318	2.387	- 172.009	- 151.034	82.921
500	24.638	45.606	36.062	4.772	- 171.550	- 145.843	63.748
600	24.390	56.026	38.031	7.184	- 171.086	- 140.744	51.466
700	24.554	53.115	41.956	12.156	- 170.204	- 130.783	38.723
800	24.554	50.071	43.404	19.639	- 169.766	- 125.856	30.563
1000	25.503	62.744	45.568	17.176	- 165.334	- 121.005	26.446
1100	25.760	63.167	47.246	15.729	- 165.505	- 119.191	23.065
1200	26.567	67.336	51.545	22.584	- 164.847	- 106.507	17.685
1300	26.567	71.463	51.787	27.589	- 164.309	- 101.766	15.491
1400	26.820	73.338	53.162	30.258	- 167.744	- 97.065	14.142

TITANIUM TRICHLORIDE (TiCl_3)

GFW = 154.259

(CRYSTAL)

$\Delta H_f^\circ = -173.1 \pm 1.0$ kcal/mol

$\Delta H_f^\circ = -172.5 \pm 1.0$ kcal/mol

$\Delta H^\circ = 0$ kcal/mol

$\Delta H_g^\circ = [39.71]$ kcal/mol

$S_{298.15}^\circ = 33.4 \pm 0.3$ gibbs/mol

$T_f = 220.1^\circ\text{K}$

$T_g = [1104.1]^\circ\text{K}$

Heat of Formation

The heat of formation, ΔH_f° , of $\text{TiCl}_3(\text{c})$ has been measured by several investigators. The results of these measurements are as follows.

Investigators

Investigator	Method	ΔH_f° kcal/mol
Schaffer et al. (1954) (1)	Calorimetric, $\text{TiCl}_4 + \text{Hg} = \text{TiCl}_3 + 1/2\text{Hg}_2\text{Cl}_2$	-171.8, -172.4
Clifton and MacLeod (1956) (2)	Solution calorimetric	-172.4
Johnson et al. (1956) (3)	Calorimetric, $\text{TiCl}_4(\text{t}) + \text{HCl}(\text{g}) = \text{TiCl}_3(\text{c}) + \text{HCl}(\text{g}) + 1/2\text{I}_2$	-172.5
Krievie et al. (1956) (4)	Solution calorimetric	-171.3
Krievie and Mason (1956) (5)	Equilibrium, $\text{TiCl}_3(\text{c}) + \text{HCl}(\text{g}) = \text{TiCl}_4(\text{g}) + 1/2\text{H}_2(\text{g})$	-172.9
Altman et al. (1956) (6)	Equilibrium, $\text{Ti}(\text{c}) + 3\text{TiCl}_4(\text{g}) = 4\text{TiCl}_3(\text{c})$	-169.4, -171.0
Head (1960) (7)	Equilibrium, $2\text{TiCl}_4(\text{g}) + \text{H}_2(\text{g}) = 2\text{TiCl}_3(\text{c}) + 2\text{HCl}(\text{g})$	-172.3
	Equilibrium, $\text{TiCl}_4(\text{t}) + \text{Hg}(\text{c}) = 1/2\text{Hg}_2\text{Cl}_2(\text{c}) + \text{TiCl}_3(\text{c})$	
	$\text{TiCl}_4(\text{t}) + \text{Ag}(\text{c}) = \text{AgCl}(\text{c}) + \text{TiCl}_3(\text{c})$	

The chosen value of -172.5 ± 1.0 kcal/mol is that reported by Johnson et al. (3).

Heat Capacity and Entropy

The heat capacity and entropy of $\text{TiCl}_3(\text{c})$ has been measured over the temperature range 54° to 1000°K by King et al. (8). The value of S_{298}° is calculated from these data based on $S_{298}^\circ = 4.29$ eu.

Transition Data

A second order transition at 220.1°K was observed by King et al. (8). The heat capacity at this temperature is in excess of 146.8 gibbs/mol. King et al. measured the value of $H_{240}^\circ - H_{200}^\circ$ as 1.213 kcal/mol.

Heat of Sublimation

The heat of sublimation is calculated from the heats of formation of $\text{TiCl}_3(\text{c})$ and $\text{TiCl}_3(\text{g})$ at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta G_r = 0$ for the process $\text{TiCl}_3(\text{c}) = \text{TiCl}_3(\text{g})$.

References

1. H. Schaffer, G. Breil, and G. Pfeffer, Z. Anorg. Chem. **275**, 325 (1954).
2. D. G. Clifton and G. E. MacLeod, J. Phys. Chem. **60**, 309 (1956).
3. W. H. Johnson, A. A. Gilliland, and E. T. Prosen, J. Res. Natl. Bur. Std. **64A**, 515 (1956).
4. W. F. Krievie, S. F. Vango, and D. M. Mason, J. Chem. Phys. **25**, 59 (1956).
5. W. F. Krievie and D. M. Mason, J. Chem. Phys. **25**, 524 (1956).
6. D. Altman, M. Farber, and D. M. Mason, J. Chem. Phys. **25**, 531 (1956).
7. R. B. Head, Aust. J. Chem. **13**, 332 (1960).
8. E. G. King et al., U. S. Bur. Mines RI5799, 1961.



Titanium Trichloride (TiCl₃)
(Ideal Gas) GFW = 154.259

Point Group = C_{3v}

S_{298.15} = [75.7 ± 1.0] gibbs/mol

ΔH_f⁰ = -128.1 ± 1.5 kcal/mol

ΔH_f^{298.15} = -128.9 ± 1.6 kcal/mol

Ground State Quantum Weight = [2]

T, °K	Cp*	S ⁰	-(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	kcal/mol	ΔH _f ⁰	Log Kp
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	10.094	60.459	91.124	3.675	-128.132	128.132	INFINITE
200	14.661	74.744	104.124	1.827	-128.482	128.482	276.621
300	17.334	79.703	111.703	1.000	-128.600	128.600	126.754
400	19.521	85.309	117.771	3.769	-128.901	128.901	91.378
500	21.324	88.908	121.927	5.744	-128.948	128.948	67.697
600	22.824	91.997	125.485	7.768	-128.953	128.953	53.806
700	24.139	94.695	127.670	9.769	-128.948	128.948	44.412
800	25.261	97.066	129.077	11.799	-128.935	128.935	37.702
900	26.233	99.231	130.634	13.834	-128.917	128.917	32.670
1000	27.097	101.175	132.342	15.873	-128.896	128.896	28.754
1100	27.880	102.951	134.192	17.915	-128.873	128.873	25.621
1200	28.604	104.584	136.184	19.958	-128.848	128.848	23.056
1300	29.284	106.101	138.324	22.002	-128.823	128.823	20.909
1400	29.924	107.512	140.612	24.047	-128.798	128.798	19.085
1500	30.531	108.832	143.052	26.092	-128.773	128.773	17.520
1600	31.112	110.072	145.648	28.137	-128.748	128.748	16.164
1700	31.673	111.241	148.401	30.182	-128.723	128.723	14.977
1800	32.214	112.346	151.314	32.228	-128.698	128.698	13.926
1900	32.734	113.395	154.395	34.273	-128.673	128.673	12.996
2000	33.234	114.395	157.559	36.317	-128.648	128.648	12.160
2100	33.714	115.354	160.802	38.362	-128.623	128.623	11.390
2200	34.174	116.274	164.132	40.406	-128.598	128.598	10.695
2300	34.614	117.154	167.552	42.450	-128.573	128.573	10.043
2400	35.034	117.994	171.062	44.493	-128.548	128.548	9.456
2500	35.434	118.794	174.662	46.537	-128.523	128.523	8.917
2600	35.814	119.554	178.352	48.580	-128.498	128.498	8.421
2700	36.174	120.274	182.132	50.623	-128.473	128.473	7.962
2800	36.514	120.954	186.002	52.665	-128.448	128.448	7.537
2900	36.834	121.594	190.062	54.707	-128.423	128.423	7.141
3000	37.134	122.194	194.312	56.749	-128.398	128.398	6.772
3100	37.414	122.754	198.762	58.790	-128.373	128.373	6.420
3200	37.674	123.274	203.412	60.832	-128.348	128.348	6.104
3300	37.914	123.754	208.162	62.873	-128.323	128.323	5.801
3400	38.134	124.194	213.012	64.914	-128.298	128.298	5.516
3500	38.334	124.594	217.962	66.954	-128.273	128.273	5.246
3600	38.514	124.954	223.012	68.995	-128.248	128.248	4.992
3700	38.674	125.274	228.162	71.035	-128.223	128.223	4.746
3800	38.814	125.554	233.412	73.074	-128.198	128.198	4.516
3900	38.934	125.794	238.762	75.114	-128.173	128.173	4.292
4000	39.034	126.004	244.212	77.153	-128.148	128.148	4.080
4100	39.114	126.174	249.762	79.191	-128.123	128.123	3.881
4200	39.174	126.314	255.412	81.230	-128.098	128.098	3.686
4300	39.214	126.424	261.162	83.267	-128.073	128.073	3.506
4400	39.244	126.504	267.012	85.305	-128.048	128.048	3.336
4500	39.264	126.554	272.962	87.342	-128.023	128.023	3.174
4600	39.274	126.584	279.012	89.379	-128.000	128.000	3.020
4700	39.274	126.594	285.162	91.415	-127.975	127.975	2.874
4800	39.264	126.584	291.412	93.451	-127.950	127.950	2.736
4900	39.244	126.554	297.762	95.486	-127.925	127.925	2.606
5000	39.214	126.504	304.212	97.521	-127.898	127.898	2.486
5100	39.174	126.424	310.762	99.555	-127.873	127.873	2.374
5200	39.114	126.314	317.412	101.589	-127.848	127.848	2.266
5300	39.034	126.174	324.162	103.623	-127.823	127.823	2.166
5400	38.934	126.004	331.012	105.656	-127.798	127.798	2.074
5500	38.814	125.804	337.962	107.689	-127.773	127.773	1.986
5600	38.674	125.554	345.012	109.721	-127.748	127.748	1.904
5700	38.514	125.274	352.162	111.751	-127.723	127.723	1.826
5800	38.334	124.954	359.412	113.784	-127.698	127.698	1.752
5900	38.134	124.594	366.762	115.814	-127.673	127.673	1.684
6000	37.914	124.194	374.212	117.848	-127.648	127.648	1.624

Dec. 31, 1960; Mar. 31, 1964; June 30, 1968; Dec. 31, 1968

Electronic Levels and Quantum Weights			
E _i , cm ⁻¹	g _i	E _i , cm ⁻¹	g _i
0	(2)	(4000)	(2)
(600)	(2)	(10000)	(2)
(1600)	(2)		

Vibrational Frequencies and Degeneracies			
ω _i , cm ⁻¹	ω _i , cm ⁻¹	ω _i , cm ⁻¹	ω _i , cm ⁻¹
(530) (1)	(590) (2)	(275) (1)	(260) (2)

Bond Distance: Ti-Cl = (2.3) Å
Bond Angle: Cl-Ti-Cl = (100°)
Products of the Moments of Inertia: I_AI_BI_C = (1.33 × 10⁻¹¹) g³ cm⁶

Heat of Formation

The heat of formation of TiCl₃(g) is calculated from the heats of reaction for the processes, (A) 3TiCl₄(g) + Ti(c) = 4TiCl₃(g) and (B) TiCl₃(c) = TiCl₃(g), combined with auxiliary JANAF heats of formation for TiCl₃(c), TiCl₃(g) and Ti(c). Equilibrium measurements of reaction (A) have been reported by Gross and Levi (1). Vapor pressure measurements for reaction (B) have been reported by Sanderson and MacKinnon (2) and by Farber and Darnell (3). Second and third law analyses of these data yield the following results.

Source	Reaction	No. Points	Range, °K	ΔH _f ²⁹⁸ , kcal/mol	Second Law	Third Law	Drift, eu	ΔH _f ²⁹⁸ *
Gross and Levi (1)	A	3	1223			31.6 ± 2.0		-128.5
Sanderson and MacKinnon (2)	B	9**	628-823		42.8 ± 1.1	42.8	-0.1 ± 1.5	-129.3
Farber and Darnell (3)	B	8	636-732		45.3 ± 2.1	45.8	0.8 ± 3.1	-126.2

*Calculation based on third law ΔH_f²⁹⁸.

**One point rejected due to failure of statistical test.

The chosen value of ΔH_f²⁹⁸ is -128.9 kcal/mol. This value is the average of the first two determinations.

Heat Capacity and Entropy

The interatomic distance is estimated from that of the solid, given as 2.46 Å by Matta et al. (4), and from comparisons of bond distances of crystal and gas phase tetrahalides of titanium. The pyramidal bond angle is estimated assuming TiCl₃(g) similar to the group V trihalides. The principal moments of inertia are I_A = I_B = 4.28 × 10⁻³⁸ g cm² and I_C = 7.26 × 10⁻³⁸ g cm². The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti³⁺ (5).

References

1. P. Gross and D. L. Levi, Congres International de Chemie Pure et Appliquees, 16e Congres, Paris, 1957; Memorias Presentes a la Section de Chemie Minerale, 627 (1959).
2. B. S. Sanderson and G. E. MacKinnon, J. Phys. Chem. 50, 314 (1956).
3. M. Farber and A. J. Darnell, J. Phys. Chem. 59, 156 (1955).
4. G. Matta, P. Corradini, and G. Allegria, J. Polym. Sci. 51, 399 (1961).
5. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Cl₃Zr

GFV = 197.579

(CRYSTAL)

ZIRCONIUM TRICHLORIDE (ZrCl₃)Zirconium Trichloride (ZrCl₃)

GFV = 197.579

(Crystal)

 $\Delta H_f^\circ = \text{Unknown}$ $\Delta H_f^\circ_{298.15} = (-170.7 \pm 15) \text{ kcal/mol}$ $\Delta H_f^\circ_{298.15} = (-145.4) \text{ kcal/mol}$ $S_{298.15}^\circ = (34.8 \pm 3) \text{ gibbs/mol}$ $T_s = (1045.9)^\circ\text{K}$ Heat of Formation

Turnbull and Watts (1) determined the equilibrium pressures for the disproportionation of ZrCl₃(c) in the temperature range from 613°K to 723°K by a modified dew point technique. Third law and second law analyses of their vapor pressure-temperature equation give the same heat of reaction $\Delta H_{298}^\circ = 30.7 \text{ kcal/mol}$ for $2\text{ZrCl}_3(\text{c}) \rightarrow \text{ZrCl}_2(\text{c}) + \text{ZrCl}_4(\text{g})$.

The adopted value, $\Delta H_f^\circ(\text{ZrCl}_3, \text{c}) = -170.7 \text{ kcal/mol}$, is calculated from the heat of reaction at 298°K, and $\Delta H_f^\circ(\text{ZrCl}_4, \text{g}) = -207.77 \text{ kcal/mol}$ (2) and $\Delta H_f^\circ(\text{ZrCl}_2, \text{c}) = -103 \text{ kcal/mol}$ (3). The assigned uncertainty, $\pm 15 \text{ kcal/mol}$ is mainly due to the uncertainty in the heat of formation of ZrCl₂(c), and also the dew point technique used.

Heat Capacity and Entropy

The heat capacities of ZrCl₃(c) are estimated from the Cp values of ZrCl₄(c) by deduction of one Cl atom Cp contributions which are calculated as $1/4(\text{Cp}(\text{ZrCl}_4, \text{c}) - \text{Cp}(\text{Zr}, \text{c}))$. The S_{298}° is calculated as 34.85 eu based on the assumption that $S_{298}^\circ(\text{ZrCl}_3, \text{c}) = S_{298}^\circ(\text{ZrCl}_4, \text{c}) - 1/4(S_{298}^\circ(\text{ZrCl}_4, \text{c}) - S_{298}^\circ(\text{Zr}, \text{c}))$.

Heat of Sublimation

The heat of sublimation is calculated from the difference in the heats of formation of gas and crystal at 298°K. The sublimation temperature is taken as the point at which $\Delta G^\circ = 0$ for $\text{ZrCl}_3(\text{c}) = \text{ZrCl}_3(\text{g})$.

References

1. A. G. Turnbull and J. A. Watts, Aust. J. Chem., **16**, 947 (1963).
2. JANAF ZrCl₄(g) table dated Dec. 31, 1969.
3. JANAF ZrCl₂(c) table dated Dec. 31, 1969.

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
100							
200							
298	22.990	34.850		.000	-170.700	-154.481	113.238
300	23.019	34.992		.043	-170.691	-154.381	112.466
400	24.069	41.768		2.400	-170.201	-149.017	81.419
500	24.730	47.212		37.524	-169.691	-143.779	62.846
600	25.235	51.767		7.340	-169.173	-138.666	50.402
700	25.664	55.690		9.886	-168.651	-133.599	41.712
800	26.064	59.143		12.472	-168.126	-128.628	35.140
900	26.433	62.234		15.097	-167.598	-123.722	30.044
1000	26.768	65.038		17.759	-167.067	-118.877	25.981
1100	27.050	67.608		20.451	-166.537	-114.083	22.466
1200	27.300	69.968		23.168	-166.006	-109.287	19.909
1300	27.550	72.163		25.911	-165.470	-104.516	17.571
1400	27.800	74.215		28.679	-164.933	-99.800	15.579
1500	28.000	76.139		31.469	-164.398	-95.134	13.861
1600	28.200	77.953		34.279	-163.868	-90.517	12.364
1700	28.370	79.668		37.108	-163.301	-85.942	11.049
1800	28.550	81.295		39.954	-162.751	-81.415	9.885
1900	28.750	82.841		42.814	-162.200	-76.924	8.848
2000	28.950	84.313		45.684	-161.614	-72.475	7.920

Cl₃Zr

Point Group: [C_{3v}]

$$\Delta H_f^\circ = -124.9 \pm 5 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -125.3 \pm 5 \text{ kcal/mol}$$

$$S_{298.15}^\circ = (81.0 \pm 3) \text{ gibbs/mol}$$

Ground State Quantum Weight = (2)

Zirconium Trichloride (ZrCl₃)

$$GF_W = 197.579$$

(Ideal Gas)

T, °K	Cp	S ^o	-(G ^o -H ^o)/T	H ^o -H ^o 298	ΔH ^o	Log Kp
100	12.920	63.612	9.210	-124.898	124.898	147.141E
200	16.668	74.086	8.261	-125.168	125.168	271.967
298	18.170	81.070	7.119	-125.278	125.278	135.131
300	18.189	81.182	7.095	-125.300	125.300	90.000
400	18.969	86.531	6.179	-122.028	122.028	89.404
500	19.487	90.623	5.185	-121.207	121.207	52.980
600	19.674	94.412	4.165	-120.365	120.365	43.650
700	20.189	97.486	3.189	-119.500	119.500	37.328
800	20.551	102.618	2.250	-117.698	117.698	26.630
900	20.669	104.780	1.328	-117.059	117.059	25.582
1000	20.756	106.784	0.219	-116.211	116.211	23.089
1100	20.817	108.573	0.507	-115.302	115.302	20.999
1200	20.869	110.178	0.855	-114.331	114.331	17.707
1300	20.907	111.730	1.003	-113.409	113.409	16.391
1400	20.935	113.230	98.000	-112.476	112.476	15.239
1500	20.953	114.579	98.000	-111.566	111.566	14.253
1600	20.961	115.853	100.000	-110.670	110.670	13.372
1700	20.963	117.063	100.000	-109.785	109.785	12.511
1800	20.966	118.173	100.960	-108.919	108.919	11.673
1900	20.969	119.245	101.848	-108.063	108.063	10.851
2000	20.972	120.285	102.701	-107.217	107.217	10.043
2100	20.975	121.296	103.521	-106.380	106.380	9.256
2200	20.978	122.278	104.307	-105.550	105.550	8.491
2300	20.981	123.230	105.057	-104.726	104.726	7.747
2400	20.983	124.153	105.774	-103.906	103.906	7.027
2500	20.985	125.048	106.458	-103.089	103.089	6.325
2600	20.987	125.915	107.105	-102.274	102.274	5.639
2700	20.989	126.754	107.717	-101.460	101.460	4.967
2800	20.991	127.566	108.294	-100.646	100.646	4.307
2900	20.993	128.341	108.836	-99.832	99.832	3.657
3000	20.995	129.088	109.343	-99.018	99.018	3.017
3100	20.997	129.807	109.815	-98.204	98.204	2.387
3200	20.999	130.498	110.252	-97.390	97.390	1.757
3300	20.999	131.161	110.653	-96.576	96.576	1.127
3400	20.999	131.796	111.018	-95.762	95.762	0.497
3500	20.999	132.403	111.348	-94.948	94.948	-0.133
3600	20.999	132.982	111.643	-94.134	94.134	-0.763
3700	20.999	133.533	111.903	-93.320	93.320	-1.393
3800	20.999	134.056	112.128	-92.506	92.506	-2.023
3900	20.999	134.551	112.318	-91.692	91.692	-2.653
4000	20.999	135.018	112.473	-90.878	90.878	-3.283
4100	20.999	135.457	112.594	-90.064	90.064	-3.913
4200	20.999	135.857	112.681	-89.250	89.250	-4.543
4300	20.999	136.218	112.734	-88.436	88.436	-5.173
4400	20.999	136.540	112.753	-87.622	87.622	-5.803
4500	20.999	136.823	112.739	-86.808	86.808	-6.433
4600	20.999	137.067	112.692	-85.994	85.994	-7.063
4700	20.999	137.272	112.613	-85.180	85.180	-7.693
4800	20.999	137.438	112.500	-84.366	84.366	-8.323
4900	20.999	137.565	112.353	-83.552	83.552	-8.953
5000	20.999	137.653	112.173	-82.738	82.738	-9.583
5100	20.999	137.702	111.959	-81.924	81.924	-10.213
5200	20.999	137.722	111.702	-81.110	81.110	-10.843
5300	20.999	137.713	111.403	-80.296	80.296	-11.473
5400	20.999	137.675	111.057	-79.482	79.482	-12.103
5500	20.999	137.608	110.673	-78.668	78.668	-12.733
5600	20.999	137.502	110.250	-77.854	77.854	-13.363
5700	20.999	137.357	110.787	-77.040	77.040	-13.993
5800	20.999	137.173	110.283	-76.226	76.226	-14.623
5900	20.999	136.950	110.739	-75.412	75.412	-15.253
6000	20.999	136.687	110.156	-74.598	74.598	-15.883

June 30, 1961; Dec. 31, 1961; June 30, 1964; Dec. 31, 1969

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	(2)
(1800)	(2)
(4500)	(2)
(12000)	(2)
(30000)	(2)

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	g_i
(490) (1)	(333) (2)
(185) (1)	(131) (2)

Bond Distance: Zr-Cl = (2.3) Å

Bond Angle: Cl-Zr-Cl = (100)°

Product of the Moments of Inertia: $I_A I_B I_C = (1.5104 \times 10^{-112}) \text{ g}^3 \text{ cm}^6$

$$\sigma = \{3\}$$

Heat of Formation

Potter (1) investigated mass spectrometrically the equilibrium $\text{CaCl}_2(\text{g}) + \text{ZrCl}_4(\text{g}) \rightleftharpoons \text{CaCl}_2(\text{g}) + \text{ZrCl}_3(\text{g})$ in the temperature range 1163-1557°K. Ion intensities were measured 2.5 eV above threshold and they were used in the calculation of equilibrium constants. Using the reported equilibrium constants, the heats of reaction at 298°K are evaluated by the third law and second law methods as -3.69 and -16.67 kcal/mol, respectively. The third law drift is 9.31 ± 1.25 eu. Using the third law $\Delta H_f^\circ = -3.69$ kcal/mol, $\Delta H_f^\circ(\text{ZrCl}_4, \text{g}) = -207.77$ kcal/mol (2), $\Delta H_f^\circ(\text{CaCl}_2, \text{g}) = -28.8$ kcal/mol (3) and $\Delta H_f^\circ(\text{ZrCl}_3, \text{g}) = -115.0$ kcal/mol (4). We obtain $\Delta H_f^\circ(\text{ZrCl}_3, \text{g}) = -125.3$ kcal/mol, which is adopted in the tabulation.

Farber et al. (5) also studied mass spectrometrically the reaction $\text{Zr}(\text{Cl}) + \text{ZrCl}_4(\text{g}) \rightleftharpoons \text{ZrCl}_3(\text{g}) + \text{ZrCl}_2(\text{g})$ in the temperature range from 1579°K to 1779°K. They reported a second law heat of reaction as $\Delta H_r^\circ = 59.2 \pm 1.6$ kcal/mol. Since the attainment of equilibrium was questionable in their studies, the heat of reaction obtained from the third law method is generally more reliable. Using their reported ion intensities of run 3 (temperature range from 1667°K to 1898°K, five points), we have calculated the equilibrium constants $K_1 = (I_{\text{ZrCl}_2})^2 / (I_{\text{ZrCl}_3}) (I_{\text{ZrCl}_4})$ for reaction (1) $\text{ZrCl}_3(\text{g}) + \text{ZrCl}_2(\text{g}) \rightleftharpoons \text{ZrCl}_4(\text{g})$, and $K_2 = (I_{\text{ZrCl}_3})^2 / (I_{\text{ZrCl}_4}) (I_{\text{ZrCl}_2})$ for reaction (2) $\text{ZrCl}_3(\text{g}) + \text{ZrCl}_3(\text{g}) \rightleftharpoons \text{ZrCl}_4(\text{g}) + \text{ZrCl}_2(\text{g})$. Third law analyses of the equilibrium constants give $\Delta H_r^\circ = -11.0$ kcal/mol for reaction (1) and its drift 4.1 ± 1.7 eu; and $\Delta H_r^\circ = 1.4$ kcal/mol for reaction (2) and its drift 11.1 ± 1.2 eu. Using the third law heats of reaction, and $\Delta H_f^\circ(\text{ZrCl}_4, \text{g}) = 49.1$ kcal/mol (5) and $\Delta H_f^\circ(\text{ZrCl}_3, \text{g}) = -207.77$ kcal/mol (2), we obtain $\Delta H_f^\circ(\text{ZrCl}_3, \text{g}) = -124.9$ kcal/mol and $\Delta H_f^\circ(\text{ZrCl}_2, \text{g}) = -43.4$ kcal/mol which are in good agreement with the values adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be a pyramid similar to the group VA trichlorides. The bond distance is assumed to be the same as that of $\text{ZrCl}_4(\text{g})$. The three principal moments of inertia are $I_A = I_B = 45.9145 \times 10^{-39}$ and $I_C = 72.6247 \times 10^{-39} \text{ g cm}^2$. The electronic levels are estimated as three times higher than those of $\text{TiCl}_3(\text{g})$, based on the ratio of the first splitting interval between Ti(IV) and Zr(IV), given by C. E. Moore (7). The quantum weights are assumed to be the same as those of $\text{TiCl}_3(\text{g})$.

Vibrational frequencies are calculated from the estimated force constants by the valence force method (8). The force constants are estimated from those of PCl_3 , AsCl_3 , and SbCl_3 listed by Herzberg (8).

References

1. N. D. Potter, Aeronutric Div., Philco-Ford Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. JANAF ZrCl₄(g) table, dated Dec. 31, 1969.
3. The heat of formation and the free energy functions of $\text{CaCl}_2(\text{g})$ are preliminary values calculated by the Thermal Laboratory, The Dow Chemical Company, Midland, Mich.
4. The heat of formation and the free energy functions of $\text{CaCl}_2(\text{g})$ are preliminary values calculated by the Thermal Laboratory, The Dow Chemical Company, Midland, Mich.
5. M. Farber, Y. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFPRJ-TR-67-244, Contract F04611-67-C-0010, Nov. 1967.
6. JANAF ZrCl₃(g) table, dated Dec. 31, 1969.
7. C. E. Moore, "Atomic Energy Levels," U. S. Natl. Bur. Std. Circ. 467.
8. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc. New York, 1945.

MAGNESIUM DICHLORIDE, DIMERIC (Mg₂Cl₄) (IDEAL GAS)

GFW = 190.436

Magnesium Dichloride, Dimeric (Mg₂Cl₄)

(Ideal Gas) GFW = 190.436

Point Group: [D_{2h}']S_{298.15} = [100.098 ± 5] gibbs/molΔH_{f,0}^o = -228.11 ± 7 kcal/molΔH_{f,298.15}^o = -228.10 ± 7 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\frac{\omega_e}{\text{cm}^{-1}}$	$\frac{\omega_e}{\text{cm}^{-1}}$	$\frac{\omega_e}{\text{cm}^{-1}}$
[500] (1)	[240] (1)	[130] (2)
[400] (1)	[200] (1)	[100] (2)
295 (1)	[150] (1)	[80] (2)

Bond Distance: Mg-Cl = [2.18] Å, Mg-Cl'(ring) = [2.3] Å

Bond Angles: Cl'-Mg-Cl (in ring) = [90°], Cl-Mg-Cl' = [135°]

Product of the Moments of Inertia: I_AI_BI_C = 1.3313 × 10⁻¹¹¹ g³ cm⁶

Heat of Formation

References relative to the monomer-dimer ratio in magnesium chloride vapor are given in the discussion for monomeric ideal gas. The selected best value for the heat of dimerization at 900°K is -39.2 kcal/mol. Combined with heat of formation data for the monomer and the heat capacity of the dimer, this yields ΔH_{f,298.15}^o = -228.10 kcal/mol.

Heat Capacity and Entropy

A planar structure with D_{2h} symmetry was assumed, with the outer Mg-Cl distance the same as in MgCl₂ and the ring Mg-Cl distance slightly larger. The ring was taken to be square, and the Cl-Mg-Cl' angle 135°. This structure gives individual moments of inertia of I_A = 31.12 × 10⁻³⁹ g cm², I_B = 191.6 × 10⁻³⁹ g cm² and I_C = I_A + I_B.

A reasonable set of frequencies was estimated by comparison with MgCl₂ monomer and other dimer molecules. The single observed frequency is from A. Buchler and W. Klemperer, J. Chem. Phys. 29, 121 (1958), who erroneously ascribed it to the bending mode of the monomer. The estimated values were adjusted until the entropy of dimerization at 900°K was -29.9 gibbs/mol, as selected in the discussion for ideal monomeric gas. The calculated thermodynamic properties of monomer and dimer give total vapor pressures in good agreement with experiment and yield a boiling point for magnesium chloride of 1624°K at one atmosphere pressure.

T, °K	Cp ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	Log Kp
0	21.680	16.141E	-	5.787	-228.107	INEFINITE
100	21.680	71.495	142.746	5.737	-228.014	463.056
200	21.529	88.672	102.748	2.815	-228.411	244.634
298	21.543	100.098	100.098	+000	-228.100	221.509
300	21.547	100.281	100.089	-055	-228.097	221.648
400	30.458	106.924	101.271	3.064	-227.979	191.349
500	30.911	115.775	103.511	6.132	-227.898	164.899
600	31.170	121.435	106.040	9.237	-227.869	142.299
700	31.331	126.253	108.592	12.363	-227.885	120.491
800	31.466	130.444	110.844	15.486	-227.923	100.426
900	31.581	134.152	113.430	18.646	-228.000	82.674
1000	31.684	137.474	115.671	21.803	-232.595	65.003
1100	31.603	140.485	117.792	24.962	-232.834	40.380
1200	31.634	143.236	119.800	28.123	-233.127	36.523
1300	31.676	145.768	121.706	31.286	-233.472	33.559
1400	31.730	148.116	123.505	34.455	-233.860	31.092
1500	31.691	150.302	125.220	37.623	-234.239	27.235
1600	31.704	152.387	126.852	40.793	-234.609	24.558
1700	31.714	154.270	128.409	43.964	-234.920	22.197
1800	31.720	155.968	129.896	47.136	-235.184	20.102
1900	31.723	157.498	131.326	50.306	-235.409	18.267
2000	31.736	159.426	132.685	53.482	-235.458	16.587
2100	31.742	160.974	133.995	56.656	-235.428	15.026
2200	31.746	162.451	135.256	59.830	-235.364	13.645
2300	31.748	163.868	136.476	63.004	-235.262	12.423
2400	31.754	165.264	137.659	66.180	-235.128	11.345
2500	31.757	166.510	138.768	69.356	-234.950	10.473
2600	31.760	167.756	139.859	72.531	-234.721	9.195
2700	31.763	168.954	140.914	75.708	-234.498	8.192
2800	31.765	170.124	141.932	78.884	-234.272	7.424
2900	31.767	171.224	142.927	82.061	-234.040	6.874
3000	31.769	172.301	143.889	85.237	-233.791	6.497
3100	31.770	173.343	144.822	88.414	-233.528	6.186
3200	31.772	174.352	145.729	91.591	-233.255	5.932
3300	31.773	175.332	146.611	94.768	-232.972	5.733
3400	31.774	176.278	147.470	97.946	-232.678	5.583
3500	31.776	177.199	148.306	101.123	-232.375	5.483
3600	31.777	178.094	149.121	104.301	-232.061	5.436
3700	31.778	178.965	149.916	107.479	-231.737	5.446
3800	31.779	179.812	150.682	110.656	-231.404	5.502
3900	31.779	180.638	151.422	113.834	-231.062	5.602
4000	31.780	181.442	152.189	117.012	-230.712	5.743
4100	31.781	182.227	152.912	120.190	-230.350	5.921
4200	31.781	182.993	153.619	123.369	-230.005	6.138
4300	31.782	183.741	154.308	126.547	-229.675	6.392
4400	31.783	184.471	154.988	129.725	-229.361	6.680
4500	31.783	185.186	155.651	132.903	-229.063	7.000
4600	31.784	185.884	156.301	136.082	-228.780	7.352
4700	31.784	186.568	156.938	139.260	-228.512	7.736
4800	31.785	187.241	157.562	142.438	-228.259	8.152
4900	31.785	187.892	158.174	145.617	-228.020	8.600
5000	31.785	188.534	158.775	148.795	-227.795	9.080
5100	31.786	189.164	159.365	151.974	-227.584	9.592
5200	31.786	189.781	159.948	155.152	-227.386	10.136
5300	31.787	190.381	160.513	158.330	-227.199	10.712
5400	31.787	190.981	161.071	161.510	-227.024	11.320
5500	31.787	191.564	161.621	164.688	-226.860	11.960
5600	31.787	192.137	162.160	167.867	-226.707	12.632
5700	31.787	192.699	162.691	171.046	-226.564	13.336
5800	31.788	193.252	163.212	174.225	-226.431	14.072
5900	31.788	193.796	163.722	177.403	-226.308	14.840
6000	31.788	194.330	164.233	180.582	-226.194	15.640

Molybdenum Tetrachloride (MoCl₄)

(Crystal)

GFW = 237.752

$$\Delta H_f^\circ = \text{Unknown}$$

$$\Delta H_{f298.15}^\circ = -114 \pm 2 \text{ kcal/mol}$$

$$\Delta H_m^\circ = [4 \pm 2] \text{ kcal/mol}$$

$$S_{298.15}^\circ = [53.5 \pm 3] \text{ gibbs/mol}$$

$$T_m = 590^\circ\text{K}$$

Heat of Formation

The adopted $\Delta H_f^\circ = -114$ kcal/mol was determined by Shchukarev et al. (1) by solution calorimetry. The authors measured the heat of solution of MoCl₄ in the aqueous solvent FeCl₃ + HCl and obtained the heat of formation from a comparison with the heat of solution of MoCl₅ measured in the same solvent.

The decomposition pressures of 2MoCl₅(c) = 2MoCl₄(c) + Cl₂(g) (80 - 150°C) were measured manometrically by Saeki and Matsuzaki (2). From the reported data we evaluate the enthalpy change for the above reaction by third law analysis.

Based on $\Delta H_{f298}^\circ(\text{MoCl}_5, c) = -126$ kcal/mol and the third law $\Delta H_{f298}^\circ = 24.132$ kcal/mol, we obtain $\Delta H_{f298}^\circ(\text{MoCl}_4, c) = -113.94$ kcal/mol, which is in very good agreement with the value reported by Shchukarev et al. (1).

Heat Capacity and Entropy

The heat capacity is estimated by comparison with that of WCl₄(c). The estimated $S_{298}^\circ = 53.5$ eu is based on the assumption that the entropy differences between MoCl₄(c) and MoCl₅(c) is about the same as that between WCl₄(c) and WCl₅(c). The entropy obtained from the second law analysis of the data of Saeki and Matsuzaki (2) agrees with the adopted one within the error of the vapor pressure data.

Melting Data

See liquid table.

References

1. S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin and A. K. Baev, Russ. J. Inorg. Chem. (English Transl.) 5, 802 (1960).
2. Y. Saeki and R. Matsuzaki, Denki Kagaku 13, 155-8 (1965).

T, °K	C _p ^o	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG_f°	Log K _p
0							
100							
200							
300	31.000	53.500	53.500	.000	-114.000	-96.136	70.470
400	31.000	53.492	53.501	.057	-113.984	-96.026	69.955
500	32.300	52.788	54.732	3.222	-113.069	-90.177	49.270
	33.600	70.135	57.100	6.517	-112.096	-84.564	36.963
600	34.900	76.376	59.605	9.942	-111.040	-79.155	26.832
700	36.200	81.652	62.572	13.497	-109.684	-73.631	23.042
800	37.600	86.779	65.294	17.187	-108.618	-68.682	18.818
900	38.900	91.285	67.935	21.015	-107.228	-63.995	15.540
1000	39.900	95.436	70.481	24.956	-105.741	-59.273	12.954
1100	40.600	98.282	72.926	28.992	-104.173	-54.700	10.869
1200	41.600	102.668	75.274	33.113	-102.538	-50.276	9.156
1300	42.200	106.222	77.527	37.304	-100.852	-45.988	7.731
1400	42.700	109.368	79.690	41.549	-99.133	-41.832	6.530
1500	43.200	112.331	81.768	45.844	-97.387	-37.799	5.507

Molybdenum Tetrachloride (MoCl₄)

(Liquid) GFW = 237.752

T, °K	Cp°	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0							
100							
200							
298	35,000	58.682	58.682	+0.00	-110.621	-94.302	69.125
300	35,000	58.699	58.683	.065	-110.597	-94.202	68.626
400	35,000	68.667	60.055	3.565	-109.347	-88.927	48.588
500	35,000	76.777	62.648	7.065	-106.169	-83.959	36.698
600	35,000	83.158	62.521	10.682	-102.035	-79.223	28.455
700	35,000	88.228	62.272	14.565	-97.997	-74.273	23.115
800	35,000	93.228	71.272	17.565	-94.861	-70.285	19.201
900	35,000	97.350	73.945	21.065	-93.799	-66.024	16.03
1000	35,000	101.038	76.473	24.565	-92.753	-61.886	13.425
1100	35,000	104.373	78.640	28.065	-91.721	-57.848	11.493
1200	35,000	107.313	80.460	31.565	-90.707	-53.906	9.418
1300	35,000	110.220	83.247	35.065	-89.712	-50.046	8.414
1400	35,000	112.814	85.268	38.565	-88.738	-46.262	7.222
1500	35,000	115.229	87.186	42.065	-87.787	-42.546	6.199

MOLYBDENUM TETRACHLORIDE (MoCl₄)

(LIQUID)

GFW = 237.752

Cl₄Mo

S°_{298.15} = [58.682] gibbs/mol

ΔHf°_{298.15} = [-110.621 ± 2] kcal/mol

Tm = 590°K

ΔHm° = [4 ± 2] kcal/mol

Tb = [680]°K

ΔHv° = [14.7] kcal/mol

Heat of Formation

The heat of formation is obtained from ΔHf°₂₉₈(c) by adding ΔHm° and the difference between H°₅₉₀ - H°₂₉₈ for crystal and liquid.

Heat Capacity and Entropy

The heat capacities are assumed to be constant at 7 gibbs/g-atom. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

Tm is taken from V. Gutmann, "Halogen Chemistry," Vol. 3, Academic Press, New York, 1967. ΔHm° is estimated such that the derived ΔG° for MoCl₄(l) yields a reasonable boiling point which is expected to be between 600 and 700°K from comparisons with related compounds.

Vaporization Data

Tb is the temperature at which the Gibbs energy change (ΔGr°) of the following process MoCl₄(l) = MoCl₄(g) approaches zero. The difference between ΔHf° for MoCl₄(l) and MoCl₄(g) at Tb is the heat of vaporization.

Molybdenum Tetrachloride (MoCl₄)
(Ideal Gas) GFW = 237.752Point Group T_d

$$\Delta H_f^\circ = -91.0 \pm 3 \text{ kcal/mol}$$

$$S_{298.15}^\circ = [86.9] \text{ gibbs/mol}$$

$$\Delta H_f^\circ = -92.0 \pm 3 \text{ kcal/mol}$$

Ground State Quantum Weight = {3}

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}	ω_i, cm^{-1}	ω_i, cm^{-1}
[390] (1)	[410] (3)	[1203] (3)
[120] (2)		

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	ϵ_i
0	(3)
[10000]	(3)
[30000]	(3)

Bond Distance: Mo-Cl = [2.27] Å

Bond Angle: Cl-Mo-Cl = [109.47]°

o = [12]

Product of the Moments of Inertia: $I_A I_B I_C = [5.2929 \times 10^{-112}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

S. A. Shchukarev, G. I. Movikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin and A. K. Baev, Zh. Neorg. Khim. **5**, 1850-4 (1960), derived the value $\Delta H_f^\circ(\text{MoCl}_4, \text{g}) = -89 \text{ kcal/mol}$ from the decomposition pressures of $2\text{MoCl}_3(\text{c}) = \text{MoCl}_2(\text{c}) + \text{MoCl}_4(\text{g})$, 480-600°C, measured by a transpiration method. However, this ΔH_f° value is adjusted to be $-92 \pm 3 \text{ kcal/mol}$, in order to obtain a reasonable boiling point (see the MoCl₄ (l) table).

Heat Capacity and Entropy

Vibrational frequencies and quantum weights are estimated by comparison with those of WCl₄(g). The molecular configuration is assumed to be tetrahedral similar to those of WCl₄(g), SiCl₄(g), TiCl₄(g) and PCl₄(g). The bond distance is estimated to be the same as that of MoCl₅(g). The three principal moments of inertia are $I_A = I_B = I_C = 80.89 \times 10^{-39} \text{ g cm}^2$. The low lying electronic levels are estimated to be 0, 10000, and 30000, all triplets, by comparison with those of WCl₄(g).

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-5.321	-91.837	-91.837	INFINITE
100	16.547	66.724	108.140	-4.142	-92.167	-89.641	195.910
200	21.366	79.088	90.959	-2.214	-92.132	-87.116	95.196
298	23.448	86.669	0.000	0.000	-92.000	-84.661	62.073
300	23.473	89.014	86.669	0.043	-91.994	-84.636	61.656
400	24.412	95.911	89.803	2.443	-91.844	-82.205	44.915
500	24.693	101.416	91.594	4.911	-91.702	-79.411	34.868
600	25.166	105.991	93.622	7.415	-91.567	-77.485	28.209
700	25.552	109.764	95.643	9.948	-91.440	-75.486	23.486
800	25.872	112.764	97.663	12.481	-91.324	-73.476	19.682
900	26.131	115.268	99.684	15.030	-91.213	-71.464	17.111
1000	26.357	118.961	101.375	17.587	-91.110	-69.467	14.698
1100	26.530	121.402	103.086	20.148	-91.017	-67.476	13.086
1200	26.661	123.691	104.743	22.720	-90.932	-65.496	11.689
1300	26.759	125.849	106.353	25.280	-90.874	-63.519	10.308
1400	26.814	127.894	107.901	27.850	-90.832	-61.547	9.216
1500	26.835	129.369	109.087	30.423	-90.806	-59.577	8.272
1600	26.756	131.030	110.407	32.997	-90.808	-57.609	7.446
1700	26.572	132.862	111.870	35.566	-90.832	-55.646	6.727
1800	26.279	134.862	113.476	38.153	-90.874	-53.688	6.087
1900	25.883	137.023	115.212	40.734	-90.942	-51.740	5.486
2000	25.404	139.378	117.083	43.317	-91.040	-49.804	4.943
2100	24.875	141.904	119.086	45.904	-91.159	-47.882	4.469
2200	24.303	144.591	121.211	48.493	-91.292	-45.973	4.052
2300	23.603	147.426	123.437	51.083	-91.440	-44.076	3.682
2400	22.807	150.401	125.759	53.680	-91.608	-42.182	3.359
2500	21.967	153.516	128.166	56.278	-91.797	-40.291	3.082
2600	21.035	156.761	130.659	58.880	-92.002	-38.404	2.851
2700	20.010	160.136	133.337	61.494	-92.224	-36.522	2.665
2800	18.904	163.631	136.099	64.123	-92.464	-34.644	2.519
2900	17.729	167.346	139.046	66.766	-92.724	-32.772	2.409
3000	16.477	171.262	142.179	69.322	-93.002	-30.912	2.326
3100	15.151	175.378	145.501	71.891	-93.292	-29.060	2.261
3200	13.756	179.691	149.016	74.476	-93.602	-27.216	2.211
3300	12.303	184.201	152.723	77.071	-93.932	-25.372	2.176
3400	10.801	188.906	156.656	79.671	-94.282	-23.528	2.151
3500	9.259	193.806	160.891	82.284	-94.654	-21.684	2.136
3600	7.687	198.901	165.426	84.914	-95.048	-19.840	2.131
3700	6.094	204.191	170.261	87.564	-95.464	-17.996	2.136
3800	4.481	209.666	175.396	90.232	-95.902	-16.152	2.151
3900	2.859	215.329	180.841	92.917	-96.362	-14.308	2.176
4000	1.236	221.186	186.596	95.644	-96.844	-12.464	2.211
4100	0.614	227.231	192.661	98.414	-97.348	-10.620	2.256
4200	0.000	233.466	199.036	101.224	-97.874	-8.776	2.311
4300	0.000	239.891	205.721	104.074	-98.424	-6.932	2.376
4400	0.000	246.506	212.726	106.964	-98.994	-5.088	2.451
4500	0.000	253.311	220.051	109.894	-99.584	-3.244	2.536
4600	0.000	260.306	227.706	112.864	-100.194	-1.396	2.631
4700	0.000	267.491	235.681	115.874	-100.824	0.452	2.736
4800	0.000	274.866	243.976	118.924	-101.474	2.308	2.851
4900	0.000	282.431	252.591	122.014	-102.144	4.164	2.976
5000	0.000	290.186	261.526	125.144	-102.834	6.020	3.111
5100	0.000	298.131	270.781	128.314	-103.544	7.876	3.256
5200	0.000	306.266	280.356	131.524	-104.274	9.732	3.411
5300	0.000	314.591	290.251	134.774	-105.024	11.588	3.576
5400	0.000	323.106	300.476	138.064	-105.794	13.444	3.751
5500	0.000	331.811	311.031	141.494	-106.584	15.296	3.936
5600	0.000	340.706	321.916	145.064	-107.394	17.152	4.131
5700	0.000	349.791	333.141	148.674	-108.224	19.008	4.336
5800	0.000	359.066	344.706	152.324	-109.074	20.864	4.551
5900	0.000	368.531	356.611	156.014	-109.944	22.720	4.776
6000	0.000	378.186	368.856	159.744	-110.834	24.576	5.011

Dec. 31, 1968

Tungsten Oxytetrachloride (WOCl₄)
(Crystal) GFW = 341.6614

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	kcal/mol H° - H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
100						
200						
298	34.954	41.300	41.300	0.00	-160.400	-131.305
300	35.000	41.516	41.501	0.065	-160.383	-131.125
400	37.500	51.928	45.703	3.650	-159.162	-121.922
500	40.500	60.584	49.435	7.395	-158.100	-112.196
600	42.500	68.088	48.596	11.695	-156.756	-103.131
700	44.350	74.786	51.868	16.043	-155.174	-94.317
800	45.500	80.796	55.115	20.545	-153.476	-85.741
900	46.300	86.208	58.274	25.141	-151.709	-77.377
1000	46.900	91.118	61.317	29.801	-149.904	-69.215

TUNGSTEN OXYTETRACHLORIDE (WOCl₄) (CRYSTAL) Cl₄OW
OPW = 341.6614

ΔHf° = Unknown
ΔHf°_{298.15} = -150.4 ± 2 kcal/mol
ΔHm° = -10.846 ± 3 kcal/mol
Tm = 484°K

Heat of Formation.

S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov¹ measured calorimetrically the heats of reaction (1) and (2) at 298°K as -131.5 ± 0.5 and -13.6 ± 0.1 kcal/mol, respectively. The reactions are given as follows:
(1) WOCl₄(c) + 6 NaOH(16.3 H₂O) → Na₂WO₄(190,000 H₂O) + 4 NaCl(50,000 H₂O) + 3 H₂O(l)
(2) H₂WO₄(c) + 2 NaOH(16.3 H₂O) → Na₂WO₄(20,000 H₂O) + 2 H₂O(l)
Based on these data and the heats of dilution for NaOH(aq)², and Na₂WO₄(aq)³, we obtain ΔHf°₂₉₈ = -118.0 ± 1.6 kcal/mol for WOCl₄(c) + 4OH⁻(∞H₂O) → H₂WO₄(c) + 4Cl⁻(∞H₂O) + H₂O(l). This leads to ΔHf°₂₉₈(WOCl₄,c) = -160.4 ± 2 kcal/mol, using ΔHf°₂₉₈(H₂WO₄,c) = -270.5 ± 0.4 kcal/mol⁵.

Heat Capacity and Entropy.

Cp₃₀₀ = 35.0 gibbs/mol is estimated using Kopp's rule. Since the melting point of WOCl₄(c) is approximately 500°K, which is relatively low for oxygen to reach its maximum contribution, we estimate Cp₅₀₀ = 40.0 gibbs/mol based on the values for WO₂(c), WO₃(c) and WCl₆(c).

The entropy, S°₂₉₈ = 41.3 eu, is calculated from ΔS°₄₅₇ = 44.5 eu for WOCl₄(c) → WOCl₄(g) obtained from the second law analysis of the vapor pressure equation given by S. A. Shchukarev and A. V. Suvorov⁴. See WOCl₄(g) table (Mar. 31, 1967) for details.

It is surprising that this entropy is smaller than the corresponding value for WOP₄(c). See WOP₄(c) table (Mar. 31, 1967) for details.

Melting Data.

Tm is calculated as the temperature at which the Gibbs energies of formation of crystal and liquid are equal. The difference between the heats of formation of crystal and liquid at the melting point is ΔHm°. This ΔHm° is derived from 2nd law analyses of the vapor pressure equation determined by Shchukarev and Suvorov⁴. See WOCl₄(l,g) tables (Mar. 31, 1967) for details.

References.

1. S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov, Zh. Neorg. Khim. **3**, 2642 (1958).
2. "Thermal Properties of Aqueous Uni-univalent Electrolytes," V. B. Parker, NBS-RS-NBS2, Natl. Bur. Std., Washington, D.C., Apr. 1965.
3. We have assumed ΔH°_{dil} = 0 ± 0.5 kcal/mol for Na₂WO₄(20,000 H₂O) → Na₂WO₄(190,000 H₂O).
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. **16**, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Earlier data reported by Shchukarev et al., Zh. Neorg. Khim. **1**, 357 (1956), **3**, 2630 (1958), **5**, 1650 (1960), have been revised and they are not used here.
5. JANAF H₂WO₄(c) table dated Mar. 31, 1967.

Tungsten Oxytetrachloride (WOCl₄)

(Ideal Gas) GFW = 341.6614

T, °K	Cp ^a	S ^b - (C ^a - H ³⁰⁰)/T	ΔH ^c	ΔG ^f	Log K ^p
0	1.000	0.000	0.000	0.000	INFINITE
100	15.252	47.704	135.776	135.776	INFINITE
200	24.608	90.333	136.501	136.501	INFINITE
250	25.367	90.037	137.068	137.068	49.811
300	25.414	90.254	137.069	137.069	89.191
400	27.395	97.859	137.024	137.024	117.551
500	29.531	104.115	136.891	136.891	149.282
600	29.436	109.412	136.711	136.711	197.981
700	29.981	113.993	136.505	136.505	252.197
800	30.362	118.022	136.291	136.291	26.864
900	30.637	121.615	136.069	136.069	93.403
1000	30.842	124.854	135.850	135.850	19.428
1100	30.998	127.802	135.633	135.633	16.732
1200	31.119	130.504	135.428	135.428	14.486
1300	31.215	132.999	135.230	135.230	12.592
1400	31.282	135.315	135.041	135.041	10.969
1500	31.334	137.476	134.865	134.865	9.564
1600	31.404	139.501	134.700	134.700	8.337
1700	31.489	141.407	134.547	134.547	7.255
1800	31.486	143.205	134.409	134.409	6.295
1900	31.517	144.909	134.283	134.283	5.436
2000	31.583	146.526	134.175	134.175	4.681
2100	31.566	148.065	134.079	134.079	3.966
2200	31.586	149.534	133.991	133.991	3.332
2300	31.504	150.939	133.920	133.920	2.753
2400	31.619	152.288	133.865	133.865	2.223
2500	31.533	153.575	133.824	133.824	1.736
2600	31.655	154.816	133.790	133.790	1.285
2700	31.656	156.011	133.762	133.762	0.861
2800	31.655	157.162	133.740	133.740	0.461
2900	31.574	158.273	133.589	133.589	0.121
3000	31.682	159.347	133.529	133.529	0.216
3100	31.689	160.386	133.484	133.484	0.531
3200	31.695	161.392	133.443	133.443	0.857
3300	31.701	162.368	133.406	133.406	1.106
3400	31.707	163.314	133.374	133.374	1.370
3500	31.712	164.234	133.346	133.346	1.619
3600	31.716	165.127	133.322	133.322	1.855
3700	31.720	165.996	133.300	133.300	2.082
3800	31.724	166.842	133.280	133.280	2.308
3900	31.728	167.666	133.261	133.261	2.523
4000	31.731	168.469	133.244	133.244	2.728
4100	31.734	169.253	133.229	133.229	2.922
4200	31.737	170.018	133.215	133.215	3.107
4300	31.740	170.765	133.202	133.202	3.284
4400	31.742	171.488	133.190	133.190	3.453
4500	31.744	172.189	133.179	133.179	3.614
4600	31.746	172.865	133.169	133.169	3.769
4700	31.748	173.518	133.160	133.160	3.918
4800	31.750	174.156	133.152	133.152	4.060
4900	31.752	174.771	133.145	133.145	4.196
5000	31.754	175.373	133.139	133.139	4.327
5100	31.755	175.962	133.133	133.133	4.454
5200	31.757	176.538	133.128	133.128	4.575
5300	31.758	177.103	133.124	133.124	4.692
5400	31.760	177.657	133.120	133.120	4.804
5500	31.761	178.200	133.116	133.116	4.914
5600	31.762	178.732	133.112	133.112	5.018
5700	31.763	179.254	133.108	133.108	5.119
5800	31.764	179.766	133.104	133.104	5.218
5900	31.765	180.266	133.100	133.100	5.312
6000	31.766	180.754	133.096	133.096	5.400

Sept. 30, 1962; Mar. 31, 1967

CI₄OW

OPW = 341.6614

TUNGSTEN OXYTETRACHLORIDE (WOCl₄) (IDEAL GAS)

Point Group [C_{2v}]

S_{298.15} = [90.1] gibbs/mol

ΔH_{f,298.15} = -137.0 ± 5 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

W, cm ⁻¹	W, cm ⁻¹	W, cm ⁻¹
[1000] (1)	[350] (1)	[200] (1)
[1000] (1)	[350] (1)	[200] (1)
[480] (1)	[300] (1)	[100] (1)
[480] (1)	[300] (1)	[100] (1)
[480] (1)	[300] (1)	[100] (1)

Bond Distance: W-Cl = [2.26] Å W-O = [1.81] Å

Bond Angle: Cl-W-O = Cl-W-Cl = [120°]

Cl-W-Cl = Cl-W-O = [90°]

Cl-W-Cl = [180°]

*Equatorial **Axial

Product of the Moments of Inertia: I_AI_BI_C = [5.873 x 10⁻¹¹²] g³ cm⁶

Heat of Formation

The heat of formation, ΔH_{f,298}(WOCl₄, g) = -137.0 kcal/mol, is calculated from ΔH_{f,298} = 23.4 kcal/mol for WOCl₄(c) → WOCl₄(g). The latter is obtained by the third law method from the vapor pressure equation given by S. A. Shchukarev* and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Second law analysis gives ΔH_{f,298} = 21.9 kcal/mol (ΔH_{f,298} = 23.4 kcal/mol).

*Earlier data reported by Shchukarev et al., Zh. Neorg. Khim. 1, 357 (1956), 3, 2630 (1956), 5, 1650 (1960), have been revised and they are not used here.

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of SOP₄(g), reported by P. L. Ogggin, H. L. Roberts and L. A. Woodward¹. The bond distance W-O and W-Cl are estimated to be the same as those in WO₃(g) and WOCl₂(g), respectively. The three principal moments of inertia are I_A = 8.260 x 10⁻³⁸, I_B = 1.052 x 10⁻³⁷ and I_C = 6.757 x 10⁻³⁸ g cm².

All vibrational frequencies are estimated by comparison with those observed in the infrared and Raman spectra for SOP₄(g)², WOCl₂(g)³, CrO₂Cl₂(g)^{4,5}, WO₃(g)⁶, and WOCl₆(g)⁶. The frequencies are not listed in point group order.

References

1. P. L. Ogggin, H. L. Roberts and L. A. Woodward, Trans. Faraday Soc. 57, 1877 (1961).
2. T. V. Iorna and P. E. Stafford, J. Am. Chem. Soc. 88, 4819 (1966).
3. C. O. Barracough and J. Stale, Aust. J. Chem. 19, 741 (1966).
4. F. A. Miller, G. L. Carlson and W. B. White, Spectrochim. Acta 1959, 709 (1959).
5. H. Stammreich, K. Kawai and Y. Taveares, Spectrochim. Acta 1959, 438 (1959).
6. JANAF WO₃(g) table (Sept. 30, 1966), WOCl₆(g) table (Dec. 31, 1966).

Lead Tetrachloride (PbCl₄)
(Ideal Gas) Mol. Wt. = 349.04

INTERIM TABLE

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0								
100	10.010	68.470	191.191	5.463	74.631	74.631	191.191	191.191
200	22.499	82.582	112.093	4.162	75.155	72.084	157.532	157.532
298	24.125	91.919	91.919	2.000	75.138	68.998	75.383	75.383
300	24.184	92.084	91.919	.045	74.997	65.957	68.007	68.007
400	24.635	99.121	92.876	2.498	74.856	62.966	34.401	34.401
500	25.180	104.704	94.703	5.000	74.733	60.007	26.228	26.228
600	25.374	109.313	96.765	7.529	74.632	57.071	20.787	20.787
700	25.528	113.284	100.845	10.073	74.544	53.961	16.887	16.887
800	25.652	116.859	104.610	12.618	74.468	50.782	13.598	13.598
900	25.748	119.999	107.751	15.161	74.404	47.544	10.974	10.974
1000	25.825	122.741	110.461	17.705	74.351	44.256	8.974	8.974
1100	25.894	125.099	112.709	20.319	74.316	40.929	7.500	7.500
1200	25.956	127.076	114.452	22.905	74.296	37.564	6.556	6.556
1300	25.999	128.784	115.808	25.466	74.288	34.179	5.957	5.957
1400	26.028	130.241	116.844	28.005	74.291	30.774	5.557	5.557
1500	26.049	131.482	117.609	30.527	74.304	27.369	5.299	5.299
1600	26.064	132.541	118.144	33.036	74.326	23.974	5.124	5.124
1700	26.074	133.451	118.492	35.536	74.354	20.609	5.000	5.000
1800	26.080	134.234	118.684	38.030	74.386	17.284	4.916	4.916
1900	26.083	134.911	118.751	40.513	74.421	14.009	4.859	4.859
2000	26.084	135.494	118.794	43.000	74.458	10.789	4.824	4.824
2100	26.084	136.000	118.820	45.486	74.496	7.624	4.800	4.800
2200	26.084	136.434	118.834	47.971	74.534	4.514	4.786	4.786
2300	26.084	136.800	118.840	50.451	74.571	1.451	4.771	4.771
2400	26.084	137.114	118.840	52.926	74.608	-1.584	4.766	4.766
2500	26.084	137.374	118.840	55.400	74.644	-4.654	4.766	4.766
2600	26.084	137.584	118.840	57.871	74.679	-7.761	4.766	4.766
2700	26.084	137.751	118.840	60.336	74.714	-10.896	4.766	4.766
2800	26.084	137.884	118.840	62.794	74.749	-14.061	4.766	4.766
2900	26.084	137.994	118.840	65.246	74.784	-17.256	4.766	4.766
3000	26.084	138.084	118.840	67.694	74.819	-20.481	4.766	4.766
3100	26.084	138.154	118.840	70.139	74.854	-23.736	4.766	4.766
3200	26.084	138.204	118.840	72.581	74.889	-27.021	4.766	4.766
3300	26.084	138.244	118.840	75.020	74.924	-30.336	4.766	4.766
3400	26.084	138.274	118.840	77.456	74.959	-33.681	4.766	4.766
3500	26.084	138.294	118.840	79.889	74.994	-37.056	4.766	4.766
3600	26.084	138.304	118.840	82.319	75.029	-40.461	4.766	4.766
3700	26.084	138.314	118.840	84.746	75.064	-43.896	4.766	4.766
3800	26.084	138.324	118.840	87.171	75.099	-47.361	4.766	4.766
3900	26.084	138.334	118.840	89.594	75.134	-50.856	4.766	4.766
4000	26.084	138.344	118.840	92.016	75.169	-54.381	4.766	4.766
4100	26.084	138.354	118.840	94.436	75.204	-57.936	4.766	4.766
4200	26.084	138.364	118.840	96.854	75.239	-61.521	4.766	4.766
4300	26.084	138.374	118.840	99.271	75.274	-65.136	4.766	4.766
4400	26.084	138.384	118.840	101.686	75.309	-68.781	4.766	4.766
4500	26.084	138.394	118.840	104.100	75.344	-72.456	4.766	4.766
4600	26.084	138.404	118.840	106.514	75.379	-76.161	4.766	4.766
4700	26.084	138.414	118.840	108.926	75.414	-79.896	4.766	4.766
4800	26.084	138.424	118.840	111.336	75.449	-83.661	4.766	4.766
4900	26.084	138.434	118.840	113.744	75.484	-87.456	4.766	4.766
5000	26.084	138.444	118.840	116.150	75.519	-91.281	4.766	4.766
5100	26.084	138.454	118.840	118.554	75.554	-95.136	4.766	4.766
5200	26.084	138.464	118.840	120.959	75.589	-99.021	4.766	4.766
5300	26.084	138.474	118.840	123.364	75.624	-102.936	4.766	4.766
5400	26.084	138.484	118.840	125.769	75.659	-106.881	4.766	4.766
5500	26.084	138.494	118.840	128.174	75.694	-110.856	4.766	4.766
5600	26.084	138.504	118.840	130.579	75.729	-114.861	4.766	4.766
5700	26.084	138.514	118.840	132.984	75.764	-118.896	4.766	4.766
5800	26.084	138.524	118.840	135.389	75.799	-122.961	4.766	4.766
5900	26.084	138.534	118.840	137.794	75.834	-127.056	4.766	4.766
6000	26.084	138.544	118.840	140.199	75.869	-131.181	4.766	4.766

June 30, 1962

Cl₄Pb

Lead Tetrachloride (PbCl₄) (Ideal Gas)

Mol. Wt. = 349.04
ΔH°_f 298.15 = [-75] kcal. mole⁻¹
ΔG°_f 298.15 = 91.9 cal. deg⁻¹ mole⁻¹
Point Group T_d

Vibrational Levels and Multiplicities

ω, cm ⁻¹	
326 (1)	
63 (2)	
341 (3)	
99 (3)	

Pb-Cl distance = 2.43 Å Cl-Pb-Cl angle = 109° 28'
I_AB₂C = 7.9660 X 10⁻¹¹² g.³ cm.⁶ σ⁻ = 12

Heat of Formation. ΔH°_f 298.15 was estimated from the value of ΔH°_f 298.15 for PbCl₂(s), using the relation between ΔH°_f 298.15 for dihalides and that for tetrahalides of titanium and zirconium as reference.

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagarajan, Bull. Soc. Chim. Belg., 71, 119 (1962).

Cl₄Pb

Titanium Tetrachloride (TiCl₄)

(Crystal)

GFW = 189.712

Cl₄Ti

(CRYSTAL)

TITANIUM TETRACHLORIDE (TiCl₄)

GFW = 189.712

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	20.000	22.000	INFINITE	6.437	-195.704	-195.704	INFINITE
100	20.000	22.000	INFINITE	6.437	-195.704	-195.704	INFINITE
200	26.859	38.329	52.654	2.645	-195.546	-195.546	43.103
298	30.943	48.927	69.927	0.000	-194.807	-194.807	127.935
300	31.000	50.119	49.928	0.057	-194.791	-175.614	127.935
400	33.350	59.380	51.174	3.202	-193.844	-169.361	92.535
500	34.800	66.994	53.600	6.697	-192.781	-163.361	71.405

$\Delta H_f^\circ = -195.7 \pm 1.0$ kcal/mol
 $\Delta H_f^\circ_{298.15} = -194.807 \pm 1.0$ kcal/mol
 $\Delta H_m^\circ = 2.382$ kcal/mol

$S^\circ_{298.15} = 49.93 \pm 0.1$ gibbs/mol
 $T_m = 249.05^\circ\text{K}$

Heat of Formation

The heat of formation, ΔH_f° of TiCl₄(c) is calculated from the corresponding quantity for TiCl₄(l) and the values of $H_{249.05}^\circ - H_{298.15}^\circ$ for both crystal and liquid.

Heat Capacity and Entropy

The heat capacity of TiCl₄(c) has been reported by Latimer (1) and by Furukawa (2). The data from the latter investigation are adopted. These data lead to a value of 44.5 eu for $S_{249.05}^\circ$. This compares with Latimer's value (1) of 43.8 eu for the same quantity. The heat capacity of the solid is extrapolated to a value of 18R at 600°K, based on the known heat capacities of TiBr₄(c) and TiI₄(c). The hypothetical entropy at 298°K is based on the integration of the extrapolated curve and the value at the melting point.

Melting Data

The triple point is reported to be 249.05°K, with a measured heat of fusion of 2.382 kcal/mol, by Furukawa (2). Latimer (1) reported values of 248.0°K and 2.233 kcal/mol for these quantities. The former data are adopted.

References

1. W. M. Latimer, J. Am. Chem. Soc. 44, 90 (1922).
2. G. T. Furukawa, private communication, U. S. Natl. Bur. Std., 1964.

Sept. 30, 1961; Mar. 31, 1964; Dec. 31, 1967

Cl₄Ti

Titanium Tetrachloride (TiCl₄)

(Liquid)

GFW = 189.712

T, °K	C _p ^o	S ^o	-(C _p ^o -H ²⁹⁸)/T	H ^o -H ²⁹⁸	ΔH ^o	ΔG ^o	Log K _p
100	34.584	46.428	63.496	-3.400	-193.496	-191.719	198.572
200	34.704	60.326	60.326	0.000	-192.200	-176.226	159.177
298							
300	34.709	60.581	60.327	-0.064	-192.177	-176.127	128.308
400	34.936	70.557	61.691	3.547	-190.972	-170.661	93.408
500	35.153	78.378	64.274	7.051	-189.420	-166.091	72.598
600	35.370	84.805	67.176	10.577	-188.098	-161.452	58.809
700	35.586	90.213	70.995	14.125	-187.205	-157.704	47.177
800	35.793	94.841	74.241	17.600	-186.540	-154.404	37.511
900	36.020	99.269	75.618	21.285	-185.430	-148.542	36.071
1000	36.237	103.075	78.177	24.898	-184.369	-144.503	31.581

TITANIUM TETRACHLORIDE (TiCl₄)

(LIQUID)

GFW = 189.712

S^o_{298,15} = 60.326 gibbs/molΔH^o_{298,15} = -192.2 ± 0.9 kcal/molT_m = 249.05°KΔH_m^o = 2.382 kcal/molT_b = 409°KΔH_v^o = 8.55 kcal/mol

Heat of Formation

The heat of formation, ΔH^o_{298,15} of TiCl₄(l) is calculated from that of TiCl₄(g) and the value of ΔH_v^o_{298,15}. The value of ΔH_v^o₂₉₈ is determined from second and third law analyses of fugacity as follows.

Source	Method	Range	No. Pts.	2nd Law	3rd Law	Drift, eu	ΔH ^o ₂₉₈
1. Pike and Foster (1959) (1)	Manometric	363-415	18*	9.82±0.02	9.83	0.0±0.1	-192.2
2. Seryakov et al. (1960) (2)	Manometric	358-412	8	9.79±0.03	9.84	0.1±0.1	-192.2
3. Schafer et al. (1953) (3)	Isoteniscope	313-358	17*	9.86±0.02	9.82	-0.1±0.0	-192.2
4. Schafer et al. (1953) (3)	Isoteniscope	313-357	16**	9.80±0.01	9.82	0.0±0.0	-192.2
5. Schafer et al. (1953) (3)	Isoteniscope	313-357	16	9.91±0.02	9.83	-0.2±0.1	-192.2
6. Schafer et al. (1953) (3)	Isoteniscope	312-359	17	9.90±0.02	9.83	-0.2±0.1	-192.2
7. Weed (1957) (4)	Manometric	298-319	***	9.79±0.01	9.82	0.1±0.0	-192.2
8. Weed (1957) (4)	Manometric	298-319	***	9.81±0.01	9.82	0.0±0.0	-192.2
9. Weed (1957) (4)	Spectra	250-302	***	9.69±0.01	9.80	0.4±0.0	-192.2

* two points rejected due to failure of a statistical test

** three points rejected due to failure of a statistical test

*** selected points from extensive data

Third law analyses of the several vapor pressure sets result in drifts which are proportional to the mean temperatures.

Conversion of these data to fugacity eliminates this temperature dependence and the drifts are then scattered randomly about a constant value. This constant value is made to be essentially zero by methods described on the TiCl₄(g) table. The conversion to fugacity was made using Pitzer's method for normal fluids (5). The calculation was carried out using the value of 45.7 atm for the critical pressure, P_c, reported by Minzer (6) and estimated values of 643 ± 15°K for the critical temperature, T_c, and 0.23 ± 0.03 for the acentric constant, a. Schafer et al. (2) reported a calorimetric determination of ΔH_v^o₂₉₈. Their value of 9.9 ± 0.2 kcal/mol was used to check the reliability of their equipment, assuming that the vapor pressure data (3) gave a more accurate determination of ΔH_v^o₂₉₈. The adopted value of ΔH_v^o₂₉₈ is 9.82 ± 0.02 kcal/mol.

Heat Capacity and Entropy

The entropy and heat capacity of TiCl₄(l) has been measured by Furukawa (8). His reported values are adopted.

Melting Data

See TiCl₄(c) table for details.

Vaporization Data

The boiling temperature, T_b, is taken as the temperature at which K_p = 1 for the reaction TiCl₄(l) = TiCl₄(g). The vapor pressure data are discussed above.

References

1. F. P. Pike and C. T. Foster, Jr., *J. Chem. Eng. Data* **1**, 305 (1959).
2. G. V. Seryakov, S. A. Vaks, L. S. Sidorina, *Zhur. Obshch. Khim* **30**, 2130 (1960).
3. H. Schafer and F. Zeppenick, *Z. Anorg. Chem.* **272**, 274 (1953).
4. H. C. Weed, Ph.D. Thesis, The Ohio State University, 1957.
5. G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1961.
6. W. Minzer, *Naturwissenschaften* **45**, 126 (1958).
7. H. Schafer, G. Breil and G. Pfeiffer, *Z. Anorg. Chem.* **276**, 325 (1954).
8. G. T. Furukawa, private communication, U. S. Natl. Bur. Std., 1964.

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	Log K ^d
0	-0.000	-0.000	INFINITE	-5.166	-182.026	INFINITE
100	16.117	63.412	105.421	4.001	-182.387	352.299
200	22.881	84.935	126.516	2.000	-182.442	157.721
298	22.882	84.935	126.516	2.000	-182.400	127.391
300	22.881	84.935	126.516	2.002	-182.399	126.516
400	24.610	97.118	147.667	8.272	-182.244	73.383
500	26.942	101.639	165.022	7.307	-182.168	60.109
600	28.942	105.504	182.102	6.815	-182.171	50.632
700	30.513	108.677	198.036	6.415	-182.058	43.526
800	31.731	111.667	212.427	6.079	-182.036	38.000
900	32.653	114.551	225.551	5.794	-182.040	33.580
1000	33.326	117.281	237.666	5.537	-182.070	29.943
1100	33.809	119.881	248.921	5.300	-182.063	26.941
1200	34.131	122.361	259.337	5.082	-182.019	24.377
1300	34.326	124.741	268.921	4.882	-182.091	22.179
1400	34.426	127.041	277.666	4.694	-182.980	20.275
1500	34.453	129.281	285.551	4.527	-182.990	18.609
1600	34.409	131.481	292.666	4.382	-183.019	17.138
1700	34.291	133.641	299.022	4.257	-183.074	15.831
1800	34.109	135.761	304.622	4.141	-183.151	14.660
1900	33.861	137.841	309.466	4.031	-183.245	13.590
2000	33.551	139.881	313.551	3.927	-183.350	12.613
2100	33.191	141.881	316.881	3.827	-183.466	11.725
2200	32.791	143.841	319.422	3.731	-183.590	10.912
2300	32.361	145.761	321.166	3.637	-183.721	10.168
2400	31.901	147.641	322.102	3.547	-183.866	9.482
2500	31.411	149.481	322.222	3.461	-184.022	8.849
2600	30.891	151.281	321.533	3.377	-184.188	8.262
2700	30.341	153.041	320.022	3.297	-184.364	7.717
2800	29.761	154.761	317.688	3.221	-184.549	7.209
2900	29.151	156.441	314.422	3.149	-184.742	6.735
3000	28.511	158.081	310.222	3.082	-184.942	6.291
3100	27.841	159.681	305.088	3.019	-185.148	5.874
3200	27.151	161.241	299.022	2.961	-185.360	5.482
3300	26.441	162.761	292.102	2.907	-185.577	5.113
3400	25.711	164.241	284.333	2.857	-185.799	4.765
3500	24.961	165.681	275.722	2.811	-186.026	4.420
3600	24.191	167.081	266.266	2.769	-186.258	4.076
3700	23.401	168.441	255.966	2.731	-186.494	3.741
3800	22.591	169.761	244.722	2.697	-186.734	3.408
3900	21.761	171.041	232.533	2.667	-186.977	3.077
4000	20.911	172.281	219.402	2.641	-187.222	2.748
4100	20.041	173.481	205.333	2.619	-187.469	2.420
4200	19.161	174.641	190.333	2.601	-187.719	2.091
4300	18.261	175.761	174.422	2.587	-187.972	1.762
4400	17.341	176.841	157.588	2.577	-188.228	1.433
4500	16.401	177.881	140.822	2.569	-188.487	1.104
4600	15.441	178.881	123.122	2.564	-188.748	0.775
4700	14.461	179.841	104.488	2.561	-189.011	0.446
4800	13.461	180.761	84.922	2.561	-189.276	0.117
4900	12.441	181.641	64.422	2.561	-189.542	-0.212
5000	11.401	182.481	42.988	2.561	-189.809	-0.541
5100	10.341	183.281	20.622	2.561	-190.076	-0.870
5200	9.261	184.041	-1.742	2.561	-190.344	-1.200
5300	8.161	184.761	-24.102	2.561	-190.611	-1.529
5400	7.041	185.441	-46.551	2.561	-190.878	-1.858
5500	5.901	186.081	-68.088	2.561	-191.145	-2.187
5600	4.741	186.681	-88.722	2.561	-191.412	-2.516
5700	3.561	187.241	-108.455	2.561	-191.679	-2.845
5800	2.361	187.761	-127.188	2.561	-191.946	-3.174
5900	1.141	188.241	-145.022	2.561	-192.213	-3.503
6000	-0.091	188.681	-161.955	2.561	-192.480	-3.832

Sept. 30, 1961; Mar. 31, 1964; Dec. 31, 1967

TITANIUM TETRACHLORIDE (TiCl₄)

(IDEAL GAS)

GFW = 189.712

Point Group T_dS₂₉₈ = 84.8 ± 0.7 gibbs/mol

Ground State Quantum Weight = 1

ΔH₀^o = -182.0 ± 0.9 kcal/molΔH_{298.15}^o = -182.4 ± 0.9 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
388 (1)	498.5 (3)
111 (2)	131 (3)

Bond Distance: Ti-Cl = 2.185 Å

Bond Angle: Cl-Ti-Cl = 109° 28'

Product of the Moments of Inertia: I_AI_BI_C = 4.2092 × 10⁻¹¹² g cm⁶

σ = 12

Heat of Formation

The heat of formation, ΔH₂₉₈^o, of TiCl₄(g) and TiCl₄(l) has been measured by several investigators. The results of these measurements are as follows.

Investigations

Investigator	Method	Reaction	ΔH ₂₉₈ ^o , kcal/mol
Johnson et al. (1959) (1)	Calorimetric	Ti(c)+2Cl ₂ (g) = TiCl ₄ (g)	-192.2
Farber and Darnell (1955) (2)	Equilibrium	TiO ₂ (c)+HCl(g) = TiCl ₄ (g)+2H ₂ O(g)	-192.7
Skinner and Ruehrwein (1955) (3)	Calorimetric	Ti(c)+xCl ₂ (g) = [TiCl ₄ (x-2)Cl ₂] soln	-190.3±3.0
Gross et al. (1957) (4)	Calorimetric	Ti(c)+xCl ₂ (g) = [TiCl ₄ (x-2)Cl ₂] soln	-191.5±0.3
Krievie et al. (1956) (5)	Calorimetric	Ti(c)+xCl ₂ (g) = [TiCl ₄ (x-2)Cl ₂] soln	-190.0±0.4
Thomsen (1982) (6)	Calorimetric	TiCl ₄ (l)+2H ₂ O(l) = 4HCl(0.002 m)+TiO ₂ (c)	-194.5

The chosen value of ΔH₂₉₈^o is that reported by Johnson et al. (1). This investigation has the advantage of being independent of the heat of vaporization of chlorins and any heats of solution in deriving the value of the heat of formation.

Heat Capacity and Entropy

The adopted value for the interatomic distance is that reported by Kimura et al. (7). The tetrahedral structure was established by the Raman work of Bhagavantam (8). The vibrational frequencies determined from the infrared and Raman spectra of TiCl₄ by Hawkins and Carpenter (9) are adjusted downward 8 cm⁻¹ for ν₂ and ν₄ so that the heats of vaporization determined by both second and third law methods are in agreement. See TiCl₄(l) table for details. The principal moments of inertia are: I_A = I_B = I_C = 74.943 × 10⁻³⁹ g cm².

References

- W. H. Johnson, R. A. Nelson, and E. J. Prosen, J. Res. Natl. Bur. Std. 52A, 49 (1959).
- M. Farber and M. Darnell, J. Chem. Phys. 23, 1460 (1955).
- G. B. Skinner and R. A. Ruehrwein, J. Phys. Chem. 59, 113 (1955).
- P. Gross, C. Hayman, and D. L. Levi, Trans. Faraday Soc. 53, 1601 (1957).
- W. F. Krievie, S. P. Vango, and D. M. Mason, J. Chem. Phys. 25, 519 (1956).
- J. Thomsen, Thermochemische Untersuchungen, I. (Verlag, J. A. Barth, Leipzig, 1882).
- M. Kimura, K. Kimura, M. Aoki, and S. Shibata, Bull. Chem. Soc. Japan 29, 95 (1956).
- S. Bhagavantam, Indian J. Phys. 2, 79 (1932).
- N. J. Hawkins and D. R. Carpenter, J. Chem. Phys. 23, 1700 (1955).

Cl₄WTungsten Tetrachloride (WCl₄)

GFW = 325.662

(Crystal)

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H°298)/T	H°-H°298	kcal/mol ΔH ^c	ΔG ^d	Log K _p
0							
100							
200							
298	31.000	47.400	47.400	.000	-105.900	-85.929	62.987
300	31.030	47.592	47.401	.057	-105.888	-85.805	62.509
400	32.335	49.468	48.463	3.558	-103.468	-83.550	61.550
500	33.440	50.953	51.004	6.558	-100.973	-80.250	61.079
600	34.645	52.302	53.712	9.954	-102.892	-76.826	60.441
700	36.250	53.786	55.485	13.513	-101.710	-70.906	59.519
800	37.555	55.712	57.208	17.208	-100.428	-55.166	58.071
900	38.840	57.212	61.590	21.025	-99.027	-49.590	56.842
1000	39.720	58.361	64.397	24.165	-97.527	-44.117	55.055
1100	40.840	59.211	65.843	29.004	-95.946	-38.920	53.733
1200	41.570	59.797	69.192	33.126	-94.299	-33.807	52.157
1300	42.170	100.148	71.445	37.313	-92.602	-28.634	50.847
1400	42.700	101.243	73.609	41.557	-90.863	-23.994	49.746
1500	43.170	102.255	75.688	45.851	-89.109	-19.219	48.609
1600	43.600	109.055	77.697	50.190	-87.285	-14.683	47.006
1700	44.000	111.710	79.611	54.570	-85.454	-10.198	45.111
1800	44.400	114.237	81.465	58.990	-83.598	-5.659	43.708
1900	44.760	116.682	83.263	63.449	-81.717	-1.556	41.799
2000	45.100	118.952	84.981	67.942	-79.810	2.614	40.280

TUNGSTEN TETRACHLORIDE (WCl₄)

(CRYSTAL)

OPW = 325.662

ΔH_f^o = UnknownΔH_f^o_{298.15} = -105.9 ± 15 kcal/molS_{298.15}^o = [47.4] gibbs/mol

Td = [771]°K

Heat of Formation.

The heat of formation, ΔH_f^o₂₉₈(WCl₄, c) = -105.9 kcal/mol, is calculated from ΔH_f^o₂₉₈ = 58.9 kcal/mol for 3WCl₄(c) = WCl₂(c) + 2WCl₅(g). The value of ΔH_f^o₂₉₈ is calculated by the third law method from decomposition pressure data in the temperature range from 354°C to 435°C reported by S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959). The second law ΔH_f^o₂₉₈ = 73.6 ± 7.9 kcal/mol and the third law drift is -24 ± 12 eu, which would correspond to a total entropy discrepancy of -8 ± 4 eu per mole of WCl₄. This entropy discrepancy is probably within the combined uncertainty of the data and the estimated entropies for the three species. S. A. Shchukarev et al., Vestnik Leningrad. Univ. 14, No. 10, Ser. Fiz. i Khim., No. 2, 78 (1959), have shown that decomposition pressures are essentially independent of the composition in the solid phase until WCl₄(c) is almost completely decomposed to WCl₂(c). This is consistent with the assumption of solid phase activities of unity which we have used in the equilibrium analysis.

Heat Capacity and Entropy.

Cp₂₉₈ = 6.2 gibbs/g-atom and Cp₇₀₀ = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. Between 298° and 700°, which is near the decomposition temperature, the heat capacity is obtained by linear interpolation.

The entropy of WCl₄(c), S₂₉₈^o = 47.4 eu, is estimated by the method of W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, 1952.

Temperature of Decomposition.

Td is calculated as the temperature at which the Gibbs energy change of the reaction 3 WCl₄(c) = WCl₂(c) + 2 WCl₅(g) approaches zero. We have also derived an approximate value of decomposition temperature, Td = 744°K, by extrapolation to one atmosphere total pressure of a log P versus 1/T fit of the decomposition pressure data reported by S. A. Shchukarev et al., Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959). The difference between the two decomposition temperatures is related to the second law entropy and the adopted entropy.

Cl₄W

ZIRCONIUM TETRACHLORIDE (ZrCl₄)

GTV = 233.032

(CRYSTAL)

Zirconium Tetrachloride (ZrCl₄)

GFW = 233.032

 $\Delta H_f^\circ = 43.36 \pm 0.7$ gibbs/mol $\Delta H_f^\circ = -234.42 \pm 0.26$ kcal/mol $\Delta H_f^\circ = -234.17 \pm 0.26$ kcal/mol $\Delta H_m = 12 \pm 3$ kcal/mol $\Delta H_{298.15}^\circ = 26.4 \pm 0.3$ kcal/mol

Ts = 506.8°K

Heat of Formation

Gal'chenko et al. (1) determined the heat of formation of ZrCl₄(c) by the direct chlorination of the highly pure Zr metal in a bomb calorimeter. Complete chlorination of the metal was accomplished as indicated by the absence of unreacted metal and of lower chlorides. Their value, ΔH_f° (ZrCl₄, c) = -234.17 ± 0.26 kcal/mol, is adopted in the tabulation.

Gross et al. (2) measured calorimetrically $\Delta H_{298}^\circ = -225.69$ kcal/mol for Zr(c) + 2Cl₂(g) = ZrCl₄(c). Corrections for the difference in heat content between liquid and gaseous chlorine at 25°C and 1 atm led to the value of standard heat of formation, ΔH_f° (ZrCl₄, c) = -234.7 ± 0.4 kcal/mol, which is in good agreement with the value adopted. Siemonsen and Siemonsen (3) also measured the heat of formation by direct chlorination of the metal in an enameled bomb calorimeter. However, they did not report their detailed experimental procedure, neither the purity of their sample, nor the corrections. The value was given as $\Delta H_{298}^\circ = -231.9 \pm 0.5$ kcal/mol.

Heat Capacity and Entropy

Todd (4) measured the low temperature heat capacities from 52.6 to 295.7°K, and made an extrapolation to 0°K which yielded an entropy of 8.12 eu at 51°K. We have adopted the measured heat capacities, but have made our own extrapolation to 0°K, based on the ratio of the measured heat capacities of ZrF₄ (5), TiF₄ (6), and TiCl₄ (7) from 6° to 50°K. This extrapolation gives $S_{50}^\circ = 6.758 \pm 0.7$ eu which is used in the table. Coughlin and King (8) measured high temperature enthalpy data from 335.9° to 566.8°K by drop calorimetry. Their data are smoothly joined with Todd's low temperature heat capacities and adopted in the table.

Melting Data

The melting point, 710°K, has been observed by Rahlfs and Fischer (9), Palko et al. (10), Denisova et al. (11, 12).

Palko et al. derived the heat of melting as 9 ± 2.5 kcal/mol from their vapor pressure data. Denisova et al. (11, 12) determined thermographically the heat of melting as 14 ± 3 kcal/mol and also determined the heat of vaporization at 710°K as 10.4 kcal/mol which combined with the heat of sublimation at 710°K (23.6 kcal/mol) gives the heat of melting as 13.4 kcal/mol. A weighted average 12 ± 3 kcal/mol is adopted for the heat of melting.

Heat of Sublimation

Several investigators have measured the vapor pressure of ZrCl₄(c) by the static method. Second and third law analyses for the vapor pressure data are summarized below:

Source	No. of Points	Temperature Range (°K)	ΔH_{298}° (kcal/mol)	Drift (eu)
Rahlfs and Fischer (9)	11	535-607	27.516	46.57
Palko et al. (10)	86*	500-689	26.255	44.573
Denisova et al. (11)	17**	626-708	26.515	44.81
				-0.29±0.51

* 4 points rejected due to failure of a statistical test.

** 1 point rejected due to failure of a statistical test.

The third law value, $\Delta H_{298}^\circ = 26.4$ kcal/mol, is adopted in the tabulation.

The sublimation temperature is obtained from the Gibbs free energy crossover between solid and gas. Rahlfs and Fischer (9) reported the sublimation temperature as 604°K.

Since the sublimation temperature is lower than the melting point, the liquid phase is thermodynamically unstable at normal conditions.

References

1. G. L. Gal'chenko, D. A. Gedakyan and B. T. Timofeev, Russ. J. Inorg. Chem. (Eng. transl.) **13**, 159 (1968).
2. P. Gross, C. Hayman and D. L. Levi, Trans. Faraday Soc. **53**, 1265 (1957).
3. H. Siemonsen and U. Siemonsen, Z. Elektrochem. **56**, 643 (1952).
4. S. S. Todd, J. Am. Chem. Soc. **72**, 2914 (1950).
5. E. F. Westrum, Jr., J. Chem. Eng. Data **10**, 140 (1965).
6. R. D. Euler and E. F. Westrum, Jr., J. Phys. Chem. **65**, 132 (1961).
7. G. T. Furukawa, private communication, U. S. Natl. Bur. Std., 1964.
8. J. P. Coughlin and E. G. King, J. Am. Chem. Soc. **72**, 2262 (1950).
9. O. Rahlfs and W. Fischer, Zeit. Anorg. Allgem. Chem. **211**, 349 (1933).
10. A. A. Palko, A. D. Ryon and D. M. Kuhn, J. Phys. Chem. **62**, 319 (1958).
11. M. D. Denisova, E. K. Safronov and O. N. Bystrova, Russ. J. Inorg. Chem. (Eng. transl.) **11**, 1171 (1966).
12. N. D. Denisova, E. K. Safronov, A. I. Pustil'nik and O. N. Bystrova, Russ. J. Phys. Chem. (Eng. transl.) **41**, 30 (1967).

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; Dec. 31, 1969

T, °K	C _p ^o	gibbs/mol S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	∞	∞	∞	5.957	234.418	234.418	INFINITE
100	16.640	16.652	66.682	4.983	235.044	227.368	466.912
200	25.680	32.485	45.905	2.692	234.735	210.772	240.156
298	28.630	43.360	43.360	∞	234.170	212.545	155.799
300	28.640	43.537	43.361	∞	234.158	212.610	154.741
400	29.970	51.982	44.503	2.991	233.503	205.259	112.148
500	30.740	56.759	46.699	6.030	232.421	194.276	66.666
600	31.340	64.420	49.193	9.136	232.131	181.432	69.799
700	31.820	69.268	51.724	12.598	231.334	164.704	57.667
800	32.200	73.080	54.256	16.440	230.536	151.536	46.655
900	32.600	77.389	56.561	19.745	230.031	141.536	36.077
1000	33.040	80.650	58.620	22.030	229.123	165.076	

ZIRCONIUM TETRACHLORIDE (ZrCl₄) (IDEAL GAS) GF_W = 233.032

Point Group = T_d

$\Delta H_f^\circ = -207.46 \pm 0.2 \text{ kcal/mol}$

$S_{298.15}^\circ = 88.0 \pm 0.2 \text{ gibbs/mol}$

$\Delta H_f^\circ = -207.77 \pm 0.2 \text{ kcal/mol}$

Ground State Quantum Weight = 1

Zirconium Tetrachloride (ZrCl₄) (Ideal Gas) GF_W = 233.032

T, °K	C _p ^a	gibbs/mol S ^b	-(C _p ^a -H ²⁹⁸)/T	H ^c -H ²⁹⁸	ΔH ^f	Log K _p
0	∞	∞	∞	∞	∞	∞
100	16.965	45.649	107.339	-207.462	-207.462	INFINITE
200	21.485	78.974	90.076	-207.434	-205.034	448.101
300	23.466	87.980	81.960	-207.463	-202.961	220.961
400	24.430	95.031	86.915	-207.468	-201.440	146.159
500	24.904	100.538	90.708	-207.468	-200.396	105.260
600	25.176	105.105	92.738	-207.467	-199.768	84.745
700	25.345	108.999	94.247	-207.467	-199.396	71.430
800	25.456	112.391	95.687	-207.467	-199.158	61.629
900	25.534	115.395	96.687	-207.467	-199.049	54.744
1000	25.590	118.088	100.494	-207.467	-199.049	49.450
1100	25.631	120.529	102.207	-207.467	-199.049	45.161
1200	25.668	122.760	103.628	-207.467	-199.049	41.651
1300	25.683	124.816	105.364	-207.467	-199.049	38.933
1400	25.708	126.720	106.822	-207.467	-199.049	36.432
1500	25.724	128.494	108.209	-207.467	-199.049	34.266
1600	25.737	130.155	109.529	-207.467	-199.049	32.370
1700	25.748	131.716	110.789	-207.467	-199.049	30.697
1800	25.757	133.188	111.993	-207.467	-199.049	29.211
1900	25.765	134.580	113.165	-207.467	-199.049	27.881
2000	25.772	135.907	114.250	-207.467	-199.049	26.604
2100	25.777	137.160	115.211	-207.467	-199.049	25.401
2200	25.782	138.359	116.132	-207.467	-199.049	24.261
2300	25.787	139.505	117.035	-207.467	-199.049	23.177
2400	25.790	140.603	117.917	-207.467	-199.049	22.142
2500	25.794	141.656	118.777	-207.467	-199.049	21.155
2600	25.797	142.667	119.611	-207.467	-199.049	20.213
2700	25.799	143.641	120.417	-207.467	-199.049	19.313
2800	25.802	144.579	121.195	-207.467	-199.049	18.452
2900	25.804	145.485	121.946	-207.467	-199.049	17.628
3000	25.806	146.359	122.671	-207.467	-199.049	16.840
3100	25.807	147.204	123.371	-207.467	-199.049	16.087
3200	25.809	148.025	124.048	-207.467	-199.049	15.369
3300	25.810	148.819	124.695	-207.467	-199.049	14.685
3400	25.812	149.590	125.317	-207.467	-199.049	14.035
3500	25.813	150.338	125.917	-207.467	-199.049	13.417
3600	25.814	151.065	126.495	-207.467	-199.049	12.831
3700	25.815	151.773	127.050	-207.467	-199.049	12.276
3800	25.816	152.461	127.583	-207.467	-199.049	11.751
3900	25.817	153.132	128.095	-207.467	-199.049	11.254
4000	25.818	153.785	128.587	-207.467	-199.049	10.784
4100	25.818	154.423	129.059	-207.467	-199.049	10.338
4200	25.819	155.045	129.503	-207.467	-199.049	9.916
4300	25.820	155.652	129.928	-207.467	-199.049	9.516
4400	25.821	156.246	130.337	-207.467	-199.049	9.137
4500	25.821	156.826	130.731	-207.467	-199.049	8.778
4600	25.821	157.394	131.110	-207.467	-199.049	8.438
4700	25.822	157.949	131.475	-207.467	-199.049	8.116
4800	25.822	158.493	131.827	-207.467	-199.049	7.811
4900	25.823	159.025	132.167	-207.467	-199.049	7.522
5000	25.823	159.547	132.495	-207.467	-199.049	7.247
5100	25.824	160.058	132.812	-207.467	-199.049	6.994
5200	25.824	160.560	133.117	-207.467	-199.049	6.752
5300	25.824	161.052	133.411	-207.467	-199.049	6.521
5400	25.825	161.534	133.694	-207.467	-199.049	6.300
5500	25.825	162.008	133.967	-207.467	-199.049	6.088
5600	25.825	162.474	134.230	-207.467	-199.049	5.885
5700	25.826	162.931	134.483	-207.467	-199.049	5.688
5800	25.826	163.380	134.727	-207.467	-199.049	5.496
5900	25.826	163.821	134.962	-207.467	-199.049	5.308
6000	25.826	164.255	135.188	-207.467	-199.049	5.124

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω_1 , cm ⁻¹	ω_2 , cm ⁻¹	ω_3 , cm ⁻¹
376 (1)	418 (3)	110 (3)
99 (2)		

Bond Distance: Zr-Cl = 2.32 ± 0.02 Å

Bond Angle: Cl-Zr-Cl = 109°28'

Product of the Moments of Inertia: I_AI_BI_C = 6.03177 × 10⁻¹¹² g³ cm⁶

σ = 12

Heat of Formation

The heat of formation of gaseous ZrCl₄, ΔH_f²⁹⁸ = -207.77 ± 0.2 kcal/mol, is calculated from the heat of formation of the crystal and the formation of gaseous ZrCl₄ from vapor pressure data. (See JANAF ZrCl₄(c) table dated Dec. 31, 1969).

Hildenbrand et al. (1) determined the equilibrium constants by the transpiration method for the reaction:



Second and third law analyses for their data are given below:

Series	No. of Points	Temp. Range (°K)	ΔH _f ²⁹⁸ (kcal/mol)	2nd law	3rd law	Drift (eu)	ΔH _f ²⁹⁸ (g)* (kcal/mol)
I	10	1171-1375	28.853	29.321			-205.8
II	9	1169-1374	31.397	30.007		-1.08±0.47	-205.0

*Derived from third law ΔH_f²⁹⁸ and ΔH_f²⁹⁸(ZrO₂, c) = -262.3 kcal/mol, ΔH_f²⁹⁸(HCl, g) = -22.063 kcal/mol and ΔH_f²⁹⁸(H₂O, g) = -57.798 kcal/mol.

The derived heat of formation is in fair agreement with the value adopted.

Heat Capacity and Entropy

Spiridonov et al. (2) measured the bond distance Zr-Cl = 2.32 ± 0.02 Å in the vapor phase by electron diffraction. The molecule was also found to be a regular tetrahedron. The same bond distance was also reported by Lister and Sutton (3) and Kimura et al. (4). The three principal moments of inertia are I_A = I_B = I_C = 84.4942 × 10⁻³⁸ g cm².

Wilmshurst (5) observed one fundamental vibrational frequency (ν₃ = 421 cm⁻¹) in the infrared spectrum of ZrCl₄ vapor, and made reasonable estimates (ν₁ = 368, ν₂ = 102 and ν₄ = 112 cm⁻¹) for the three remaining unobserved fundamentals, based on observed overtone and combination bands. Godnev et al. (6) calculated the four fundamental vibrational frequencies (382, 108, 423 and 114 cm⁻¹) from data for related group IV halides through the use of a 5-parameter potential function. Büchler et al. (7) also found in the infrared spectrum the vibrational frequency, ν₃ = 423 cm⁻¹. Delvaule and Francois (8) observed the symmetric stretching vibration ν₁ at 383 cm⁻¹ from the Raman spectrum of ZrCl₄ in PCl₃ and POC₂, both of which form complexes with ZrCl₄. Bobovich (9) reported the symmetric stretching vibration ν₁ at 315 cm⁻¹ from a partially polarized band in his Raman spectrometric studies.

Pontrelli (10) observed in the Raman spectrum all four fundamental vibrational frequencies (376, 99, 418 and 110 cm⁻¹) which are adopted in the tabulation.

References

1. D. L. Hildenbrand, L. P. Theard, W. F. Hall, F. Ju, F. S. La Viola and M. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport, Calif., Pub. No. U-1734, N0661-0905-C, June, 1962.
2. V. P. Spiridonov, P. A. Akishin and V. I. Tsirel'nikov, Zh. Strukt. Khim. **3**, 329 (1962).
3. M. W. Lister and L. E. Sutton, Trans. Faraday Soc. **37**, 393 (1941).
4. M. Kimura, R. Kimura, M. Aoki and S. Shibata, Bull. Chem. Soc. Japan **29**, 95 (1956).
5. J. K. Wilmshurst, J. Mol. Spectrosc. **5**, 343 (1960).
6. I. N. Godnev, A. M. Aleksandrovskaya, I. V. Rignina, Optics and Spectroscopy (Eng. transl.) **2**, 172 (1959).
7. A. Büchler, J. B. Berkowitz-Hattuck and D. H. Dugre, J. Chem. Phys. **34**, 2202 (1961).
8. M. L. Devalle and F. Francois, Bull. Soc. Chim. **13**, 205 (1946); J. Phys. Radium **7**, 15 (1946).
9. Ya. S. Bobovich, Optics and Spectroscopy (Eng. transl.) **11**, 85 (1961).
10. G. M. Pontrelli, Dissertation Abstract **23**, 4130 (1963).

Cl₅Mo

GFW = 273.205

(CRYSTAL)

MOLYBDENUM PENTACHLORIDE (MoCl₅)

Molybdenum Pentachloride (MoCl₅)
(Crystal) GFW = 273.205

$\Delta H_f^\circ = \text{unknown}$

$\Delta H_{298.15}^\circ = -126 \pm 2 \text{ kcal/mol}$

$\Delta H_m^\circ = [4.5 \pm 1.5] \text{ kcal/mol}$

$S_{298.15}^\circ = [57 \pm 3] \text{ gibbs/mol}$

$T_m = 467^\circ\text{K}$

Heat of Formation

The heat of formation is obtained from S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zh. Neorg. Khim. 5, 1650 (1960). The authors derived the ΔH_f° (MoCl₅, c) = -126 kcal/mol by measuring the heat of solution of MoCl₅ in NaOH(aq), which was compared with the heats of solution of MoO₃ and NaCl measured in the same solvent.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with that of MoCl₃ (c). S_{298}° is estimated as 57 eu from the vapor pressure data for MoCl₅ (c) + MoCl₅ (g) measured by S. A. Shchukarev, I. V. Vasil'kova and B. N. Sharupin, J. Gen. Chem. USSR (English Transl.) 26, 2335 (1956).

Melting Data

See liquid table.

T, °K	Cp°	$-\int_0^T \frac{C_p^\circ}{T} dT$	$H^\circ - H_{298}^\circ$	ΔH_f°	Log Kp
0					
100					
200					
298	37,220	57,000	57,000	0.000	74,208
300	37,220	57,230	57,001	0.069	73,639
400	40,000	68,320	58,494	3,931	50,791
500	42,700	77,536	61,405	6,068	37,223
600	45,400	85,569	64,777	12,476	28,287
700	46,500	91,723	70,256	17,956	21,348
800	47,500	96,723	75,256	23,436	16,368
900	50,100	105,016	83,549	31,729	13,795
1000	50,900	110,337	88,374	36,554	11,005
1100	51,500	115,221	92,800	40,980	8,769
1200	52,050	119,725	96,325	45,005	6,820
1300	52,500	123,900	99,500	48,730	5,147
1400	52,650	127,809	102,419	52,119	3,768
1500	52,600	131,447	105,057	55,025	2,606

Cl₅Mo

MOLYBDENUM PENTACHLORIDE (MoCl₅) (LIQUID) GFW = 273.205

$$S_{298.15}^{\circ} = [65.441] \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} = [-121.9705] \text{ kcal/mol}$$

$$T_m = 487^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = [4.5 \pm 1.5] \text{ kcal/mol}$$

$$T_b = 537^{\circ}\text{K}$$

$$\Delta H_v^{\circ} = [12.0] \text{ kcal/mol}$$

Heat of Formation

The heat of formation is obtained from $\Delta H_f^{\circ}(c)$ by adding ΔH_m° and the difference between $H_m^{\circ} - H_{298}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed constant and estimated as 42 gibbs/mol or 7 gibbs/g-atm. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

T_m is taken from S. A. Shechukarev, G. I. Novikov, A. V. Suvorov and V. K. Mokeimov, Russ. J. Inorg. Chem. (English Transl.) 4, 935 (1959). ΔH_m° is estimated by comparison with that of WCl₅(c).

Vaporization Data

T_b is the temperature at which the difference between the Gibbs energy of formation for MoCl₅(l) and MoCl₅(g) approaches zero. The difference between $\Delta H_f^{\circ}(\text{MoCl}_5, l)$ and $\Delta H_f^{\circ}(\text{MoCl}_5, g)$ is ΔH_v° .

Molybdenum Pentachloride (MoCl₅)

(Liquid) GFW = 273.205

T, °K	C _p ^o	S ^o - (C ^o - H ²⁹⁸)/T	gibbs/mol	H ^o - H ²⁹⁸	kcal/mol	ΔH ^o	ΔG ^o	Log K _p
0								
100								
200								
298	42.000	65.441	65.441	.000	121.921	99.673	99.673	73.062
300	42.000	65.701	65.442	.076	121.681	99.535	99.535	72.511
400	42.000	77.763	67.069	4.276	120.356	92.431	92.431	59.440
500	42.000	87.158	76.200	8.476	116.905	83.481	83.481	47.222
600	42.000	94.613	73.663	12.676	117.506	76.922	76.922	26.747
700	42.000	101.267	77.176	16.676	116.146	72.600	72.600	22.667
800	42.000	106.896	80.349	21.076	114.613	66.473	66.473	16.159
900	42.000	111.643	83.756	25.276	113.486	60.507	60.507	14.693
1000	42.000	116.266	86.790	29.476	112.197	54.691	54.691	11.953
1100	42.000	120.271	89.455	33.676	110.914	49.002	49.002	9.736
1200	42.000	123.925	92.160	37.676	109.650	43.431	43.431	7.910
1300	42.000	127.267	94.919	42.076	106.406	37.963	37.963	6.382
1400	42.000	130.400	97.344	46.276	107.164	32.500	32.500	5.066
1500	42.000	133.297	99.645	50.476	105.966	27.304	27.304	3.976

MOLYBDENUM PENTACHLORIDE (MoCl_5)

(IDEAL GAS)

 $GFW = 273.205$ Point Group D_{3h}
$$\Delta M f_0^\circ = -106.6 \pm 1 \text{ kcal/mol}$$
$$\Delta H_{298.15}^{\circ} = -107.0 \pm 1 \text{ kcal/mol}$$
$$\Delta G_{298.15}^\circ = [95 \pm 3] \text{ gibbs/mol}$$

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[490] (1)	[350] (2)
[400] (1)	[170] (2)
[410] (1)	[100] (2)
[150] (1)	[190] (2)

Electronic Levels and Quantum Weights

6.2 CM

[7000] (2)

Meat of Formation

The adopted $\Delta H_{f298}^\circ = -107.0$ kcal/mol is obtained from the vapor pressure data for $\text{HocCl}_5(\text{c}) = \text{HocCl}_5(\text{g})$ measured by Shchukarev et al. (1) and Saeki and Matsuzaki (2).

Source	Method	Reaction	Temperature range, °K	$\Delta H_{298.15}^{\circ}$ Second law	$\Delta H_{298.15}^{\circ}$ Third law	Drift e.u.	ΔH_{298}° Kcal/mol
Shchukarev	Transpiration	$\text{MoCl}_5(\text{c}) = \text{MoCl}_5(\text{g})$	343 - 435	19.04 ± 0.45	19.18	0.3	-106.82
Saeki	Manometric	$\text{MoCl}_5(\text{c}) = \text{MoCl}_5(\text{g})$	298 - 474	16.79 ± 0.06	18.94	5.6	-107.06

* Calculation based on third law ΔH_{298}° .

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those of NbCl_5 obtained from infrared and Raman spectra by Carlson (4). Structure, bond distance and bond angle are taken from Evans et al. (4). The three principal moments of inertia are $I_A = I_B = 106.1682 \times 10^{-39}$ and $I_C = 91.0074 \times 10^{-39} \text{ g cm}^2$. The electronic levels are estimated to be 0, 7000 and 14000 cm^{-1} , all doublets, by comparison with those of WCl_6 (5).

1. S. A. Shekhurev, I. V. Vasil'kova and B. N. Sharupin, J. Gen. Chem. USSR (English Transl.), **26**, 2335-9 (1956).
2. Y. Saeki and R. Matsuzaki, Denki Kagaku **23**, 155-8 (1965).
3. G. L. Carlson, Spectrochim. Acta **19**, 1291 (1963).
4. R. V. G. Ewens and W. H. Lister, Trans. Faraday Soc. **34**, 1358-62 (1938).

Molybdenum Pentachloride (MoCl_5)
(Ideal Gas) GFW = 273.205

$$GFW = 273.205$$

T, °K	C _p ²	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	H ² -H ²⁹⁸	kcal/mol ΔH°	ΔG°	Log K _p
100	16.497	68.762	INFINITE	4.6167	104.584	104.584	INFINITE
200	25.708	84.166	97.581	2.683	107.223	102.664	221.338
288	28.556	95.043	95.043		107.215	98.039	101.132
300	28.580	95.220	95.043		107.000	93.578	68.595
350	30.592	110.384	98.372	2.083	104.976	93.495	68.111
400	32.612	125.546	103.654	2.893	102.733	91.252	65.867
500	36.695	155.985	100.854	9.079	106.187	86.462	34.997
600	41.126	182.766	103.365	12.181	105.193	86.304	29.251
700	45.750	206.433	105.600	15.301	104.269	86.146	24.732
800	50.520	227.933	107.600	18.421	103.400	86.000	20.400
900	55.400	247.333	109.357	21.541	102.571	85.863	16.163
1000	60.350	264.755	110.927	24.661	101.782	85.735	12.015
1100	65.360	280.200	112.457	27.781	101.035	85.616	8.868
1200	70.410	293.766	113.947	30.901	100.326	85.500	6.711
1300	75.500	306.450	115.393	34.021	99.657	85.387	5.554
1400	80.630	318.266	116.800	37.141	99.030	85.278	4.397
1500	85.800	329.200	118.167	40.261	98.437	85.173	3.240
1600	91.010	339.266	119.500	43.381	97.870	85.072	2.083
1700	96.260	348.466	120.800	46.501	97.327	84.975	0.926
1800	101.550	356.800	122.066	49.621	96.806	84.882	-0.231
1900	106.880	364.266	123.293	52.741	96.306	84.793	-1.388
2000	112.250	370.866	124.483	55.861	95.823	84.708	-2.545
2100	117.660	376.600	125.633	58.981	95.356	84.627	-3.702
2200	123.110	381.466	126.743	62.101	94.903	84.550	-4.859
2300	128.600	386.466	127.813	65.221	94.463	84.477	-6.016
2400	134.130	391.600	128.843	68.341	94.036	84.407	-7.173
2500	139.700	396.866	129.833	71.461	93.623	84.340	-8.330
2600	145.310	402.266	130.783	74.581	93.223	84.276	-9.487
2700	150.960	407.800	131.703	77.701	92.836	84.215	-10.644
2800	156.650	413.466	132.583	80.821	92.463	84.157	-11.801
2900	162.380	419.266	133.423	83.941	92.103	84.102	-12.958
3000	168.150	425.200	134.223	87.061	91.756	84.050	-14.115
3100	173.960	431.266	135.000	90.181	91.423	84.000	-15.272
3200	179.810	437.466	135.743	93.301	91.103	83.952	-16.429
3300	185.700	443.800	136.453	96.421	90.796	83.907	-17.586
3400	191.630	450.266	137.123	99.541	90.503	83.865	-18.743
3500	197.600	456.866	137.753	102.661	90.223	83.826	-19.900
3600	203.610	463.600	138.343	105.781	90.956	83.790	-21.057
3700	209.660	470.466	138.893	108.901	90.703	83.757	-22.214
3800	215.750	477.466	139.403	112.021	90.463	83.726	-23.371
3900	221.880	484.600	139.873	115.141	90.233	83.697	-24.528
4000	228.050	491.866	140.303	118.261	90.016	83.672	-25.685
4100	234.260	499.266	140.693	121.381	89.800	83.647	-26.842
4200	239.950	506.866	141.059	124.501	89.587	83.622	-27.999
4300	245.700	514.500	141.333	127.621	89.373	83.597	-29.156
4400	251.500	522.166	141.600	130.741	89.159	83.572	-30.313
4500	257.350	530.000	141.867	133.861	88.946	83.547	-31.470
4600	263.250	538.000	142.133	136.981	88.732	83.522	-32.627
4700	269.200	546.166	142.400	140.101	88.518	83.497	-33.784
4800	275.200	554.500	142.667	143.221	88.304	83.472	-34.941
4900	281.250	563.000	142.933	146.341	88.090	83.447	-36.098
5000	287.350	571.666	143.200	149.461	87.876	83.422	-37.255
5100	293.500	580.500	143.467	152.581	87.662	83.397	-38.412
5200	299.700	589.500	143.733	155.701	87.448	83.372	-39.569
5300	305.950	598.666	144.000	158.821	87.234	83.347	-40.726
5400	312.250	608.000	144.267	161.941	87.020	83.322	-41.883
5500	318.600	617.500	144.533	165.061	86.806	83.297	-43.040
5600	325.000	627.166	144.800	168.181	86.592	83.272	-44.197
5700	331.450	637.000	145.067	171.301	86.378	83.247	-45.354
5800	337.950	647.000	145.333	174.421	86.164	83.222	-46.511
5900	344.500	657.166	145.600	177.541	85.950	83.197	-47.668
6000	351.100	667.500	145.867	180.661	85.736	83.172	-48.825

Dec. 31, 1968

T, °K.	C _p	S° - (F° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f ⁰	Log K _p
0	0.000	INFINITE	- 5.462	- 81.027	INFINITE
100	15.058	4.014	- 4.391	- 81.800	167.739
200	22.874	77.094	- 2.458	- 81.988	78.242
298	26.743	87.043	- 1.000	- 81.913	48.758
300	26.792	87.209	- 0.950	- 81.909	48.387
400	28.698	95.208	88.121	- 81.732	33.484
500	29.717	101.732	90.211	- 81.510	24.564
600	30.313	107.207	92.600	- 81.280	18.634
700	30.639	111.846	94.603	- 81.042	14.166
800	30.839	115.025	96.403	- 80.792	10.272
900	31.114	116.680	99.679	- 80.630	9.634
1000	31.240	122.965	101.846	- 80.386	9.192
1100	31.335	125.947	105.904	- 80.941	5.202
1200	31.405	128.458	109.458	- 80.685	2.160
1300	31.462	130.193	112.710	- 80.402	0.943
1400	31.509	131.527	115.715	- 80.092	0.520
1500	31.546	132.972	118.477	- 79.638	0.073
1600	31.576	137.739	112.747	- 79.987	6.902
1700	31.622	139.461	117.134	- 79.410	6.411
1800	31.640	140.671	117.715	- 78.842	5.943
1900	31.655	142.764	118.477	- 78.292	5.501
2000	31.658	146.339	119.767	- 77.727	5.089
2100	31.668	149.221	122.205	- 77.150	4.700
2200	31.689	150.570	125.359	- 76.563	4.324
2300	31.706	151.864	128.473	- 75.968	3.957
2400	31.712	153.107	125.551	- 75.362	3.592
2500	31.724	154.458	127.404	- 74.747	3.237
2600	31.729	155.771	129.584	- 74.116	2.892
2700	31.733	157.647	128.435	- 73.476	2.557
2800	31.737	158.688	130.459	- 72.826	2.237
2900	31.744	159.672	131.230	- 72.166	1.937
3000	31.747	161.620	133.081	- 71.496	1.657
3500	31.750	162.540	133.910	- 70.819	1.377
3600	31.752	163.435	134.717	- 70.142	1.107
3700	31.757	164.351	135.574	- 69.465	0.847
3800	31.759	165.076	137.025	- 68.788	0.587
3900	31.761	166.780	137.759	- 68.111	0.327
4000	31.762	167.565	138.477	- 67.434	0.067
4100	31.766	168.078	139.865	- 66.757	0.002
4200	31.767	169.808	140.537	- 66.080	0.000
4300	31.768	170.422	141.196	- 65.403	0.000
4400	31.769	171.220	141.941	- 64.726	0.000
4500	31.772	172.272	142.703	- 64.049	0.000
4600	31.773	173.227	143.702	- 63.372	0.000
4700	31.774	173.869	144.299	- 62.695	0.000
4800	31.774	174.498	144.885	- 62.018	0.000
4900	31.776	175.115	145.460	- 61.341	0.000
5000	31.777	175.315	146.563	- 60.664	0.000
5100	31.778	176.898	147.127	- 59.987	0.000
5200	31.778	177.470	147.664	- 59.310	0.000
5300	31.779	178.581	148.191	- 58.633	0.000
5400	31.779	179.129	149.222	- 57.956	0.000
5500	31.780	179.129	149.222	- 57.279	0.000
5600	31.781	179.663	149.725	- 56.602	0.000
5700	31.781	179.663	149.725	- 55.925	0.000
5800	31.781	179.663	149.725	- 55.248	0.000
5900	31.781	179.663	149.725	- 54.571	0.000
6000	31.781	179.663	149.725	- 53.894	0.000

Dec. 31, 1960/ Sept. 30, 1962

PHOSPHORUS PENTACHLORIDE (PCl₅) (IDEAL GAS)

ΔH_f⁰ = -81.0 ± 1.0 kcal. mole⁻¹
Point group D_{3h}
ΔH_f⁰ 298.15 = -81.9 ± 1.0 kcal. mole⁻¹
S_{298.15}⁰ = 87.0 cal. deg.⁻¹ mole⁻¹

MOL. WT. = 208.260

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
394 (1)	394 (1)	465 (1)
176 (1)	592 (2)	335 (2)
100 (2)	280 (2)	

Bond angles: Cl₂(equatorial)-P-Cl(equatorial) = 120° Cl(axial)-P-Cl(equatorial) = 180° Cl(equatorial)-P-Cl(equatorial) = 90°

Bond distance: P-Cl(equatorial) = 2.04 Å P-Cl(axial) = 2.19 Å

Product of moment of inertia: I_AI_BI_C = 6.3873 X 10⁻¹¹² g.³ cm.⁶

σ = 6

Heat of Formation.

ΔH_f⁰ 298.15 was calculated from the ΔH_f⁰ 298.15 for the reaction: PCl₃(g) + Cl₂(g) → PCl₅(g). Third law calculations using experimental equilibrium constants, and free energy functions from JANAF Tables gave a ΔH_f⁰ 298.15 = -20.884 kcal. mole⁻¹. This ΔH_f⁰ is the average of (1) ΔH_f⁰ 298.15 = -20.768 ± 0.26 kcal. mole⁻¹ and (2) ΔH_f⁰ 298.15 = -21.001 ± 0.24 kcal. mole⁻¹. The first, ΔH_f⁰(1), was obtained from eleven experimental equilibrium constants measured by C. Holland, Z. Elektrochem. 18, 234 (1912) as corrected by W. Nernst, Z. Elektrochem. 22, 37 (1916). The second, ΔH_f⁰(2), was obtained from thirteen experimental equilibrium constants measured by W. Fischer and O. Jüßmann, Z. anorg. u. allgem. Chem. 235, 337 (1935).

For the same reaction, PCl₃(g) + Cl₂(g) = PCl₅(g), a third law calculation by D. P. Stevenson and D. M. Yost, J. Chem. Phys. 9, 403 (1941) gave a ΔH_f⁰ = -21.320 ± 0.107 kcal. mole⁻¹. With a new assignment of fundamental frequencies J. K. Wilhamurst and H. J. Bernstein, J. Chem. Phys. 27, 661 (1957) reported a ΔS₀⁰ = -20.525 ± 0.16 kcal. mole⁻¹.

The ΔH_f⁰ 298.15 values corresponding to these heats of reaction are:

Source
ΔH _f ⁰ 298.15
-82.9 kcal. mole ⁻¹
-82.1 kcal. mole ⁻¹
-81.9 kcal. mole ⁻¹
D. P. Stevenson and D. M. Yost (loc. cit.).
J. K. Wilhamurst and H. J. Bernstein (loc. cit.).
Calculated using free energy functions from JANAF Tables.

Heat Capacity and Entropy.

The fundamental vibrational frequencies were assigned by Wilhamurst and Bernstein (loc. cit.) from their infrared and Raman spectral data, except the frequency, 176 cm.⁻¹, which they calculated. Electron diffraction data of M. Rouault, Ann. Phys. 14, 78 (1940) and Sargent and Schomaker, (quoted in) J. Chem. Phys. 9, 403 (1941), show the free PCl₅ molecule to be a trigonal bipyramid of D_{3h} symmetry. The bond lengths were calculated from force constants and Badger's rule by Wilhamurst and Bernstein (loc. cit.). Their values are in good agreement with the electron diffraction bond lengths of M. Rouault, (loc. cit.). The calculated moments of inertia are I_A = I_B = 93.2177 X 10⁻³⁹ g. cm.² and I_C = 73.5053 X 10⁻³⁹ g. cm.².

TUNGSTEN PENTACHLORIDE (WCl₅)

(CRYSTAL)

GFW = 361.115

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	—kcal/mol— ΔH°	ΔG°	Log Kp
0						
100						
200						
298	37.200	52.000	52.000	122.600	96.056	70.411
300	37.255	52.030	52.001	122.500	95.892	69.957
400	40.015	61.320	54.995	122.300	87.172	47.629
500	42.781	72.553	56.408	119.973	78.777	34.434
600	45.400	80.591	59.792	119.344	70.687	25.748
700	47.450	87.751	63.276	116.513	62.987	19.634
800	49.000	94.134	66.735	114.534	55.363	15.174
900	50.400	99.835	70.185	112.424	47.924	11.244
1000	50.900	105.355	73.485	110.279	41.055	8.973
1100	51.580	110.239	76.516	108.061	34.240	6.803
1200	52.080	114.750	79.517	105.802	27.683	5.032
1300	52.420	118.423	82.340	103.517	21.207	3.595
1400	52.420	121.423	84.916	101.220	14.816	2.394
1500	52.800	126.468	87.776	98.920	8.879	1.294

 $\Delta H_f^\circ = \text{Unknown}$ $\Delta H_f^\circ_{298.15} = -122.6 \pm 10 \text{ kcal/mol}$ $\Delta H_m^\circ = 4.917 \pm 1 \text{ kcal/mol}$ $\Delta H_s^\circ_{298.15} = 24.0 \text{ kcal/mol}$ $S^\circ_{298.15} = [52.0] \text{ gibbs/mol}$ $T_m = 526^\circ\text{K}$ Heat of Formation.

The heat of formation, ΔH_f° (WCl₅, c) = -122.6 kcal/mol, is calculated from that of the gas less the heat of sublimation, $\Delta H_s^\circ = 24.0 \text{ kcal/mol}$. The latter is calculated by the third law method from partial pressures of WCl₅(g) derived from the total pressure data* of S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4 Ser. Fiz. i Khim., No. 1, 120 (1959). Dimer pressures, calculated from the same authors' dimer-monomer dissociation data, are subtracted from the total pressures in order to obtain the monomer pressures. Analyses of the monomer pressures over both crystal and liquid give similar results and the average values for ΔH_s° are 20.6 (second law) and 24.0 kcal/mol (third law) with a drift of about 7 eu.

*Earlier data reported by Shchukarev et al., Zhur. Neorg. Khim. 1, 357 (1956); 2, 2630 (1958), have been revised and are not used here.

Heat Capacity and Entropy.

$CP_{298} = 6.2 \text{ gibbs/g-atom}$ and $CP_{526} = 7.25 \text{ gibbs/g-atom}$ are estimated using the method described by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. Between 298° and 526°, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, $S^\circ_{298} = 52 \text{ eu}$, is estimated by comparison with those of WCl₂ (c), WCl₄ (c) and WCl₆ (c).

Melting Data.

The melting point was determined from vapor pressure data by Shchukarev et al., loc. cit. The heat of melting is the difference at the melting point between the second law heats of vaporization and sublimation derived from total vapor pressure data of Shchukarev et al., loc. cit.

Heat of Sublimation.

See the heat of formation of WCl₅(g) for details.

Tungsten Pentachloride (WCl₅)
(Liquid)
GFW = 361.115

T, °K	C _p ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{H^\circ - H^\circ_{298}}$	ΔG°	Log K _p
0						
100						
200						
298	43.500	59.393	59.393	+0.000	-118.400	-94.060
300	43.500	59.326	59.326	+0.890	-118.368	-93.910
400	43.500	72.077	72.077	+4.760	-118.482	-88.813
500	43.500	81.583	81.583	+8.780	-115.066	-78.535
600	43.500	89.814	89.814	+13.130	-113.499	-71.376
700	43.500	96.520	96.520	+17.480	-111.265	-64.477
800	43.500	102.359	102.359	+21.480	-108.483	-57.709
900	43.500	107.459	107.459	+25.180	-105.265	-51.028
1000	43.500	112.035	112.035	+30.530	-107.519	-44.975
1100	43.500	116.181	116.181	+34.880	-106.076	-38.791
1200	43.500	119.966	119.966	+39.230	-104.651	-32.736
1300	43.500	123.427	123.427	+43.580	-103.242	-26.801
1400	43.500	126.608	126.608	+47.840	-101.848	-21.004
1500	43.500	129.673	129.673	+52.280	-100.472	-15.245

Dec. 31, 1962; Dec. 31, 1966

TUNGSTEN PENTACHLORIDE (WCl₅)

$S^\circ_{298.15} = [59.393] \text{ gibbs/mol}$
 $T_m = 526^\circ\text{K}$
 $T_b = 561.4^\circ\text{K}$

Heat of Formation.

The heat of formation, $\Delta H^\circ_{298}(\text{WCl}_5, l) = -118.4 \text{ kcal/mol}$, is calculated from that of $\text{WCl}_5(c)$ by adding the heat of melting and the difference between $H^\circ_{526} - H^\circ_{298}$ for the crystal and liquid.

Heat Capacity and Entropy.

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom.

The entropy of $\text{WCl}_5(l)$, $S^\circ_{298.15} = 59.393 \text{ eu}$, is calculated in a manner analogous to that of the heat of formation.

Melting Data.

See $\text{WCl}_5(c)$ table for details.

Vaporization Data.

The boiling point, 561.4°K , is calculated as the temperature at which the Gibbs energy of formation for both $\text{WCl}_5(l)$ and $\text{WCl}_5(g)$ are equal. The difference in the heats of formation of $\text{WCl}_5(l)$ and $\text{WCl}_5(g)$ at the boiling point is the heat of vaporization. S. A. Shchukarev, G. I. Novikov and N. V. Andreeva¹ revised their previous data² and derived the boiling point as 561.2°K from their vapor pressure measurements.

References:

1. S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959).
2. S. A. Shchukarev and G. I. Novikov, Zhur. Neorg. Khim. 1, 357 (1956).

Cl₅W

OPW = 361.115

(LIQUID)

$\Delta H^\circ_{298.15} = -118.4 \text{ kcal/mol}$
 $\Delta H_m^\circ = 4.917 \pm 1 \text{ kcal/mol}$
 $\Delta H_v^\circ = 16.266 \text{ kcal/mol}$

Cl₅W

Tungsten Pentachloride (WCl₅)
(Ideal Gas) GFW = 361.115

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	enthalpy/mol H° - H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	- 5.073	98.199	98.199	INFINITE
100	26.024	95.961	2.707	98.437	98.163	206.187
200	26.024	95.961	2.707	98.437	98.163	98.156
298	26.736	96.935	0.000	98.600	85.454	62.639
300	26.769	97.113	0.053	98.595	85.372	62.194
400	28.919	105.516	2.105	98.115	80.450	42.600
500	30.596	112.339	6.030	98.016	74.713	33.531
600	30.947	117.951	9.104	97.721	72.480	26.401
700	31.166	122.740	12.215	97.431	68.297	21.323
800	31.311	126.911	15.339	97.154	64.156	17.527
900	31.433	130.595	18.466	96.885	60.045	14.591
1000	31.540	133.919	21.621	96.629	55.968	12.632
1100	31.553	136.924	24.773	96.383	51.915	10.315
1200	31.608	139.671	27.931	96.150	47.882	8.720
1300	31.660	142.204	31.095	95.927	43.869	7.375
1400	31.708	144.566	34.266	95.714	39.873	6.229
1500	31.761	146.781	37.437	95.515	35.890	5.229
1600	31.817	148.793	40.616	95.325	31.922	4.360
1700	31.873	150.723	43.800	95.144	27.960	3.595
1800	31.930	152.577	46.991	94.973	24.017	2.916
1900	31.987	154.356	49.188	94.811	20.076	2.308
2000	32.047	156.071	51.384	94.661	16.146	1.764
2100	32.107	157.722	53.576	94.518	12.226	1.272
2200	32.166	159.317	55.761	94.384	8.313	0.826
2300	32.224	160.856	57.929	94.266	4.400	0.418
2400	32.281	162.341	59.485	94.162	0.485	0.045
2500	32.337	163.780	61.030	94.069	- 3.404	- 0.298
2600	32.392	165.179	62.562	93.971	- 7.303	- 0.614
2700	32.444	166.533	64.084	93.870	- 11.194	- 0.906
2800	32.493	167.843	65.593	93.761	- 15.092	- 1.178
2900	32.540	169.109	67.084	93.642	- 18.987	- 1.430
3000	32.584	169.019	68.571	93.597	- 22.866	- 1.666
3100	32.632	170.088	69.980	93.592	- 26.759	- 1.887
3200	32.673	171.125	71.324	93.580	- 30.655	- 2.094
3300	32.712	172.129	72.604	93.561	- 34.549	- 2.289
3400	32.748	173.104	73.824	93.536	- 38.442	- 2.473
3500	32.782	174.057	75.000	93.507	- 42.335	- 2.647
3600	32.814	174.981	76.139	93.474	- 46.226	- 2.813
3700	32.843	175.881	77.244	93.437	- 50.117	- 2.973
3800	32.869	176.754	78.314	93.396	- 54.007	- 3.125
3900	32.891	177.601	79.350	93.351	- 57.896	- 3.270
4000	32.917	178.444	80.351	93.302	- 61.784	- 3.416
4100	32.934	179.257	81.314	93.249	- 65.664	- 3.557
4200	32.956	180.051	82.244	93.193	- 69.544	- 3.707
4300	32.973	180.824	83.144	93.134	- 73.423	- 3.853
4400	32.987	181.577	84.014	93.071	- 77.302	- 3.994
4500	33.000	182.327	84.854	93.006	- 81.181	- 4.130
4600	33.012	183.052	85.664	92.938	- 85.060	- 4.261
4700	33.021	183.762	86.444	92.867	- 88.939	- 4.388
4800	33.028	184.454	87.194	92.792	- 92.818	- 4.511
4900	33.036	185.139	87.914	92.714	- 96.697	- 4.630
5000	33.041	185.806	88.604	92.625	- 100.576	- 4.745
5100	33.045	186.460	89.264	92.526	- 104.455	- 4.856
5200	33.048	187.104	89.894	92.418	- 108.334	- 4.962
5300	33.050	187.734	90.504	92.300	- 112.213	- 5.064
5400	33.051	188.354	91.094	92.174	- 116.092	- 5.162
5500	33.049	188.956	91.664	92.049	- 120.000	- 5.254
5600	33.044	189.551	92.214	91.914	- 123.918	- 5.341
5700	33.045	190.136	92.744	91.774	- 127.836	- 5.424
5800	33.043	190.704	93.254	91.624	- 131.754	- 5.501
5900	33.038	191.274	93.744	91.464	- 135.672	- 5.574
6000	33.034	191.831	94.214	91.294	- 139.590	- 5.641

Dec. 31, 1962 Dec. 31, 1966

TUNGSTEN PENTACHLORIDE (WCl₅)

(IDEAL GAS)

GFW = 361.116

Point Group [D_{3h}]S°_{298,15} = [96.9] gibbs/mol

Ground State Quantum Weight = [2]

ΔH°₀ = -98.2 ± 8 kcal/molΔH°_{298,15} = -98.6 ± 8 kcal/mol

Electronic Levels and Quantum Weights

E ₁ , cm ⁻¹	E ₂
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[480] (1)	[350] (2)
[400] (1)	[150] (2)
[380] (1)	[100] (2)
[130] (1)	[180] (2)

Bond Distance: W-Cl = [2.26] Å

Bond Angle: Cl-W-Cl = [120]° Cl-W-Cl** = [90]° Cl**W-Cl** = [180]°

* Equatorial ** Axial

Product of the Moments of Inertia: I_AI_BI_C = [9.98 x 10⁻¹¹²] g³ cm⁶

Heat of Formation.

The heat of formation, ΔH°₂₉₈ (WCl₅, g) = -98.6 kcal/mol, is calculated from ΔH°₂₉₈ = 19.4 kcal/mol for WCl₆(g) → WCl₅(g) + 1/2 Cl₂(g). The value of ΔH°₂₉₈ is calculated by the third law method from the equation for log Kp given by S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). The second law ΔH°₂₉₈ is 24.6 kcal/mol and the third law drift is -8.5 eu.

Heat Capacity and Entropy.

The molecular configuration is assumed to be a trigonal bipyramid similar to that of MoCl₅ determined by electron diffraction by R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. 34, 1358 (1938). The bond distance is estimated to be the same as that in WCl₆(g). The three principal moments of inertia are: I_A = I_B = 105.23 x 10⁻³⁹ and I_C = 90.20 x 10⁻³⁹ g cm².

All vibrational frequencies are estimated from those of SbCl₅, PCl₅, NbCl₅ and TaCl₅ obtained from infrared and Raman spectra by G. L. Carlson, Spectrochim. Acta 19, 1291 (1963).

If it is considered that the metal atoms are effectively ionized, then the W⁵⁺ will have a single d electron in a field of chloride ions. The electronic splitting would be roughly the inverse of that in CuCl₂(g) as given by C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966), where Cu has a d⁹ configuration. By analogy with the splitting in CuCl₂, the low lying electronic levels are estimated to be 7000 cm⁻¹ and 14000 cm⁻¹, both doublets.

Molybdenum Hexachloride (MoCl₆)

(Crystal) GFW = 308.658

MOLYBDENUM HEXACHLORIDE (MoCl₆)

(CRYSTAL)

GFW = 308.658

 $\Delta H_f^\circ = \text{unknown}$ $\Delta H_f^\circ_{298.15} = [-125 \pm 10] \text{ kcal/mol}$ $S^\circ_{298.15} = [61.0 \pm 4.0] \text{ gibbs/mol}$ $T_s = [527]^\circ\text{K}$

Heat of Formation

G. I. Novikov and N. V. Galitskii, Zh. Neorg. Khim. **10**, 576-8 (1965), assumed that the equilibrium $\text{MoCl}_5(\text{c}) = \text{MoCl}_5(\text{g}) + 1/2 \text{Cl}_2(\text{g})$ exists. They then calculated values for the constant of the above equilibrium and estimated the thermodynamic characteristics, $\Delta H_f^\circ = 4 \text{ kcal/mol}$ and $\Delta S_f^\circ = 8 \text{ eu}$, of the equilibrium $\text{MoCl}_5(\text{c}) = \text{MoCl}_5(\text{c}) + 1/2 \text{Cl}_2(\text{g})$, from which they obtained the $\Delta H_f^\circ_{298}(\text{MoCl}_5, \text{c}) = -125 \text{ kcal/mol}$.

Heat Capacity and Entropy

The adopted heat capacity is the same as that of $\text{WCl}_6(\text{g}, \text{c})$, since the heat capacities of W and Mo are almost the same. The entropy is estimated from that of $\text{MoCl}_5(\text{c})$ by the addition of 4 eu due to one extra chlorine atom in the molecule.

Vaporization Data

The sublimation point is calculated from the free energy crossover between crystal and gas. However, it should be noted that $\text{MoCl}_6(\text{c})$ is unstable with respect to $\text{MoCl}_5(\text{c})$ at all temperatures and thus sublimation could occur only under an atmosphere of Cl_2 .

T, °K	Cp°	gibbs/mol S°	$-(G^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0							
100							
200							
298							
300							
400							
500							
600							
700							
800							
900							
1000							
1100							
1200							
1300							
1400							
1500							

Molybdenum Hexachloride (MoCl₆)(Ideal Gas) GF_W = 308.658Point Group O_h $\Delta H_f^\circ = [-104.7 \pm 20]$ kcal/mol $S_{298.15}^\circ = [100.3 \pm 4]$ gibbs/mol $\Delta H_f^\circ = [-105.0 \pm 20]$ kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
[347] (1)	[144] (3)	
[326] (2)	[171] (3)	
[390] (3)	[106] (3)	
Bond Distance: Mo-Cl = [2.26] Å		
Bond Angle: Cl-Mo-Cl = [90°]		
Product of the Moments of Inertia: $I_A I_B I_C = [1.7398 \times 10^{-111}]$ g ³ cm ⁶		

 $\sigma = 24$

Heat of Formation

G. I. Novikov and N. V. Galitskii, Zh. Neorg. Khim. **10**, 576-82 (1965), assumed that the equilibrium MoCl₆(g) = MoCl₅(g) + 1/2 Cl₂(g) exists. They then calculated values for the constant of the above equilibrium and estimated the thermodynamic characteristics, $\Delta H_f^\circ = 2.5$ kcal/mol and $\Delta S_f^\circ = 10$ eu of the equilibrium MoCl₆(g) = MoCl₅(g) + 1/2 Cl₂(g), from which they obtained the ΔH_f° (MoCl₆, g) = -105 kcal/mol.

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those of MoF₆ and WF₆, given by K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York - London, 1963, and WCl₆ given by J. C. Evans and G. Y. S. Lo, J. Mol. Spectrosc. **26**, 147 (1968).

Structure, bond distance and bond angle are estimated to be the same as those of WCl₆. The three principal moments of inertia are $I_A = I_B = I_C = 120.2684 \times 10^{-39}$ g cm².

Dec. 31, 1968

Tungsten Hexachloride, Alpha (α -WCl₆)
(Crystal) GFW = 396.568

T, °K	Cp	$\frac{\text{gibbs/mol}}{S^\circ}$	$\frac{-(G^\circ - H^\circ_{298})}{T}$	$\frac{\text{kcal/mol}}{H^\circ - H^\circ_{298}}$	ΔG°	Log Kp
0						
200						
288	41.926	57.000	57.000	.000	- 141.900	79.028
300	42.000	57.200	57.001	.078	- 141.878	79.167
400	46.000	60.800	58.656	4.478	- 140.557	53.452
500	50.000	62.807	62.231	10.274	- 137.917	36.221
600	53.100	67.224	66.478	15.444	- 135.965	26.238
700	54.820	100.551	70.657	20.552	- 131.876	16.016
800	55.950	114.510	78.943	31.565	- 129.309	12.074
900	56.000	120.408	82.845	37.563	- 127.044	9.962
1000	56.000	125.745	86.506	43.163	- 124.799	8.459
1100	56.000	130.618	89.252	48.163	- 122.564	7.110
1200	56.000	135.250	91.420	52.963	- 120.366	6.001
1300	56.000	139.250	93.420	57.263	- 118.175	5.173
1400	56.000	143.114	95.405	61.001	- 116.001	4.57
1500	56.000					

TUNGSTEN HEXACHLORIDE, ALPHA (α -WCl₆) (CRYSTAL) GFW = 396.568

$\Delta H^\circ_f = \text{Unknown}$
 $\Delta H^\circ_{298.15} = -141.9 \pm 6 \text{ kcal/mol}$
 $\Delta H^\circ (a_1 \rightarrow a_2) = [1.0] \text{ kcal/mol}$
 $\Delta H^\circ (a_2 \rightarrow \beta) = 3.77 \text{ kcal/mol}$
 $\Delta H^\circ_{298.15} = 23.9 \text{ kcal/mol}$

$S^\circ_{298.15} = [57.0] \text{ gibbs/mol}$
 $Tt (a_1 \rightarrow a_2) = 450 \pm 10^\circ K$
 $Tt (a_2 \rightarrow \beta) = 503^\circ \pm 3^\circ K$

Heat of Formation.

S. A. Shchukarev, I. V. Vasilkova and G. I. Novikov, Zh. Neorg. Khim., 3, 2642 (1958), have measured calorimetrically the heat of solution of WCl₆(c) and also of H₂WO₄(c) in a 12% solution of NaOH as -188.0 ± 0.3 and -13.6 ± 0.11 kcal/mol, respectively. Based on these data and a heat of dilution value for Na₂WO₄ which is essentially zero, we obtain $\Delta H^\circ_{298} = -174.4 \pm 0.3 \text{ kcal/mol}$ for WCl₆(c) + 6NaOH(16.3H₂O) → H₂WO₄(c) + 6NaCl(22.00H₂O) + 2H₂O(l). This reaction gives $\Delta H^\circ_{298}(WCl_6, c) = -141.9 \pm 6 \text{ kcal/mol}$, using a revised $\Delta H^\circ_{298}(H_2WO_4, c) = -270.5 \text{ kcal/mol}$, and other auxiliary data from JANAP Tables and from V. B. Parker, "Thermal Properties of Aqueous Unit-univalent Electrolytes," NBS-RS-NBS-2, Natl. Bur. Std., Washington, D.C., April, 1965. The authors have suggested a possible uncertainty of the order of 5 kcal/mol due to the slowness of the dissolution of WCl₆(c).

Heat Capacity and Entropy.

J. R. Welty¹ has measured the enthalpy changes for WCl₆(a, c) in the temperature range from 406° to 502.4°K by drop calorimetry. Few points were measured in the region of the $a_1 \rightarrow a_2$ transition and no attempt was made to investigate the phase present at the conclusion of the drop. Thus, these data appear to be inadequate to define the heat capacities of the a_1 and a_2 phases. The adopted heat capacities are estimated so that they are reasonably consistent with the enthalpy data.

The entropy $S^\circ_{298} = 57.0 \text{ eu}$, is calculated from that of the gas using $\Delta S^\circ_{298} = 43.155 \text{ eu}$ from the vaporization and sublimation data given in the WCl₆(g) table (December 31, 1966).

Transition Data.

Transition temperatures and heats of transition have been reported by the following investigators, and their results are summarized as follows:

Investigator	Method	$a_1 \rightarrow a_2$ transition		$a_2 \rightarrow \beta$ transition	
		Temperature (°K)	ΔH° (kcal/mol)	Temperature (°K)	ΔH° (kcal/mol)
Ketelaar ² et al.	Vapor pressure	441	-	500	3.4
Stevenson ³	Cooling curve	458	-	503	-
Welty ¹	Vapor Pressure	-	-	503	1.9
Shchukarev ⁴ et al.	Drop calorimetric	-	-	504	3.4
Dobrotin ⁵	Vapor pressure	-	-	504	3.4
	Approximate calorimetric	-	-	493 ± 10	5.5

The adopted $\Delta H^\circ_{450} (a_1 \rightarrow a_2)$ and $\Delta H^\circ_{503} (a_2 \rightarrow \beta)$ are calculated as 1.0 and 3.77 kcal/mol, respectively, based on the adopted heat capacities and the enthalpy data. The enthalpies are assumed to refer to a_1 phase as the final state, although no experimental evidence for this is given.

Melting Data.

See WCl₆ (p.c) table (December 31, 1966).

Heat of Sublimation.

See WCl₆(g) table (December 31, 1966) for detailed information about sublimation data.

References:

1. J. R. Welty, Ph.D. Thesis, Oregon State University (1962).
2. J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim., 62, 597 (1943).
3. F. D. Stevenson, Ph.D. Thesis, Oregon State University (1962); U.S. Bur. Mines Rept. Invest. 6367 (1964).
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).
5. R. B. Dobrotin, A. V. Suvorov and Y. V. Kondrat'ev, Vestnik Leningrad. Univ. 19, No. 4, Fiz. i Khim. No. 1, 95 (1964).

Cl₆W

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log Kp
100							
200							
298	45,000	67,066	67,066	.000	- 136,921	- 106,925	78.376
300	45,000	67,344	67,067	.083	- 136,894	- 106,739	77.759
400	45,000	80,790	68,832	4,583	- 135,473	- 96,906	52.947
500	45,000	94,136	73,497	13,583	- 132,851	- 78,197	28.483
600	45,000	105,473	79,640	18,083	- 131,606	- 69,187	21.601
700	45,000	111,482	83,253	22,583	- 130,387	- 60,357	16.489
800	45,000	116,792	86,689	27,083	- 129,268	- 51,620	12.924
900	45,000	121,323	89,740	31,583	- 128,195	- 43,110	9.691
1000	45,000	125,812	93,009	36,083	- 126,900	- 34,683	6.691
1100	45,000	129,728	95,908	40,583	- 125,775	- 26,350	4.799
1200	45,000	133,330	98,650	45,083	- 124,667	- 18,110	3.045
1300	45,000	136,664	101,248	49,583	- 123,576	- 9,493	1.554
1400	45,000	139,769	103,714	54,083	- 122,502	- 1,875	.273
1500	45,000						

ΔH°_0 = Unknown
 $\Delta H^\circ_{298.15} = [-136.921] \text{ kcal/mol}$
 $\Delta H^\circ (\alpha_2 \rightarrow \beta) = 3.77 \text{ kcal/mol}$
 $\Delta H^\circ = 1.60 \text{ kcal/mol}$
 $\Delta H^\circ_{298.15} = 18.921 \text{ kcal/mol}$

$S^\circ_{298.15} = [67.066] \text{ gibbs/mol}$
 $T_f (\alpha_2 \rightarrow \beta) = 503 \pm 3^\circ \text{K}$
 $T_m = 555 \pm 2^\circ \text{K}$

Heat of Formation.
The heat of formation, $\Delta H^\circ_{298} (\text{WCl}_6, \beta, c) = -136.921 \text{ kcal/mol}$, is calculated from that of $\text{WCl}_6(\alpha, c)$ by adding the heat of $\alpha_2 = \beta$ transition and the difference between $H^\circ_{503} - H^\circ_{298.15}$ for $\text{WCl}_6(\alpha, c)$ and $\text{WCl}_6(\beta, c)$.

Heat Capacity and Entropy.
J. R. Welty¹ has measured the enthalpy changes for $\text{WCl}_6(\beta, c)$ in the temperature range from 508° to 553°K by drop calorimetry. Because of the short temperature range, poor distribution of points, and lack of identification of the phase present at the conclusion of each drop, we feel that the enthalpy data are insufficient to define the heat capacity accurately. The adopted heat capacities are estimated so that they are consistent with the enthalpy data within their probable uncertainty.

The entropy of $\text{WCl}_6(\beta, c)$, $S^\circ_{298.15} = 67.066 \text{ eu}$, is calculated in a manner analogous to that of the heat of formation.

Transition Data.

See $\text{WCl}_6(\alpha, c)$ table (Dec. 31, 1966).

Melting Data.

Melting point and heat of melting have been reported by the following investigators, and their results are summarized as follows:

Investigator	Method	Melting Point (°K)	ΔH_m° (kcal/mol)
Ketelaar ² et al.	Vapor pressure	557	2.3
Stevenson ³	Cooling curve	555	-
Welty ¹	Vapor pressure	555	1.5
Shchukarev ⁴ et al.	Drop calorimetric	556	1.6
Dobrotin ⁵ et al.	Vapor pressure	564	2.0
	Approximate calorimetric	545 $\pm$ 12	4.2

The adopted heat of melting, $\Delta H^\circ_{555} = 1.6 \text{ kcal/mol}$, is calculated from the adopted heat capacities and the enthalpy data. The enthalpies are assumed to refer to α_1 phase as the final state, although no experimental evidence for this is available.

Heat of Sublimation.

$\Delta H^\circ_{298.15}$ is calculated as the difference between $\Delta H^\circ_{298.15}$ for $\text{WCl}_6(\beta, c)$ and $\text{WCl}_6(g)$.

References.

1. J. R. Welty, Ph.D. Thesis, Oregon State University (1962).
2. J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 62, 597 (1943).
3. T. D. Stevenson, Ph.D. Thesis, Oregon State University, (1962); U.S. Bur. Mines Rept. Invest. 6367 (1964).
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).
5. R. B. Dobrotin, A. V. Suvorov and Y. V. Kondrat'ev, Vestnik Leningrad. Univ. 19, No. 4, Ser. Fiz. i Khim., No. 1, 95 (1964).

Dec. 31, 1966

Tungsten Hexachloride (WCl₆)

(Liquid)

GF_W = 396.568

T, °K	C _p ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{H^\circ - H^\circ_{298}}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log K _p
100							
200							
298	48.000	68.095	68.085	.000	-136.091	-106.399	77.992
300	48.000	68.382	68.086	.089	-136.058	-106.215	77.378
400	48.000	82.191	59.469	9.669	-134.357	-97.531	72.182
500	48.000	97.502	33.524	9.669	-132.637	-87.531	31.182
600	48.000	101.653	77.505	16.489	-131.115	-76.332	28.532
700	48.000	109.052	81.497	19.289	-129.570	-65.657	21.748
800	48.000	115.462	85.451	24.089	-128.061	-61.205	16.720
900	48.000	121.115	89.017	28.869	-126.573	-56.934	11.720
1000	48.000	126.173	92.484	33.669	-125.109	-47.634	6.799
1100	48.000	130.747	95.758	38.489	-123.664	-36.876	7.327
1200	48.000	134.924	98.850	43.289	-122.239	-29.050	5.291
1300	48.000	138.766	101.775	48.089	-120.831	-21.341	3.568
1400	48.000	142.323	104.546	52.869	-119.440	-13.740	2.400
1500	48.000	145.635	107.176	57.669	-118.066	-6.739	

TUNGSTEN HEXACHLORIDE (WCl₆)

(LIQUID)

GF_W = 396.568

S_{298.15}^o = [68.085] gibbs/mol

T_m = 555 ± 2 °K

T_b = 613.6 °K

ΔH_f^o_{298.15} = -136.091 kcal/mol

ΔH_m^o = 1.60 kcal/mol

ΔH_v^o = 14.319 kcal/mol

Heat of Formation.

The heat of formation, ΔH_f^o_{298.15}(WCl₆(l)) = -136.091 kcal/mol, is calculated from that of WCl₆(β,c) by adding the heat of melting and the difference between H_{298.15}^o for WCl₆(β,c) and WCl₆(l).

Heat Capacity and Entropy.

J. R. Welty, Ph.D. Thesis, Oregon State University (1962), has measured the enthalpy changes for WCl₆(l) in the temperature range from 560° to 603°K by drop calorimetry. Since the temperature range was very short and no attempt was made to investigate the phase present at the conclusion of the drop, we feel that the enthalpy data are insufficient to define the heat capacity accurately. The adopted heat capacities are estimated so that they are reasonably consistent with the enthalpy data.

The entropy of WCl₆(l), S_{298.15}^o = 68.085 eu, is calculated in a manner analogous to that of the heat of formation.

Melting Data.

See WCl₆(β,c) table dated Dec. 31, 1966.

Vaporization Data.

The boiling point, 613.6°K, is calculated as the temperature at which the Gibbs energies of formation for both WCl₆(l) and WCl₆(g) are equal. The difference in the heats of formation of WCl₆(l) and WCl₆(g) at the boiling point is the heat of vaporization.

J. A. A. Ketelaar, G. M. Oosterhout and P. B. Braun, Rec. Trav. Chim. 82, 597 (1943), have determined the boiling point and the heat of vaporization as 603.7°K and 15.24 kcal/mol, respectively, from vapor pressure measurements. S. A. Shchukarev and A. V. Suvorov revised their previous data^{1,3} and gave the boiling point and the heat of vaporization as 616.2°K and 14.7 kcal/mol, respectively, from their vapor pressure measurements.

See WCl₆(g) table, dated Dec. 31, 1966, for detailed information about vaporization data.

References:

1. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).
2. S. A. Shchukarev and G. I. Novikov, Zh. Neorg. Khim. 1, 357 (1956).
3. S. A. Shchukarev, G. I. Novikov, A. V. Suvorov and A. K. Baev, Zh. Neorg. Khim. 3, 2630 (1958).

Point Group O_h
ΔH_f^o_{298.15} = [100.2] gkcal/mol
ΔH_f^o_{298.15} = -117.6 ± 6 kcal/mol
ΔH_f^o_{298.15} = -118.0 ± 6 kcal/mol

Vibrational Frequencies and Degeneracies

WCl ₆ cm ⁻¹	WCl ₆ cm ⁻¹
[360] (1)	[140] (3)
[340] (2)	[180] (3)
375 (3)	[120] (3)

Bond Distance: W-Cl = 2.26 Å

Bond Angle: Cl-W-Cl = 90°

Product of the Moments of Inertia: I_AI_BI_C = 1.7396 x 10⁻¹¹¹ g³ cm⁶

σ = 24

Heats of Formation

The heat of formation of WCl₆(g), ΔH_f^o₂₉₈ = -118.0 kcal/mol, is calculated from that of the crystal plus the adopted heat of sublimation, ΔH_{sub}^o₂₉₈ = 23.9 kcal/mol for WCl₆(s,c). The latter was obtained from third law analysis of the vapor pressure data 1,2,3,4, using all JANAF functions (Dec. 31, 1966).

Investigator	Phase Studied	Temp. range (K)	No. of Points	ΔH _f ^o ₂₉₈ (kcal/mol)	Drift (eu)	ΔH _f ^o ₂₉₈ (WCl ₆ /g)***
Stevenson ¹	α, e	462 - 502	38	20.9 ± 0.5	23.74	-118.16
	β*, e	503 - 551	15	23.1 ± 0.2	23.89	-118.01
	1*	557 - 598	13	24.2 ± 0.1	23.89	-118.01
Shchukarev ² et al.	α, c	**	-	22.0	23.80	-118.10
	β*, c	-	-	23.8	23.98	-117.92
	1*	-	-	24.1	23.98	-117.92
Ketelaar ³ et al.	α, c	425 - 500	21	23.1 ± 0.1	23.94	-117.96
	β*, c	504 - 554	21	24.4 ± 0.1	23.91	-117.99
	1*	523 - 635	21	24.4 ± 0.1	23.85	-118.05
Vernon ⁴	α, c	298 - 423	4	16.1 ± 4.1	21.02	-120.88

A. A. Vernon⁴ has also determined the equilibrium constants in the temperature range from 1350° to 1600°K for the decomposition of WCl₆(g) to W(c) and Cl₂(g) by reaction of the sample with a hot tungsten filament in a vacuum bulb. Using the reported equilibrium constants, the heat of formation of WCl₆(g) at 298°K is calculated by the second and third law method as -131.8 ± 2.9 kcal/mol and -135.2 kcal/mol, respectively. The third law drift is 2.4 ± 1.9 au. Unfortunately, the reported equilibrium constants may be seriously in error, since atomic chlorine is the main species at the pressure and temperature studied.

* Enthalpy changes are converted to ΔH_f^o₂₉₈ for WCl₆(α, c) → WCl₆(g).

** Vapor pressure equations for the crystal (α,β) and the liquid to gas are given.

*** The third law ΔH_f^o₂₉₈ is used in calculation.

References:

1. F. D. Stevenson, Ph.D Thesis, Oregon State University (1962); U.S. Bur. Mines Rept. Invest. 6367 (1961).
2. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. 1 Khim., No. 1, 87 (1961).
3. J. A. A. Ketelaar, O. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 52, 597 (1943).
4. A. A. Vernon, J. Am. Chem. Soc. 59, 1832 (1937).

Heat Capacity and Entropy

R. O. Evans and W. Lister, Trans. Faraday Soc. 34, 1358 (1938), have determined the octahedral structure for WCl₆(g) by electron diffraction and found the bond length to be 2.26 Å.

The vibrational frequency of W₂, 375 cm⁻¹, was observed in the infrared spectra by J. C. Evans, The Dow Chemical Company, private communication, Dec. 1, 1966. The values of V₁, V₂ and V₃ (360, 340 and 180 cm⁻¹, respectively) are estimated, based on those of the aqueous ion PtCl₆²⁻ reported by L. A. Woodward and J. A. Creighton, Spectrochim. Acta 17, 594 (1961). The values of V₄ and V₆ (140 and 120 cm⁻¹, respectively) are estimated by comparison with those of W₂(g).

The three principal moments of inertia are I_A = I_B = I_C = 120.2684 x 10⁻³⁹ g cm².

Dec. 31, 1962; Dec. 31, 1966

T, °K	Cp ^o	S ^o	-(G°-H°)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔG _f ^o	Log Kp
0	-0.00	1.00	INFINITE	-7.359	-117.588	-117.588	INFINITE
100	22.253	68.266	178.247	-5.996	-117.469	-117.469	743.733
200	31.228	106.977	103.221	-3.245	-118.376	-118.376	114.260
298	34.402	100.155	100.155	-0.000	-118.000	-97.670	71.740
300	34.439	100.168	100.156	-0.064	-117.992	-97.745	71.207
400	35.793	110.486	101.526	3.584	-117.551	-97.054	49.754
500	36.468	118.553	104.152	7.200	-117.095	-84.492	36.931
600	36.850	125.239	107.126	10.868	-116.695	-73.014	28.416
700	37.085	130.638	110.110	14.565	-116.358	-61.610	22.358
800	37.239	135.901	113.048	18.282	-116.077	-50.272	17.031
900	37.346	140.284	115.836	22.017	-115.859	-38.981	14.323
1000	37.423	144.233	118.482	25.750	-115.697	-27.742	11.527
1100	37.481	147.402	120.888	29.486	-115.566	-16.539	9.266
1200	37.524	150.326	123.360	33.246	-115.461	-5.370	7.552
1300	37.558	153.070	125.609	37.000	-115.375	5.755	6.191
1400	37.585	155.655	127.742	40.758	-115.300	16.234	5.091
1500	37.607	158.049	129.770	44.517	-115.247	26.700	4.121
1600	37.625	160.312	131.702	48.279	-115.208	37.164	3.282
1700	37.640	162.458	133.595	52.042	-115.182	47.628	2.546
1800	37.653	164.510	135.406	55.807	-115.166	58.096	1.916
1900	37.663	166.486	137.144	59.573	-115.158	68.568	1.386
2000	37.672	168.376	138.808	63.339	-115.156	79.046	0.946
2100	37.680	170.186	140.400	67.107	-115.160	89.528	0.607
2200	37.687	171.923	141.893	70.875	-115.169	100.012	0.367
2300	37.693	173.598	143.360	74.644	-115.181	110.500	0.227
2400	37.698	175.214	144.816	78.414	-115.195	121.000	0.187
2500	37.702	176.768	146.264	82.184	-115.210	131.500	0.147
2600	37.706	178.261	147.707	85.954	-115.226	142.000	0.107
2700	37.710	179.698	149.144	89.724	-115.242	152.500	0.067
2800	37.713	181.081	150.570	93.494	-115.258	163.000	0.027
2900	37.716	182.416	151.994	97.264	-115.274	173.500	0.007
3000	37.719	183.703	153.416	101.034	-115.290	184.000	0.000
3100	37.721	184.948	154.834	104.804	-115.306	194.500	0.000
3200	37.723	186.155	156.250	108.574	-115.322	205.000	0.000
3300	37.725	187.323	157.663	112.344	-115.338	215.500	0.000
3400	37.727	188.458	159.070	116.114	-115.354	226.000	0.000
3500	37.729	189.563	160.476	119.884	-115.370	236.500	0.000
3600	37.730	190.638	161.876	123.654	-115.386	247.000	0.000
3700	37.732	191.683	163.273	127.424	-115.402	257.500	0.000
3800	37.733	192.698	164.668	131.194	-115.418	268.000	0.000
3900	37.734	193.683	166.063	134.964	-115.434	278.500	0.000
4000	37.735	194.638	167.458	138.734	-115.450	289.000	0.000
4100	37.736	195.563	168.853	142.504	-115.466	299.500	0.000
4200	37.737	196.458	170.248	146.274	-115.482	310.000	0.000
4300	37.738	197.323	171.643	150.044	-115.498	320.500	0.000
4400	37.739	198.158	173.038	153.814	-115.514	331.000	0.000
4500	37.740	198.963	174.433	157.584	-115.530	341.500	0.000
4600	37.740	199.738	175.828	161.354	-115.546	352.000	0.000
4700	37.741	200.483	177.223	165.124	-115.562	362.500	0.000
4800	37.742	201.198	178.618	168.894	-115.578	373.000	0.000
4900	37.742	201.883	180.013	172.664	-115.594	383.500	0.000
5000	37.743	202.538	181.408	176.434	-115.610	394.000	0.000
5100	37.743	203.173	182.803	180.204	-115.626	404.500	0.000
5200	37.744	203.788	184.198	183.974	-115.642	415.000	0.000
5300	37.744	204.383	185.593	187.744	-115.658	425.500	0.000
5400	37.745	204.958	187.000	191.514	-115.674	436.000	0.000
5500	37.745	205.513	188.405	195.284	-115.690	446.500	0.000
5600	37.745	206.048	189.810	199.054	-115.706	457.000	0.000
5700	37.746	206.563	191.215	202.824	-115.722	467.500	0.000
5800	37.746	207.058	192.620	206.594	-115.738	478.000	0.000
5900	37.746	207.533	194.025	210.364	-115.754	488.500	0.000
6000	37.747	207.988	195.430	214.134	-115.770	499.000	0.000

Tungsten Pentachloride, Dimeric (W₂Cl₁₀)
(Ideal Gas) GFW = 722.230

T, °K	Cp°	S°	-G°-H° ²⁹⁸ /T	H°-H° ²⁹⁸	ΔH°	Log Kp
0	0.000	INFINITE	INFINITE	-10.438	-208.690	INFINITE
100	97.951	104.851	223.358	-197.345	-208.695	431.296
200	56.922	146.124	170.521	-6.010	-207.644	202.692
298	67.969	170.521	170.521	0.000	-207.600	127.799
300	43.017	170.911	170.522	6.117	-207.560	126.661
400	55.754	203.495	177.758	13.053	-206.539	94.145
500	66.612	215.934	183.172	19.654	-204.401	66.032
600	76.233	228.278	186.632	26.304	-203.387	51.701
700	84.816	239.590	191.048	32.976	-202.411	41.000
800	92.591	249.041	194.484	39.671	-201.454	33.172
900	99.699	256.932	197.001	46.371	-200.524	27.041
1000	106.377	263.481	199.604	53.084	-199.625	22.161
1100	112.771	269.728	202.228	59.805	-198.757	18.166
1200	118.933	275.691	204.901	66.531	-197.913	14.688
1300	124.899	281.384	207.621	73.261	-197.087	12.109
1400	130.701	286.828	210.394	79.994	-196.276	9.779
1500	136.351	292.049	213.221	86.731	-195.481	7.600
1600	141.861	297.054	216.099	93.469	-194.699	5.906
1700	147.233	301.861	219.021	100.210	-193.929	4.336
1800	152.477	306.481	222.001	106.954	-193.169	3.311
1900	157.599	310.921	225.031	113.699	-192.421	2.598
2000	162.601	315.191	228.111	120.441	-191.681	2.003
2100	167.481	319.311	231.241	127.187	-190.949	1.510
2200	172.233	323.291	234.421	133.934	-190.229	1.137
2300	176.861	327.121	237.651	140.681	-189.511	0.861
2400	181.361	330.811	240.921	147.429	-188.799	0.651
2500	185.731	334.361	244.241	154.179	-188.099	0.481
2600	189.981	337.781	247.611	160.929	-187.409	0.341
2700	194.121	341.071	251.021	167.679	-186.729	0.221
2800	198.151	344.241	254.471	174.429	-186.059	0.131
2900	202.071	347.291	257.961	181.180	-185.399	0.071
3000	205.891	350.241	261.491	187.931	-184.749	0.031
3100	209.611	353.091	265.061	194.683	-184.109	0.011
3200	213.241	355.841	268.671	201.434	-183.479	0.001
3300	216.781	358.491	272.321	208.184	-182.849	0.000
3400	220.241	361.041	276.011	214.939	-182.219	0.000
3500	223.611	363.491	279.641	221.691	-181.589	0.000
3600	226.901	365.841	283.211	228.444	-180.959	0.000
3700	230.111	368.091	286.721	235.194	-180.329	0.000
3800	233.241	370.241	290.171	241.944	-179.699	0.000
3900	236.301	372.291	293.561	248.694	-179.069	0.000
4000	239.291	374.241	296.891	255.444	-178.439	0.000
4100	242.211	376.091	300.161	262.194	-177.809	0.000
4200	245.061	377.841	303.371	268.944	-177.179	0.000
4300	247.841	379.491	306.521	275.694	-176.549	0.000
4400	250.561	381.041	309.611	282.444	-175.919	0.000
4500	253.211	382.491	312.641	289.194	-175.289	0.000
4600	255.791	383.841	315.611	295.944	-174.659	0.000
4700	258.301	385.091	318.521	302.694	-174.029	0.000
4800	260.741	386.241	321.371	309.444	-173.399	0.000
4900	263.111	387.291	324.161	316.194	-172.769	0.000
5000	265.421	388.241	326.891	322.944	-172.139	0.000
5100	267.671	389.091	329.561	329.694	-171.509	0.000
5200	269.861	390.741	332.171	336.444	-170.879	0.000
5300	271.991	392.291	334.721	343.194	-170.249	0.000
5400	274.061	393.741	337.211	350.044	-169.619	0.000
5500	276.071	395.091	339.641	356.794	-168.989	0.000
5600	278.021	396.341	342.011	363.544	-168.359	0.000
5700	279.911	397.491	344.321	370.294	-167.729	0.000
5800	281.741	398.541	346.571	377.044	-167.099	0.000
5900	283.511	399.491	348.761	383.794	-166.469	0.000
6000	285.221	400.341	350.891	390.544	-165.839	0.000

Dec. 31, 1966

Cl₁₀W₂

GFW = 722.230

TUNGSTEN PENTACHLORIDE, DIMERIC (W₂Cl₁₀) (IDEAL GAS)

Point Group [D_{2h}]
S_{298.15} = [1.70] gibbs/mol
Ground State Quantum Weight = [3]
ΔH_f⁰ = -208.7 ± 10 kcal/mol
ΔH_f^{298.15} = -207.6 ± 10 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
[500] (2)	[150] (2)	[90] (2)
[400] (2)	[125] (4)	[80] (2)
[350] (2)	[100] (6)	[60] (4)
[250] (2)		[40] (2)

Bond Distance: W-Cl = [2.26] Å

Bond Angle: Cl-W-Cl = [90]° W-Cl-W-Cl = [90]°

Cl-W-Cl = [180]° Cl-W-Cl = [90]°

*Equatorial **Axial

Product of the Moments of Inertia: I_AI_BI_C = [8.638] x 10⁻¹¹⁰ g³ cm⁶

Heat of Formation

The heat of formation, ΔH_f²⁹⁸ (W₂Cl₁₀/g) = -207.6 kcal/mol, is calculated from ΔH_f²⁹⁸ = 10.4 kcal/mol for W₂Cl₁₀(g) = 2 WCl₅(g), using all JANAP Functions (Dec. 31, 1966). The value of ΔH_f²⁹⁸ is obtained from third law analysis of the partial pressures of WCl₅(g) and W₂Cl₁₀(g) derived from PVT data determined by S. A. Shchukarev, G. I. Novikov and N. V. Andreev, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959). The second law ΔH_f²⁹⁸ is 10.4 ± 0.3 kcal/mol.

Heat Capacity and Entropy

The molecular configuration is estimated by analogy with that of Mo₂Cl₁₀ reported by D. Z. Sands and P. Zaikin, Acta Cryst. 12, 723 (1959). Chlorine atoms are placed octahedrally around two tungsten atoms and these two octahedra share one common edge with six chlorine and two tungsten atoms in a plane. The bond length is estimated to be the same as that in WCl₆(g). The three principal moments of inertia are I_A = 210.5 x 10⁻³⁹, I_B = 576.8 x 10⁻³⁹ and I_C = 566.8 x 10⁻³⁹ g cm².

All vibrational frequencies are estimated, based on those of WCl₅ (AlCl₃)₂ and Cs₂Cl₂, such that S₂₉₈(W₂Cl₁₀/g) = 216.65 eu. This entropy is derived from ΔS₂₉₈ = 19.92 + 0.5 eu for W₂Cl₁₀(g) = 2WCl₅(g), obtained by second law analysis of the data of Shchukarev et al., loc. cit. The frequencies are not in point group order.

Cl₁₀W₂

Cobalt (Co)

(Reference State) GFW = 58.9332

COBALT (Co)

GFW = 58.9332

(REFERENCE STATE)

0 to 700°K Crystal alpha
 700 to 1768°K Crystal beta
 1768 to 3170°K Liquid
 3170 to 8000°K Ideal Monatomic gas

See crystal, liquid and monatomic gas tables for details.

T, °K	Cp*	$\mu\text{Btu/mol}$ S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$ kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	.0000	.0000	INFINITE	- 1.139	.000	.000
100	3.330	1.840	11.990	- 1.015	.000	.000
200	4.940	2.920	7.410	.000	.000	.000
298	5.330	3.160	7.160	.000	.000	.000
300	5.937	7.217	7.160	.011	.000	.000
400	6.340	6.980	7.418	.625	.000	.000
500	6.740	10.439	7.680	1.279	.000	.000
600	7.090	11.699	8.414	1.971	.000	.000
700	7.420	12.817	8.944	2.697	.000	.000
800	7.750	13.975	9.559	3.557	.000	.000
900	8.250	14.916	10.075	4.356	.000	.000
1000	8.680	15.815	10.605	5.210	.000	.000
1100	9.520	16.488	11.118	6.127	.000	.000
1200	10.330	17.594	11.618	7.115	.000	.000
1300	11.630	18.424	12.108	8.211	.000	.000
1400	10.570	19.337	12.592	9.443	.000	.000
1500	9.500	20.021	13.065	10.835	.000	.000
1600	9.150	20.622	13.519	11.345	.000	.000
1700	9.030	21.222	13.933	11.972	.000	.000
1800	9.680	21.869	14.407	17.067	.000	.000
1900	9.680	24.413	14.920	18.035	.000	.000
2000	9.680	24.909	15.407	19.003	.000	.000
2100	9.680	25.381	15.871	19.971	.000	.000
2200	9.680	25.832	16.314	20.939	.000	.000
2300	9.680	26.262	16.737	21.907	.000	.000
2400	9.680	26.674	17.143	22.875	.000	.000
2500	9.680	27.069	17.532	23.843	.000	.000
2600	9.680	27.449	17.906	24.811	.000	.000
2700	9.680	27.814	18.266	25.779	.000	.000
2800	9.680	28.166	18.613	26.747	.000	.000
2900	9.680	28.506	18.949	27.715	.000	.000
3000	9.680	28.834	19.273	28.683	.000	.000
3100	9.680	29.151	19.586	29.651	.000	.000
3200	9.680	29.458	19.891	30.619	.000	.000
3300	6.304	27.763	21.268	120.368	.000	.000
3400	6.319	27.959	22.364	120.999	.000	.000
3500	6.333	28.135	23.383	121.632	.000	.000
3600	6.351	28.314	24.351	122.266	.000	.000
3700	6.372	28.488	25.281	122.900	.000	.000
3800	6.396	28.658	26.184	123.540	.000	.000
3900	6.423	28.825	26.983	124.181	.000	.000
4000	6.453	28.988	27.781	124.825	.000	.000
4100	6.487	29.147	28.584	125.472	.000	.000
4200	6.523	29.304	29.295	126.122	.000	.000
4300	6.563	29.458	29.975	126.777	.000	.000
4400	6.605	29.609	30.647	127.435	.000	.000
4500	6.650	29.758	31.292	128.098	.000	.000
4600	6.697	29.905	31.913	128.765	.000	.000
4700	6.746	30.050	32.510	129.437	.000	.000
4800	6.796	30.192	33.085	130.114	.000	.000
4900	6.852	30.333	33.640	130.797	.000	.000
5000	6.907	30.472	34.175	131.485	.000	.000
5100	6.965	30.609	34.692	132.178	.000	.000
5200	7.025	30.745	35.192	132.876	.000	.000
5300	7.085	30.876	35.675	133.583	.000	.000
5400	7.147	31.012	36.143	134.295	.000	.000
5500	7.210	31.144	36.596	135.013	.000	.000
5600	7.275	31.273	37.036	135.737	.000	.000
5700	7.340	31.400	37.462	136.466	.000	.000
5800	7.406	31.532	37.876	137.205	.000	.000
5900	7.474	31.659	38.278	137.949	.000	.000
6000	7.541	31.786	38.669	138.700	.000	.000

Sept. 30, 1967

Cobalt (Co)

Co

(Crystal)

GFW = 58.9332

T, °K	Cp°	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	.000	.000	INFINITE	-	.000	.000	.000
100	3.330	1.840	11.990	-1.015	.000	.000	.000
200	5.340	4.920	7.710	-.558	.000	.000	.000
298	5.930	7.180	7.180	.000	.000	.000	.000
300	5.937	7.217	7.180	.011	.000	.000	.000
400	6.740	8.680	7.410	.625	.000	.000	.000
500	7.240	10.439	7.880	1.279	.000	.000	.000
600	7.690	11.699	8.414	1.971	.000	.000	.000
700	7.920	12.617	8.964	2.697	.000	.000	.000
800	8.050	13.315	9.456	3.356	.000	.000	.000
900	8.100	13.915	10.075	4.056	.000	.000	.000
1000	8.140	14.415	10.805	4.810	.000	.000	.000
1100	8.170	14.815	11.618	5.618	.000	.000	.000
1200	8.190	15.115	12.500	6.480	.000	.000	.000
1300	8.200	15.315	13.450	7.395	.000	.000	.000
1400	8.210	15.435	14.470	8.365	.000	.000	.000
1500	8.210	15.465	15.565	9.390	.000	.000	.000
1600	8.210	15.465	16.735	10.470	.000	.000	.000
1700	8.210	15.465	17.980	11.610	.000	.000	.000
1800	8.210	15.465	19.295	12.810	.000	.000	.000
1900	8.210	15.465	20.680	14.070	.000	.000	.000
2000	8.210	15.465	22.135	15.390	.000	.000	.000
2100	8.210	15.465	23.660	16.770	.000	.000	.000
2200	8.210	15.465	25.255	18.200	.000	.000	.000
2300	8.210	15.465	26.920	19.680	.000	.000	.000
2400	8.210	15.465	28.655	21.210	.000	.000	.000
2500	8.210	15.465	30.460	22.790	.000	.000	.000

COBALT (Co)

(CRYSTAL)

GFW = 58.9332

 $\Delta H_f^\circ = 0$ kcal/mol $\Delta H_{298.15}^\circ = 0$ kcal/mol $\Delta H_t^\circ = 0.108$ kcal/mol $\Delta H_m^\circ = 3.87 \pm 0.06$ kcal/mol $\Delta H_{298.15}^\circ = 101.5 \pm 0.5$ kcal/mol $S_{298.15}^\circ = 7.18 \pm 0.1$ gibbs/mol $T_t = (700^\circ) \text{ K}$ $T_m = 1768^\circ \text{ K}$

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity of Co(c) is adopted from Hultgren et al. (1). Their selected values are based on the data from nineteen investigations. The entropy values are based on $S_t^\circ = 0.0011$ eu. The heat capacity has a maximum value of 13.14 gibbs/mol at the Curie point (1394°K).

Transition Data

The exact nature of the $\alpha(\text{hcp})$ - $\beta(\text{fcc})$ transition is yet to be clearly elucidated. Three investigations (2,3,4) indicate that it is not a simple time- and temperature-dependent phenomenon. Crystalline cobalt exists as pure β -phase above 700°K whereas mixtures of α and β cobalt commonly coexist in varying proportions below this temperature. The values of T_t° and ΔH_t° are those selected by Hultgren et al. (1).

Melting Data

The temperature and heat of melting are those selected by Hultgren et al. (1).

Heat of Sublimation

The heat of sublimation is calculated from the data of Edwards et al. (5). See Co(g) table for details.

References

1. R. Hultgren, R. L. Orr and K. K. Kelley "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," University of California, Berkeley, Calif., (1966).
2. O. S. Edwards and H. Lipson, J. Inst. Metals 89, 177 (1943).
3. A. R. Troiano and J. L. Tokich, Trans. Am. Inst. Mining Met. Engrs. 175, 728 (1946).
4. P. R. Rao, Proc. Indian Acad. Sci. Sect. A, 51, 230 (1965).
5. J. W. Edwards, H. L. Johnston and W. E. Dittmars, J. Am. Chem. Soc. 73, 4729 (1951).

Cobalt (Co)

GFW = 58.9332

COBALT (Co) (LIQUID)

GFW = 58.9332

T, °K	C _p ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(C_p^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log K _p
0						
100						
200						
298	5.930	9.793	9.793	.000	4.303	3.524 - 2.563
300	5.937	9.830	9.793	.011	4.303	3.519 - 2.564
400	6.340	11.593	10.011	.625	4.303	3.258 - 1.780
500	6.740	13.052	10.493	1.279	4.303	2.997 - 1.310
600	7.090	14.312	11.027	1.971	4.303	2.735 - .996
700	7.380	15.426	11.577	2.664	4.300	2.473 - .772
800	7.750	16.434	12.122	3.450	4.195	2.228 - .609
900	8.250	17.375	12.654	4.249	4.166	1.982 - .481
1000	8.840	18.274	13.172	5.103	4.195	1.736 - .379
1100	9.520	19.148	13.675	6.020	4.196	1.490 - .296
1200	9.560	19.978	14.166	6.974	4.142	1.246 - .227
1300	9.600	20.745	14.643	7.932	4.024	1.007 - .169
1400	9.640	21.458	15.105	8.894	3.754	.785 - .122
1500	9.680	22.124	15.551	9.860	3.728	.574 - .084
1600	9.680	22.740	15.981	10.828	3.724	.383 - .050
1700	9.680	23.316	16.397	11.796	3.627	.198 - .019
1800	9.680	23.850	16.798	12.764	.000	.000
1900	9.680	24.417	17.185	13.732	.000	.000
2000	9.680	24.909	17.559	14.700	.000	.000
2100	9.680	25.381	17.920	15.668	.000	.000
2200	9.680	25.832	18.270	16.636	.000	.000
2300	9.680	26.262	18.608	17.604	.000	.000
2400	9.680	26.674	18.935	18.572	.000	.000
2500	9.680	27.069	19.253	19.540	.000	.000
2600	9.680	27.440	19.561	20.508	.000	.000
2700	9.680	27.814	19.860	21.476	.000	.000
2800	9.680	28.166	20.150	22.444	.000	.000
2900	9.680	28.506	20.433	23.412	.000	.000
3000	9.680	28.834	20.707	24.380	.000	.000
3100	9.680	29.151	20.974	25.348	.000	.000
3200	9.680	29.453	21.235	26.316	.000	.000
3300	9.680	29.757	21.489	27.284	.000	.000
3400	9.680	30.045	21.736	28.252	.000	.000
3500	9.680	30.326	21.977	29.220	.000	.000
3600	9.680	30.599	22.213	30.188	.000	.000
3700	9.680	30.864	22.444	31.156	.000	.000
3800	9.680	31.122	22.668	32.124	.000	.000
3900	9.680	31.374	22.888	33.092	.000	.000
4000	9.680	31.619	23.104	34.060	.000	.000

Sept. 30, 1967

Co

$$\Delta H_f^\circ_{298.15} = 9.79 \text{ gibbs/mol}$$

$$\Delta H_f^\circ_{298.15} = 4.303 \pm 0.1 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 3.87 \pm 0.06 \text{ kcal/mol}$$

$$\Delta H_v^\circ = 89.219 \text{ kcal/mol}$$

$$T_m = 1768^\circ\text{K}$$

$$T_b = 3170.29^\circ\text{K}$$

Heat of Formation

The heat of formation (ΔH_f°) of Co(l) is obtained from that of the crystal by adding ΔH_m° and the differences between $H_{1768}^\circ - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity of Co(l) selected by Hultgren et al. (1) is used at temperatures above 1768°K. The heat capacities at temperatures below the melting point are estimated by assuming a glass transition at 1100°K and heat capacities similar to those of the crystal below 1100°K.

Melting Data

See Co(c) table for details.

Vaporization Data

The boiling point is calculated from the adopted thermodynamic functions and the chosen heat of sublimation at 298°K so that the free energy functions calculated by integration of the crystal liquid data and by statistical methods from the gas phase are equal at the boiling point.

Reference

1. R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," University of California, Berkeley, Calif. (1966).

Cobalt (Co)
(Ideal Gas)

GFV = 58.9332

T, °K	Cp	S° -(C°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal/mol	ΔG° kcal/mol	Log Kp
0	∞	∞	∞	∞	∞
100	4.270	37.290	101.119	101.119	INFINITE
200	5.127	40.764	101.482	97.947	-214.065
298	5.503	42.879	101.537	94.368	-103.121
300	5.510	42.879	101.500	90.857	-66.600
400	5.850	42.879	101.489	80.791	-66.141
500	6.077	45.461	101.359	68.727	-36.575
600	6.188	47.000	101.321	53.617	-36.575
700	6.236	47.958	101.216	38.483	-29.191
800	6.259	48.793	101.081	23.357	-23.277
900	6.265	49.543	100.918	8.231	-16.445
1000	6.261	50.213	100.733	6.1205	-16.445
1100	6.309	50.793	100.528	62.780	-12.473
1200	6.329	51.343	100.304	59.388	-10.416
1300	6.347	51.870	99.940	56.017	-9.416
1400	6.363	52.380	99.487	52.673	-8.416
1500	6.375	52.761	98.956	49.357	-7.416
1600	6.383	53.172	98.343	46.073	-6.416
1700	6.386	53.559	97.656	42.826	-5.416
1800	6.385	53.924	96.906	39.615	-4.416
1900	6.380	54.266	96.106	36.440	-3.416
2000	6.374	54.597	95.261	33.300	-2.416
2100	6.365	54.904	94.382	30.193	-1.416
2200	6.355	55.203	93.478	27.120	-0.416
2300	6.343	55.496	92.550	24.083	0.584
2400	6.329	55.783	91.600	21.083	1.584
2500	6.312	56.061	90.628	18.120	2.584
2600	6.304	56.329	89.636	15.193	3.584
2700	6.294	56.586	88.624	12.300	4.584
2800	6.284	56.832	87.592	9.440	5.584
2900	6.273	57.068	86.540	6.612	6.584
3000	6.263	57.295	85.468	3.824	7.584
3100	6.252	57.513	84.376	1.076	8.584
3200	6.240	57.722	83.264	-1.720	9.584
3300	6.228	57.922	82.132	-4.556	10.584
3400	6.215	58.113	80.980	-7.432	11.584
3500	6.202	58.295	79.808	-10.348	12.584
3600	6.189	58.468	78.616	-13.304	13.584
3700	6.176	58.632	77.404	-16.300	14.584
3800	6.163	58.787	76.172	-19.336	15.584
3900	6.150	58.932	74.920	-22.412	16.584
4000	6.137	59.068	73.648	-25.528	17.584
4100	6.124	59.195	72.356	-28.684	18.584
4200	6.111	59.313	71.044	-31.880	19.584
4300	6.098	59.422	69.712	-35.116	20.584
4400	6.085	59.522	68.360	-38.392	21.584
4500	6.072	59.613	66.988	-41.708	22.584
4600	6.059	59.695	65.596	-45.064	23.584
4700	6.046	59.768	64.184	-48.460	24.584
4800	6.033	59.832	62.752	-51.896	25.584
4900	6.020	59.887	61.300	-55.372	26.584
5000	6.007	59.932	59.828	-58.888	27.584
5100	5.994	59.968	58.336	-62.444	28.584
5200	5.981	59.995	56.824	-66.040	29.584
5300	5.968	60.013	55.292	-69.676	30.584
5400	5.955	60.022	53.740	-73.352	31.584
5500	5.942	60.022	52.168	-77.068	32.584
5600	5.929	60.013	50.576	-80.824	33.584
5700	5.916	60.000	48.964	-84.620	34.584
5800	5.903	60.000	47.332	-88.456	35.584
5900	5.890	60.000	45.680	-92.332	36.584
6000	5.877	60.000	44.008	-96.248	37.584

Sept. 30, 1967

COBALT, MONATOMIC (Co)

Ground State Configuration $4f_7/2$

(IDEAL GAS)

GFV = 58.9332

$\Delta H_f^\circ = 101.1 \pm 0.5$ kcal/mol
 $\Delta H_f^\circ_{298.15} = 101.5 \pm 0.5$ kcal/mol

Electronic Levels and Multiplicities

ϵ_i cm ⁻¹	g_i	ϵ_i cm ⁻¹	g_i	ϵ_i cm ⁻¹	g_i	ϵ_i cm ⁻¹	g_i
0	10	5076	4	15774	4	23184	10
816	8	7442	8	16196	2	23208	8
1407	6	8461	6	16467	10	24466	42
1809	4	13796	6	17234	8	25590	30
3483	10	14036	4	16471	4	25987	54
4143	8	14399	2	16778	6	27983	10
4690	6	15184	6	18390	4	28975	28

Heat of Formation

The heat of formation is the heat of sublimation at 298°K. The adopted value is that reported by Edwards et al. (1). Their value is used because their vapor pressure measurements for Fe (1) and Cu (2) have proved to be very reliable. The results obtained by Vintaikin and Tomash (3) are rejected because their vapor pressure data for Fe (4) resulted in a value for the heat of sublimation which was higher than the accepted value [see JANAF Fe(g) Table for details]. The remaining vapor pressure data are rejected either because the drift was too large or because there were not enough points. Second and third law analyses of the available vapor pressure data gave the following results, with reaction A corresponding to $\text{Co(c)} = \text{Co(g)}$ and reaction B corresponding to $\text{Co(l)} = \text{Co(g)}$.

Source	Reaction	Method	No. Pts.	Range, T°K	$\Delta H_f^\circ_{298.15}$ 2nd Law	$\Delta H_f^\circ_{298.15}$ 3rd Law	Drift, eu
Edwards (1)	A	Langmuir	9	1363-1522	101.0 ± 1.0	101.54	$+0.4 \pm 0.7$
Kornev (5)	A	Knudsen	8*	1323-1523	98.8 ± 0.8	95.37	-2.4 ± 0.6
Dancy (6)	B	Langmuir	1	1823	--	90.61	--
Ruff (7)	B	Boiling Pt.	1	2648	--	99.35	--
Nesmeyanov (8)	A	Knudsen	3	1391-1540	82.4 ± 2.4	82.31	-0.1 ± 1.6
Nesmeyanov (9)	A	Knudsen	12*	1345-1541	91.7 ± 2.4	83.19	-5.9 ± 1.7
Vintaikin (3)	A	Knudsen	Eqn.	1373-1523	102.9	103.34	+0.3

*One point rejected due to failure of a statistical test.

**Calculation based on third law $\Delta H_f^\circ_{298}$.

Heat Capacity and Entropy

The electronic levels are taken from Moore (10). Levels above 25,000 cm⁻¹ are averaged. Unobserved levels below 20,000 cm⁻¹ are estimated.

References

- J. W. Edwards, H. L. Johnston and W. E. Dimars, J. Am. Chem. Soc. **73**, 4729 (1951).
- J. W. Edwards, H. L. Johnston and W. E. Dimars, J. Am. Chem. Soc. **75**, 2467 (1953).
- E. Z. Vintaikin and Ya. Tomash, Russ. J. Phys. Chem. (English Transl.) **35**, 1042 (1961).
- E. Z. Vintaikin, Dokl. Akad. Nauk SSSR **117**, 632 (1957).
- Iu. V. Kornev and V. N. Golubkin, Dokl. Akad. Nauk SSSR **53**, 565 (1954).
- T. E. Dancy, J. Iron Steel Inst. (London) **167**, 160 (1951).
- O. Ruff and F. Keilig, Z. Anorg. Chem. **129**, 321 (1914).
- A. N. Nesmeyanov and D. D. Man, Dokl. Akad. Nauk SSSR **123**, 1064 (1959).
- A. N. Nesmeyanov and D. D. Man, Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk, No. 1 (1960).
- C. E. Moore, U. S. Natl. Bur. Std. Circ. **467** (1949).

Sept. 30, 1967

Ground State Configuration $3F_4$
 $\Delta H_f^\circ = 282.50 \pm 0.5 \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = 42.6 \pm 0.1 \text{ gibbs/mol}$
 $\Delta H_f^\circ = 282.50 \pm 0.5 \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = 284.34 \pm 0.5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	8	13761	5	27484	7
950	7	13405	3	28112	5
1597	5	13594	1	27585	3
3351	11	17772	7	41738	25
4029	9	18032	5	45972	35
4561	7	18339	3	47667	69
4950	5	24075	5	49865	48
5205	3	24268	3	52230	15
9813	9	24412	1	56011	5
10708	7	24887	5	62670	58
11322	5	26000	4	84127	131

Heat of Formation

The heat of formation, ΔH_f° , is calculated from the equation $\text{Co(g)} = e^- + \text{Co}^+(\text{g})$ with the JANAF auxiliary value for Co(g) ; using an ionization potential of 69438 cm^{-1} (191.377 kcal/mol) obtained from C. E. Moore, "Atomic Energy Levels," Vol. II, U. S. Natl. Bur. Std. Circ. 467, 1949. The value of $H_0^\circ - H_{298}^\circ$ is -1.504 kcal/mol .

Heat Capacity and Entropy

The electronic levels and quantum weights are taken from C. E. Moore, loc. cit. Levels above $30,000 \text{ cm}^{-1}$ are averaged.

T, °K	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°	Log Kp
0							
100	5.123	42.599	62.599	.000	284.341	272.293	-199.596
200	5.320	42.632	62.590	.010	284.349	272.219	-199.311
300	5.482	42.609	62.612	.559	284.110	264.110	-196.608
400	5.617	42.595	62.628	1.115	285.200	263.894	-115.348
500	5.715	42.579	62.645	1.740	285.600	259.595	-94.457
600	5.785	42.561	62.661	2.337	285.977	255.977	-78.464
700	5.831	42.545	62.675	2.903	286.330	252.903	-65.464
800	5.867	42.531	62.687	3.437	286.552	249.363	-55.330
900	5.895	42.518	62.697	3.942	286.682	245.904	-47.868
1000	5.915	42.506	62.704	4.418	286.728	242.628	-42.167
1100	5.928	42.495	62.709	4.865	286.788	239.548	-37.167
1200	5.936	42.485	62.713	5.285	286.850	236.660	-32.860
1300	5.940	42.476	62.716	5.680	286.912	233.962	-29.155
1400	5.942	42.468	62.718	6.052	286.972	231.452	-25.950
1500	5.943	42.461	62.720	6.408	287.030	229.130	-23.150
1600	5.944	42.455	62.721	6.748	287.085	226.995	-20.750
1700	5.945	42.450	62.722	7.072	287.138	225.048	-18.750
1800	5.946	42.445	62.723	7.382	287.188	223.280	-17.050
1900	5.947	42.441	62.724	7.678	287.235	221.680	-15.600
2000	5.948	42.437	62.725	7.960	287.278	220.230	-14.350
2100	5.949	42.434	62.726	8.228	287.318	218.930	-13.250
2200	5.950	42.431	62.727	8.482	287.355	217.780	-12.250
2300	5.951	42.428	62.728	8.722	287.388	216.780	-11.350
2400	5.952	42.426	62.729	8.948	287.418	215.930	-10.550
2500	5.953	42.424	62.730	9.162	287.445	215.230	-9.850
2600	5.954	42.422	62.731	9.365	287.468	214.680	-9.250
2700	5.955	42.420	62.732	9.558	287.488	214.280	-8.750
2800	5.956	42.418	62.733	9.740	287.505	213.930	-8.350
2900	5.957	42.416	62.734	9.912	287.518	213.630	-8.050
3000	5.958	42.414	62.735	10.075	287.528	213.380	-7.800
3100	5.959	42.412	62.736	10.228	287.535	213.180	-7.600
3200	5.960	42.410	62.737	10.372	287.540	213.030	-7.450
3300	5.961	42.408	62.738	10.508	287.543	212.930	-7.350
3400	5.962	42.406	62.739	10.635	287.545	212.880	-7.300
3500	5.963	42.404	62.740	10.755	287.546	212.880	-7.250
3600	5.964	42.402	62.741	10.868	287.546	212.930	-7.200
3700	5.965	42.400	62.742	10.975	287.545	213.030	-7.150
3800	5.966	42.398	62.743	11.075	287.543	213.180	-7.100
3900	5.967	42.396	62.744	11.168	287.540	213.380	-7.050
4000	5.968	42.394	62.745	11.255	287.535	213.630	-7.000
4100	5.969	42.392	62.746	11.338	287.528	213.930	-6.950
4200	5.970	42.390	62.747	11.415	287.518	214.280	-6.900
4300	5.971	42.388	62.748	11.488	287.505	214.680	-6.850
4400	5.972	42.386	62.749	11.558	287.488	215.130	-6.800
4500	5.973	42.384	62.750	11.625	287.468	215.630	-6.750
4600	5.974	42.382	62.751	11.688	287.445	216.180	-6.700
4700	5.975	42.380	62.752	11.748	287.418	216.780	-6.650
4800	5.976	42.378	62.753	11.805	287.388	217.430	-6.600
4900	5.977	42.376	62.754	11.858	287.355	218.130	-6.550
5000	5.978	42.374	62.755	11.908	287.318	218.880	-6.500
5100	5.979	42.372	62.756	11.955	287.278	219.680	-6.450
5200	5.980	42.370	62.757	12.000	287.235	220.530	-6.400
5300	5.981	42.368	62.758	12.042	287.188	221.430	-6.350
5400	5.982	42.366	62.759	12.082	287.138	222.380	-6.300
5500	5.983	42.364	62.760	12.118	287.085	223.380	-6.250
5600	5.984	42.362	62.761	12.152	287.030	224.430	-6.200
5700	5.985	42.360	62.762	12.183	286.972	225.530	-6.150
5800	5.986	42.358	62.763	12.212	286.912	226.680	-6.100
5900	5.987	42.356	62.764	12.238	286.850	227.880	-6.050
6000	5.988	42.354	62.765	12.262	286.788	229.130	-6.000

(CRYSTAL)

COBALT DIFLUORIDE (CoF₂)

GFW = 96.9300

$$\Delta H_f^\circ = -160.2 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -160.5 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 14.058 \pm 3.0 \text{ kcal/mol}$$

$$\Delta H_s^\circ = 75.3 \pm 3.0 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 19.60 \pm 0.10 \text{ gibbs/mol}$$

$$T_m = 1400^\circ\text{K}$$

Cobalt Difluoride (CoF₂)

(Crystal)

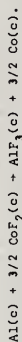
GFW = 96.9300

T, °K	Cp ^a	gibbs/mol S ^b	-(G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K ^e
0	0.000	INFINITE	-	2.978	-160.229	-160.229	INFINITE
100	6.005	5.976	32.192	2.652	-160.692	-157.036	343.201
200	13.763	13.563	21.032	1.494	-160.721	-153.341	167.563
298	16.470	19.605	19.605	0.000	-160.500	-149.760	109.777
300	16.501	19.707	19.605	0.31	-160.494	-149.494	109.052
400	18.096	24.701	20.275	1.770	-160.139	-146.144	79.849
500	18.864	28.630	21.586	3.652	-159.748	-142.691	62.370
600	19.309	32.312	23.091	5.533	-159.361	-139.316	50.746
700	19.616	35.846	24.611	7.414	-158.974	-135.949	40.600
800	19.816	39.244	26.131	9.290	-158.587	-132.580	31.446
900	19.979	42.487	27.576	11.160	-158.199	-129.212	23.602
1000	20.115	45.600	28.954	13.035	-157.812	-125.844	16.802
1100	20.231	48.622	30.265	14.906	-157.425	-122.476	11.100
1200	20.329	51.566	31.521	16.771	-157.038	-119.108	6.465
1300	20.412	54.436	32.741	18.529	-156.651	-115.740	2.742
1400	20.476	57.236	33.928	20.287	-156.264	-112.372	0.000
1500	20.525	59.975	35.083	22.045	-155.877	-109.004	-2.742
1600	20.578	62.666	36.226	23.803	-155.490	-105.636	-5.484
1700	20.625	65.312	37.351	25.561	-155.103	-102.268	-8.226
1800	20.667	67.916	38.467	27.319	-154.716	-98.900	-10.968
1900	20.699	70.489	39.571	29.077	-154.329	-95.532	-13.710
2000	20.726	73.032	40.667	30.835	-153.942	-92.164	-16.452

June 30, 1970

Heat of Formation

Heus and Egan (1) measured the electromotive force of a solid state galvanic cell which involved the reactions



$$E_{973} = 1.611 \text{ volts}$$

$$E_{973} = 2.231 \text{ volts}$$

Combining these results with auxiliary thermodynamic data (2) for the reactants and products, we derive $\Delta H_f^\circ(\text{CoF}_2, \text{c}) = -160.2$ and -159.5 kcal/mol .

Several equilibrium studies (3, 4, 5) involving $\text{CoF}_2(\text{c})$ have been reported in the literature. Second and third law analyses of these equilibrium data are summarized below, auxiliary data for Co(c) and $\text{CoCl}_2(\text{c})$ are from (6).

Reference	Chemical Reaction	Temp. Range °K	Points	ΔH_{298}° kcal/mol	2nd law gibbs/mol	3rd law gibbs/mol	Drift gibbs/mol	$\Delta H_f^\circ(\text{CoF}_2, \text{c})$ kcal/mol
(3)	$\text{CoF}_2(\text{c}) + 2\text{HCl(g)} \rightleftharpoons \text{CoCl}_2(\text{c}) + 2\text{HF(g)}$	588-605	3	4.1	1.75±0.4	-1.7±0.1	-162.5±2.0	
(4)	$\text{CoF}_2(\text{c}) + \text{H}_2(\text{g}) \rightleftharpoons \text{Co(c)} + 2\text{HF(g)}$	673-673	3	35.2	31.5±1.0	-4.2±3.5	-161.8±2.0	
(5)	$\text{CoF}_2(\text{c}) + \text{H}_2\text{O(g)} \rightleftharpoons \text{CoO(c)} + 2\text{HF(g)}$	773-1023	5	30.2	31.1±0.2	0.9±0.3	-160.4±2.0	

*Third law values except for the first reaction.

We note that Heus and Egan (1), in the same paper, measured $\Delta H_f^\circ(\text{AlF}_3, \text{c}) = -360.2 \text{ kcal}$ in excellent agreement with the JANAF value (2). Domange (5) also measured similar equilibria for MgF_2 and CaF_2 , which were very consistent with the JANAF heats of formation (2). Jellinek and Rudat (4) reported similar equilibria for $\text{PbF}_2(\text{c})$, which show excellent consistency with the JANAF heat of formation (2). Thus, it is apparent that these three sets are probably quite reliable, and we adopt $\Delta H_f^\circ(\text{CoF}_2, \text{c}) = -160.5 \pm 1 \text{ kcal/mol}$.

Heat Capacity and Entropy

Catalano and Stout (7) measured low temperature heat capacities in the temperature range 10° to 300°K . Heat capacity data above 300°K are calculated from the high temperature (458-1400°K) enthalpy data of Binford et al. (8). Both sets of data were smoothed by computer and joined at 298.15°K .

The value of $S_{298.15}^\circ$ is obtained from the low temperature heat capacity data of Catalano and Stout (7) and is based on $S_{10}^\circ = 0.013 \text{ gibbs/mol}$.

Melting Data

$T_m = 1400^\circ\text{K}$ is from the high temperature enthalpy studies of Binford et al. (8). ΔH_m is calculated from their enthalpy data. Premelting of the sample is assumed to be responsible for the rapid rise in the enthalpy near the melting point. This enthalpy is included in ΔH_m .

Heat of Sublimation

Kana'an et al. (9) made sublimation studies of CoF_2 using Knudsen and Langmuir techniques over the temperature range 972° to 1241°K . Second and third law analyses of these sublimation pressures are summarized below.

Method	Temp. Range °K	No. of Points	ΔH_{298}° kcal/mol	2nd law gibbs/mol	3rd law gibbs/mol	Drift gibbs/mol
Knudsen	1058-1242	17	75.0	75.1±0.1	0.1±0.2	
Langmuir	972-1032	6	72.8	75.5±0.2	2.6±1.4	

The selected value is $\Delta H_{298}^\circ = 75.3 \pm 3.0 \text{ kcal/mol}$.

References

1. R. J. Heus and J. J. Egan, *Z. Phys. Chem.*, **23**, 38 (1956).
2. JANAF Thermochemical Tables; AlF_3 dated 6-30-70; MgF_2 dated 3-31-66; PbF_2 dated 6-30-69; CaF_2 dated 12-31-68.
3. K. Jellinek and R. Koop, *Z. Phys. Chem.*, **23**, 305 (1929).
4. K. Jellinek and A. Rudat, *Z. Anorg. Chem.*, **23**, 281 (1928).
5. L. Domange, *Ann. Chim.*, **2**, 225 (1947).
6. U. S. Natl. Bur. Std. Techn. Note 270-4, 1969.
7. E. Catalano and J. M. Stout, *J. Chem. Phys.*, **23**, 1803 (1955).
8. J. S. Binford, Jr., J. M. Stout, J. H. Strohmenger, and T. H. Hebert, *J. Phys. Chem.*, **71**, 2404 (1967).
9. A. S. Kana'an, G. Besenbruch, and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **25**, 1035 (1966).

(LIQUID)

COBALT DIFLUORIDE (CoF₂)

GFW = 96.9300

$$S_{298.15}^{\circ} = 20.61 \pm 2.5 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = -152.412 \pm 4.0 \text{ kcal/mol}$$

$$T_m = 1400^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 14.058 \pm 3.0 \text{ kcal/mol}$$

$$T_b = 12012^{\circ}\text{K}$$

$$\Delta H_v^{\circ} = [48.0] \text{ kcal/mol}$$

Heat of Formation

$\Delta H_f^{\circ}(l)$ is calculated from $\Delta H_f^{\circ}(c)$ by adding the heat of melting and the difference in $(H_{1400}-H_{298})$ between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of liquid CoF₂ is estimated by comparison with those for FeCl₂(l), MgF₂(l), and PbF₂(l) and is assumed constant in the temperature range 298°-3000°K. Binford et al. (1) reported $C_p = 30.3$ gibbs/mol for liquid CoF₂ at 1444°K. This value is based on only two enthalpy points near the melting point and appears high in comparison with heat capacities for other liquid metal dihalides. Therefore, the value is not adopted.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the CoF₂(c) table for details.

Vaporization Data

T_b is the temperature at which the Gibbs energy change for the process CoF₂(l) + CoF₂(g) approaches zero. The difference between the heat of formation of the gas and liquid at T_b is ΔH_v° .

Reference

1. J. S. Binford, Jr., J. M. Strohmenger, and T. H. Hebert, J. Phys. Chem., **71**, 2404 (1967).

Cobalt Difluoride (CoF₂)

(Liquid) GFW = 96.9300

T, °K	C _p ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0							
100							
200							
298	25.000	20.611	20.611	0.000	-152.412	-141.972	104.068
300	25.000	20.766	20.611	.066	-152.391	-141.908	103.300
400	25.000	27.958	21.592	2.546	-151.275	-138.535	95.741
500	25.000	33.536	23.484	5.046	-150.236	-135.532	87.241
600	25.000	38.094	25.517	7.546	-149.260	-132.684	80.330
700	25.000	41.948	27.596	10.046	-148.337	-129.995	74.586
800	25.000	45.266	29.604	12.546	-147.563	-127.421	69.810
900	25.000	48.231	31.513	15.046	-146.836	-124.952	65.783
1000	25.000	50.865	33.319	17.546	-146.157	-122.574	62.368
1100	25.000	53.248	35.024	20.046	-145.526	-120.286	59.495
1200	25.000	55.423	36.634	22.546	-144.941	-118.020	57.049
1300	25.000	57.424	38.158	25.046	-144.400	-115.821	54.971
1400	25.000	59.277	39.601	27.546	-143.903	-113.682	53.122
1500	25.000	61.002	40.971	30.046	-143.450	-111.620	51.468
1600	25.000	62.615	42.274	32.546	-143.046	-109.629	50.000
1700	25.000	64.131	43.515	35.046	-142.685	-107.707	48.697
1800	25.000	65.560	44.701	37.546	-142.366	-105.849	47.530
1900	25.000	66.911	45.834	40.046	-142.088	-104.051	46.480
2000	25.000	68.194	46.921	42.546	-141.850	-102.313	45.530
2100	25.000	69.413	47.963	45.046	-141.650	-100.625	44.680
2200	25.000	70.576	48.964	47.546	-141.485	-99.000	43.920
2300	25.000	71.688	49.928	50.046	-141.350	-97.437	43.250
2400	25.000	72.752	50.857	52.546	-141.240	-95.930	42.660
2500	25.000	73.772	51.754	55.046	-141.150	-94.477	42.140
2600	25.000	74.753	52.620	57.546	-141.080	-93.070	41.680
2700	25.000	75.696	53.457	60.046	-141.020	-91.707	41.280
2800	25.000	76.605	54.268	62.546	-140.970	-90.380	40.930
2900	25.000	77.483	55.053	65.046	-140.930	-89.087	40.630
3000	25.000	78.330	55.815	67.546	-140.900	-87.820	40.380

June 30, 1970

GF_N = 96.9300

(IDEAL GAS)

COBALT DIFLUORIDE (CoF₂)Point Group (C_{2v})JHf₀^{*} = -85.0 ± 3.0 kcal/molJHf_{298.15}^{*} = -85.2 ± 3.0 kcal/molS_{298.15}^{*} = [66.42 ± 3.0] gibbs/molGround State Configuration [³Σ]Cobalt Difluoride (CoF₂)(Ideal Gas) GF_N = 96.9300

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	9.821	54.359	INFINITE	3.093	-85.044	-85.044	INFINITE
100	11.156	57.876	76.866	2.231	-85.001	-86.183	186.353
200	12.239	60.421	68.421	1.000	-85.000	-86.416	93.439
300	12.252	66.497	66.422	-0.23	-85.202	-84.427	64.427
400	12.793	70.102	66.909	1.277	-85.332	-84.439	48.899
500	13.126	72.996	67.847	2.574	-85.486	-84.522	39.567
600	13.341	75.409	68.912	3.899	-85.695	-84.509	33.332
700	13.494	77.478	69.991	5.241	-85.930	-84.459	28.687
800	13.613	79.288	71.042	6.596	-86.301	-84.360	25.505
900	13.713	80.897	72.059	7.963	-86.609	-84.223	22.861
1000	13.803	82.347	73.008	9.338	-86.973	-84.051	20.773
1100	13.865	83.666	73.918	10.723	-87.397	-83.839	19.041
1200	13.960	84.877	74.781	12.115	-87.600	-83.584	17.590
1300	14.029	85.998	75.602	13.515	-87.849	-83.286	16.355
1400	14.093	87.040	76.382	14.921	-88.222	-82.935	15.268
1500	14.150	88.014	77.125	16.333	-88.713	-82.540	14.357
1600	14.202	88.929	77.835	17.751	-89.140	-82.115	13.536
1700	14.250	89.791	78.513	19.173	-89.543	-81.662	12.812
1800	14.293	90.607	79.162	20.601	-89.832	-81.119	12.156
1900	14.331	91.361	79.785	22.032	-89.999	-80.539	11.569
2000	14.366	92.117	80.383	23.467	-90.055	-100.655	10.999
2100	14.397	92.819	80.959	24.905	-90.213	-100.690	10.500
2200	14.425	93.469	81.513	26.346	-90.673	-101.102	10.084
2300	14.450	94.131	82.048	27.790	-91.132	-101.484	9.625
2400	14.473	94.746	82.565	29.236	-91.592	-101.804	9.240
2500	14.493	95.337	83.064	30.684	-92.053	-101.616	8.883
2600	14.510	95.906	83.547	32.134	-92.514	-101.749	8.553
2700	14.526	96.454	84.015	33.586	-92.975	-101.604	8.245
2800	14.539	96.983	84.468	35.040	-93.436	-101.963	7.959
2900	14.551	97.493	84.909	36.494	-93.900	-102.044	7.690
3000	14.561	97.987	85.337	37.950	-94.365	-102.113	7.439
3100	14.569	98.464	85.752	39.406	-94.831	-102.163	7.202
3200	14.576	98.927	86.157	40.864	-95.294	-101.382	6.929
3300	14.582	99.375	86.551	42.321	-95.759	-101.362	6.629
3400	14.586	99.811	86.934	43.780	-96.082	-95.789	6.157
3500	14.589	100.234	87.308	45.239	-96.620	-92.994	5.487
3600	14.591	100.645	87.673	46.698	-96.980	-90.197	5.476
3700	14.592	101.044	88.029	48.157	-97.105	-87.366	5.162
3800	14.592	101.434	88.377	49.616	-97.1254	-84.590	4.865
3900	14.591	101.813	88.716	51.075	-97.1409	-81.784	4.563
4000	14.590	102.182	89.046	52.534	-97.1568	-78.969	4.315
4100	14.588	102.542	89.373	53.993	-97.1733	-76.153	4.059
4200	14.585	102.894	89.691	55.452	-97.1903	-73.332	3.816
4300	14.581	103.237	90.002	56.910	-97.2080	-70.505	3.583
4400	14.577	103.572	90.307	58.368	-97.2264	-67.677	3.362
4500	14.573	103.900	90.605	59.825	-97.2455	-64.845	3.149
4600	14.568	104.220	90.898	61.282	-97.2652	-62.006	2.946
4700	14.563	104.533	91.184	62.739	-97.2857	-59.164	2.751
4800	14.557	104.860	91.466	64.195	-97.3069	-56.315	2.564
4900	14.551	105.180	91.742	65.650	-97.3291	-53.464	2.385
5000	14.545	105.434	92.013	67.105	-97.3520	-50.609	2.212
5100	14.539	105.722	92.279	68.559	-97.3757	-47.751	2.046
5200	14.532	106.004	92.540	70.013	-97.4003	-44.882	1.886
5300	14.526	106.281	92.796	71.466	-97.4257	-42.010	1.732
5400	14.519	106.552	93.049	72.918	-97.4522	-39.140	1.584
5500	14.512	106.816	93.297	74.370	-97.4794	-36.259	1.441
5600	14.505	107.080	93.540	75.821	-97.5076	-33.372	1.302
5700	14.498	107.337	93.780	77.271	-97.5368	-30.482	1.169
5800	14.491	107.589	94.016	78.720	-97.5668	-27.587	1.039
5900	14.483	107.836	94.246	80.169	-97.5978	-24.689	0.915
6000	14.476	108.080	94.477	81.617	-97.6296	-21.783	0.793

Juna 30, 1970

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	4
[300]	[4]
[4000]	[4]
[8000]	[4]

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹
[600] (1)
[1511] (1)
762 (1)

Bond Distance: Co-F = [1.72] Å

Bond Angle: F-Co-F = [165°]

Product of Moments of Inertia: $I_A I_B I_C = 6.5424 \times 10^{-116} \text{ g cm}^6$ $\sigma = 2$

Heat of Formation

The heat of formation of gaseous CoF₂, $\Delta H_f^\circ = -88.1 \pm 7.0$ kcal/mol, is calculated from the heat of formation of the crystal, $\Delta H_{298}^\circ = -163.4 \pm 4.0$ kcal/mol, and the heat of sublimation, $\Delta H_{298}^\circ = 75.3 \pm 3.0$ kcal/mol. The sublimation value is determined from a third law analysis of the vapor pressure data for CoF₂ reported by Kana'an at al. (1). See CoF₂(c) table for details.

Heat Capacity and Entropy

Büchler et al. (2) investigated the deflection of a molecular beam of CoF₂(g) by an electric field and found that within the sensitivity of the apparatus the molecule was nonpolar and consequently possessed a linear structure. Hastie et al. (3) recently investigated the infrared absorption spectra of several transition metal difluorides through the use of matrix isolation techniques. Isotopic shift measurements for matrix isolated NiF₂, ZnF₂, and CuF₂ in neon and argon indicated that these species were slightly bent. Based upon these results, the authors estimated the F-Co-F angle as 165°. This value is adopted here. The bond length was estimated by Bravar at al. (4). Individual moments of inertia are $I_A = 0.1925 \times 10^{-39}$, $I_B = 18.341 \times 10^{-39}$, and $I_C = 18.533 \times 10^{-39} \text{ g cm}^2$. Hastie et al. (3) isolated CoF₂ in neon and argon matrices and observed the ν_3 fundamental at 762 cm⁻¹. They also calculated $\nu_1 = 600 \text{ cm}^{-1}$ by a valence force field method and estimated ν_2 as 151 cm⁻¹ by applying the variation in the frequencies for the chlorides of Co, Ni, Cu, and Zn to the fluorides. The electronic levels and quantum weights are estimated by comparison with the electronic energy levels for Co²⁺(g) ion (5) and those for CoCl₂(g) observed by Hough et al. (6).

References

1. A. S. Kana'an, G. Basanbruch, and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **28**, 1035 (1966).
2. A. Büchler, J. L. Stauffer, and W. Kienparar, *J. Chem. Phys.*, **40**, 3471 (1964).
3. J. W. Hastie, R. H. Hauge, and J. L. Margrave, *High Temperature Science*, **1**, 76 (1969).
4. L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Rev.*, **63**, 111 (1963).
5. C. E. Moore, *U. S. Natl. Bur. Std. Circ.* 467, Vol. II, 1952.
6. J. T. Hough, G. E. Larosi, and T. C. James, *J. Chem. Phys.*, **34**, 1670 (1961).

Cesium (Cs)

(Reference State) GFW = 132.905

CESIUM (Cs)

(REFERENCE STATE)

GFW = 132.905

T, °K	Cp ^o	S ^o gibbs/mol	-(G ^o -H ^o)/T	H ^o -H ^o 298	ΔH ^o kcal/mol	ΔG ^o	Log Kp
0	.000	.000	INFINITE	-1.844	.000	.000	.000
100	6.16 ^a	13.13 ^a	26.443	-1.331	.000	.000	.000
200	6.665	21.007	1.690	.000	.000	.000	.000
298	7.655	26.351	.000	.000	.000	.000	.000
300	7.733	26.359	20.351	.014	.000	.000	.000
400	7.533	24.265	21.059	1.276	.000	.000	.000
500	7.446	23.920	21.871	2.025	.000	.000	.000
600	7.405	23.674	22.685	2.767	.000	.000	.000
700	7.395	23.485	23.505	3.507	.000	.000	.000
800	7.394	23.402	24.094	4.247	.000	.000	.000
900	7.357	23.253	24.733	4.986	.000	.000	.000
1000	7.358	23.146	25.414	5.725	.000	.000	.000
1100	7.358	23.078	26.142	6.464	.000	.000	.000
1200	7.358	23.033	26.910	7.203	.000	.000	.000
1300	7.358	23.000	27.718	7.942	.000	.000	.000
1400	7.358	23.000	28.566	8.681	.000	.000	.000
1500	7.358	23.000	29.454	9.420	.000	.000	.000
1600	7.358	23.000	30.382	10.159	.000	.000	.000
1700	7.358	23.000	31.350	10.947	.000	.000	.000
1800	7.358	23.000	32.358	11.785	.000	.000	.000
1900	7.358	23.000	33.406	12.673	.000	.000	.000
2000	7.358	23.000	34.494	13.611	.000	.000	.000
2100	7.358	23.000	35.622	14.599	.000	.000	.000
2200	7.358	23.000	36.790	15.637	.000	.000	.000
2300	7.358	23.000	38.000	16.725	.000	.000	.000
2400	7.358	23.000	39.250	17.863	.000	.000	.000
2500	7.358	23.000	40.540	19.051	.000	.000	.000
2600	7.358	23.000	41.870	20.289	.000	.000	.000
2700	7.358	23.000	43.250	21.577	.000	.000	.000
2800	7.358	23.000	44.670	22.915	.000	.000	.000
2900	7.358	23.000	46.130	24.303	.000	.000	.000
3000	7.358	23.000	47.630	25.741	.000	.000	.000
3100	7.358	23.000	49.170	27.229	.000	.000	.000
3200	7.358	23.000	50.750	28.767	.000	.000	.000
3300	7.358	23.000	52.370	30.355	.000	.000	.000
3400	7.358	23.000	54.030	31.993	.000	.000	.000
3500	7.358	23.000	55.730	33.681	.000	.000	.000
3600	7.358	23.000	57.470	35.419	.000	.000	.000
3700	7.358	23.000	59.250	37.207	.000	.000	.000
3800	7.358	23.000	61.070	39.045	.000	.000	.000
3900	7.358	23.000	62.930	40.933	.000	.000	.000
4000	7.358	23.000	64.830	42.871	.000	.000	.000
4100	7.358	23.000	66.770	44.859	.000	.000	.000
4200	7.358	23.000	68.750	46.897	.000	.000	.000
4300	7.358	23.000	70.770	48.985	.000	.000	.000
4400	7.358	23.000	72.830	51.123	.000	.000	.000
4500	7.358	23.000	74.930	53.311	.000	.000	.000
4600	7.358	23.000	77.070	55.549	.000	.000	.000
4700	7.358	23.000	79.250	57.837	.000	.000	.000
4800	7.358	23.000	81.470	60.175	.000	.000	.000
4900	7.358	23.000	83.730	62.563	.000	.000	.000
5000	7.358	23.000	86.030	64.901	.000	.000	.000
5100	7.358	23.000	88.370	67.289	.000	.000	.000
5200	7.358	23.000	90.750	69.727	.000	.000	.000
5300	7.358	23.000	93.170	72.215	.000	.000	.000
5400	7.358	23.000	95.630	74.753	.000	.000	.000
5500	7.358	23.000	98.130	77.341	.000	.000	.000
5600	7.358	23.000	100.670	79.979	.000	.000	.000
5700	7.358	23.000	103.250	82.667	.000	.000	.000
5800	7.358	23.000	105.870	85.405	.000	.000	.000
5900	7.358	23.000	108.530	88.193	.000	.000	.000
6000	7.358	23.000	111.230	91.031	.000	.000	.000

June 30, 1968

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	kcal/mol H° - H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	INFINITE	- 1.644	.000	.000	INFINITE
100	6.169	13.134	- 1.331	.000	.000	.000
200	6.445	17.536	- .980	.000	.000	.000
298	7.495	26.351	.000	.000	.000	.000
300	7.733	26.395	.014	.000	.000	.000
400	8.620	22.775	.842	.434	.156	.585
500	8.850	24.733	1.792	.305	.289	.724
600	8.670	26.361	2.614	.153	.394	.844
700	8.590	27.746	3.512	.005	.473	.948
800	8.595	28.647	4.411	.000	.528	1.044
900	8.600	30.006	5.311	.000	.565	1.137
1000	8.600	30.455	6.211	.000	.596	1.204

CESIUM (Cs)

(CRYSTAL)

GFW = 132.905

$$\Delta H_f^\circ = 0 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = 0 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 0.499 \pm 0.001 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = 18.32 \text{ kcal/mol}$$

$$S^\circ_{298.15} = 20.351 \pm 0.05 \text{ gibbs/mol}$$

$$T_m = 301.55 \pm 0.01^\circ \text{K}$$

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Lien (4), Filby (3), and Horgan (5). The adopted values are derived based on the Cp data reported by Filby (3) and Lien (4). Lien measured the heat capacities in the temperature range 0.1874 to 1.20°K in the adiabatic demagnetization cryostat and at higher temperatures, 1.2 to 4.09°K, in the liquid-helium temperature cryostat. The Cs sample was obtained from a commercial source of 99.8 per cent purity. Filby determined the Cp values in the temperature ranges 0.4-1.5°K, 3-26°K and 20-320°K, using commercial samples of 99.9 per cent purity. These two sets of measurements are joined smoothly at 4°K. S_{298.15} is derived from the adopted heat capacities, based on S_{0,20} = 0.0002 eu.

Dauphinee (1) determined the heat capacities of Cs(c) employing a sample badly contaminated with oxygen. In the temperature range of approximately 100 to 200°K, an anomaly of Cp curve somewhat similar to those found for sodium and potassium was reported. This anomaly was not observed by Filby who used the higher purity cesium sample. The Cp values reported by Dauphinee are lower than the adopted ones by about 0.5 to 1.5 per cent in the temperatures 55 to 220°K; above 270°K his reported heat capacities are unreasonably high. Therefore the data are not adopted for evaluation. McCollum (2) calculated the Debye 8 values from the measured low temperature heat capacities and plotted them, since no numerical data were reported these were not used. The low temperature Cp values determined by Martin (3) and Horgan (5) are in good agreement with the adopted ones.

Melting Data

See Cs(4) table for details.

Heat of Sublimation

ΔH_{sub}[°]_{298.15} is calculated as the difference between ΔH_f[°]_{298.15} for Cs(g) and Cs(c).

References

1. T. M. Dauphinee, D. L. Martin and H. Preston-Thomas, Proc. Roy. Soc. (London) **A233**, 214 (1955), 20-320°K.
2. D. C. McCollum, Jr. and H. B. Silsbee, Phys. Rev. **127**, 119 (1962), 1.3-12°K.
3. B. D. Martin, D. A. Zych and C. V. Heer, Phys. Rev. **135**, A871 (1964), 0.36-1.63°K.
4. W. H. Lien and N. E. Phillips, Phys. Rev. **133**, A1370 (1964), 0.19-4.09°K.
5. J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) **A284**, 83 (1965), 0.7-320°K.
6. J. A. Horgan and J. C. Thompson, J. Chem. Phys. **47**, 4607 (1967), 2.1-4.2°K.

T, °K	Cp*	S° - (G° - H° ₂₉₈)/T	gibbs/mol	ΔG°	Log Kp
0	∞	INFINITE	1.481	18.683	INFINITE
100	4.968	36.515	16.328	16.328	35.666
200	4.968	39.397	14.067	14.067	15.330
298	4.968	41.942	11.983	11.983	8.770
300	4.968	41.973	11.843	11.843	8.628
400	4.968	43.402	10.009	10.009	5.403
500	4.968	44.511	8.2505	8.2505	3.498
600	4.968	45.417	6.709	6.709	2.246
700	4.968	46.162	5.330	5.330	1.345
800	4.968	46.816	4.129	4.129	0.713
900	4.968	47.431	3.109	3.109	0.321
1000	4.968	47.958	2.268	2.268	0.000
1100	4.968	48.428	1.604	1.604	0.000
1200	4.968	48.860	1.127	1.127	0.000
1300	4.971	49.258	0.849	0.849	0.000
1400	4.975	49.627	0.646	0.646	0.000
1500	4.981	49.970	0.508	0.508	0.000
1600	4.982	50.292	0.424	0.424	0.000
1700	5.008	50.595	0.369	0.369	0.000
1800	5.031	50.882	0.330	0.330	0.000
1900	5.062	51.154	0.302	0.302	0.000
2000	5.102	51.415	0.280	0.280	0.000
2100	5.158	51.645	0.260	0.260	0.000
2200	5.218	51.846	0.242	0.242	0.000
2300	5.295	52.100	0.224	0.224	0.000
2400	5.385	52.367	0.207	0.207	0.000
2500	5.481	52.589	0.192	0.192	0.000
2600	5.613	52.807	0.178	0.178	0.000
2700	5.752	53.021	0.165	0.165	0.000
2800	5.908	53.233	0.153	0.153	0.000
2900	6.085	53.444	0.142	0.142	0.000
3000	6.282	53.653	0.132	0.132	0.000
3100	6.502	53.863	0.122	0.122	0.000
3200	6.747	54.073	0.112	0.112	0.000
3300	7.018	54.285	0.102	0.102	0.000
3400	7.317	54.498	0.092	0.092	0.000
3500	7.647	54.715	0.082	0.082	0.000
3600	8.004	54.936	0.072	0.072	0.000
3700	8.403	55.160	0.062	0.062	0.000
3800	8.831	55.390	0.052	0.052	0.000
3900	9.284	55.625	0.042	0.042	0.000
4000	9.760	55.867	0.032	0.032	0.000
4100	10.261	56.115	0.022	0.022	0.000
4200	10.786	56.370	0.012	0.012	0.000
4300	11.341	56.633	0.002	0.002	0.000
4400	11.926	56.903	0.000	0.000	0.000
4500	12.541	57.182	0.000	0.000	0.000
4600	13.187	57.468	0.000	0.000	0.000
4700	13.872	57.761	0.000	0.000	0.000
4800	14.612	58.062	0.000	0.000	0.000
4900	15.408	58.370	0.000	0.000	0.000
5000	15.265	58.684	0.000	0.000	0.000
5100	16.484	59.008	0.000	0.000	0.000
5200	16.994	59.328	0.000	0.000	0.000
5300	17.516	59.657	0.000	0.000	0.000
5400	17.989	59.989	0.000	0.000	0.000
5500	18.411	60.323	0.000	0.000	0.000
5600	18.780	60.658	0.000	0.000	0.000
5700	19.051	60.994	0.000	0.000	0.000
5800	19.343	61.328	0.000	0.000	0.000
5900	19.536	61.660	0.000	0.000	0.000
6000	19.668	61.990	0.000	0.000	0.000

June 30, 1968

Ground State Configuration $2s^2_{1/2}$ $S^{\circ}_{298.15} = 41.942 \pm 0.01$ gibbs/mol $\Delta H^{\circ}_0 = 18.68 \pm 0.5$ kcal/mol $\Delta H^{\circ}_{298.15} = 18.32 \pm 0.5$ kcal/mol

Electronic Levels and Quantum Weights

g_i , cm ⁻¹	g_i , cm ⁻¹	g_i , cm ⁻¹
0.00	22588.89	4
11178.24	22631.83	6
11732.35	24317.17	2
14499.49	24472.29	8
14597.08	24472.46	6
18535.51	25784.23	6
21765.65	26616.40	26
21946.66	27363.68	34

Heat of Formation

The total pressures of Cs(g) and Cs₂(g) over Cs(c) and Cs(l) in the temperature range 738.6 to 1268.3°K have been measured, using the boiling point method, by Bonilla (4), Tepper (3) and Achener (2); using the static method, by Kröner (10), Scott (7) and Stone (11); and the positive ion method by Taylor (6). Fichtbauer (8) and Hacksapill (9) have determined the vapor pressures of Cs(l) by a spectroscopic method and P-V-T relationships, respectively. Based on the reported total pressures, the partial pressures of Cs(g) and Cs₂(g) are evaluated by use of dimer-monomer ratios calculated from JANAF free energy functions and $\Delta H^{\circ}_{298.15} = 11.24$ kcal/mol for the reaction $Cs_2(g) = 2Cs(g)$. The value of $\Delta H^{\circ}_{298.15}$ is adopted such that the derived monomer partial pressures give consistent second and third law heats of vaporization. The results are presented in the table below.

Stone et al. (3) measured the vapor pressures of Cs(l) at temperatures 920-1682°K and pressures 0.811-33.53 atm in both the saturation and superheat regions, using a static method and a refractory metal apparatus with a diaphragm as a null-point detector. These vapor pressures reported at temperatures 920-1267.3°K and total pressure below 10 atm are used for evaluation and are reasonably represented by a mixture of monomer and dimer ideal gases. The value of ΔH°_{298} (Cs, g) is adopted as 18.32±0.5 kcal/mol which is derived based on the vapor pressures reported by Stone et al. The results obtained are in reasonable agreement with the values derived from the other vapor pressure sets.

Investigator	Temperature, °K	Points	No. of ΔH°_{298} , kcal/mol	Drift, eu	ΔH°_{298} , kcal/mol*
1. Stone (1966)	920.6-1267.7	79	18.19±0.02	-0.37±0.02	18.32
2. Achener (1964)	751.5-1144.3	15	18.15±0.04	-0.30±0.05	18.38
3. Tepper (1963)	729.3-1268.3	21	18.11±0.02	-0.27±0.02	18.36
4. Bonilla (1962)	674.3-1199.2	41	18.16±0.03	-0.42±0.03	18.26
5. Wathford (1961)	722.2-1277.8	11	18.01±0.01	0.08±0.01	18.59
6. Taylor (1937)	238.6-298.5	8	18.41±0.03	-0.22±0.11	18.35
	303.3-345.8	6	17.75±0.10	0.32±0.31	18.36
7. Scott (1924)	321.4-386.6	8	17.28±0.28	-0.43±0.79	17.63
8. Fichtbauer (1921)	464.1-505.5	4	17.20±0.74	1.86±1.54	18.60
9. Hacksapill (1913)	503.2-670.2	10	18.33±0.47	-0.56±0.80	18.50
10. Kröner (1913)	522.7-628.7	12	18.67±0.44	-1.00±0.76	18.60

*Calculation based on the third law ΔH°_{298} and $\Delta H^{\circ}_{298} = 0$ and 0.499 kcal/mol for Cs(c) and Cs(l), respectively.

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights ($n \leq 10$) are obtained from Moore (11). The electronic levels above 25000 cm⁻¹ are average values calculated from those given by Moore. The missing electronic levels, where quantum number $n = 7, 8, 9$ and 10, and the corresponding quantum weights are estimated according to the method recommended by Gurvich (12). The calculated values at 6000°K, e.g. Cp = 19.668 gibbs/mol and S° = 61.980 eu, are not significantly different from the corresponding values, Cp = 19.650 gibbs/mol and S° = 61.871 eu, obtained from using all the electronic levels reported by Moore for calculation without cutting or adding any levels.

References

1. J. P. Stone, C. T. Ewing, J. R. Spann, E. W. Steinkuller, D. D. Williams, and R. R. Miller, J. Chem. Eng. Data **11**, 309 and 315 (1966).
2. P. Y. Achener, Aerojet-General Nuclear, AGN-8090, January 1964.
3. J. Tepper, A. Hurchison, J. Zelenak, and F. Koehlich, NSA Research Corporation, Callery, Pennsylvania, RTD-TDR-63-4018, 1964; J. Tepper, A. Hurchison, J. Zelenak, and F. Koehlich, NSA Research Corporation, Callery, Pennsylvania, RTD-TDR-63-4018, 1964.
4. F. Bonilla, D. Seckner, and W. M. Wakana, J. Soc. Metals Trans. Quart. **55**, 877 (1962).
5. Vapor pressure data measured by W. D. Weatherford, Jr., and quoted by Tepper (2).
6. J. B. Taylor and I. Langmuir, Phys. Rev. **51**, 753 (1937).
7. D. H. Scott, Phil. Mag. **47**, 32 (1924).
8. C. Fichtbauer, and H. Barthelemy, Z. Physik **4**, 337 (1921).
9. A. Hacksapill, Ann. Chem. Phys. **40**, 438 (1913).
10. C. Kröner, Ann. U. S. Natl. Bur. Std. Circ. **467**, 1958.
11. C. E. Moore, U. S. Natl. Bur. Std. Circ. **35**, 108 (1962).
12. L. V. Gurvich, V. A. Kvitidze, and N. P. Rtsisheva, Russ. J. Phys. Chem. **35**, 108 (1962).

T, °K Cp^o $\frac{\text{cal}}{\text{mole}} \frac{\text{S}^o}{\text{K}} - (\text{G}^o - \text{H}^o_{298})/T$ $\text{H}^o - \text{H}^o_{298}$ $\frac{\text{kcal}}{\text{mole}} \Delta \text{HF}^o$ ΔG^o Log Kp

100									
200	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
250	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
300	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
350	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
400	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
450	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
500	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
600	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
700	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
800	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
900	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
1000	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
1100	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
1200	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
1300	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
1400	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
1500	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
1600	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
1700	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
1800	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
1900	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
2000	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
2100	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
2200	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
2300	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
2400	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
2500	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
2600	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
2700	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
2800	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
2900	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
3000	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
3100	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
3200	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
3300	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
3400	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
3500	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
3600	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
3700	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
3800	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
3900	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
4000	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
4100	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
4200	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
4300	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
4400	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
4500	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
4600	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
4700	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
4800	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
4900	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
5000	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
5100	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
5200	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
5300	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
5400	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
5500	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
5600	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
5700	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
5800	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
5900	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		
6000	4.568	40.545	40.545	.000	108.100	108.586	- 73.732		

June 30, 1968

Cs⁺Ground State Configuration ¹S₀S^o_{298.15} = 40.565 ± 0.0005 gibbs/molΔHf^o = 108.5 ± 1 kcal/molΔHf^o_{298.15} = 108.1 ± 1 kcal/mol

Electronic Levels and Quantum Weights

$$\frac{\epsilon_i, \text{cm}^{-1}}{0} \frac{g_i}{1}$$

Heat of Formation

The ionization potential of Cs(g) was reported as 3.893 eV or 89.776 kcal/mol by C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, 1958. Based on this data we derived ΔHf^o_{298.15} = 108.1 ± 1 kcal/mol for Cs⁺(g).

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights were reported by Moore, loc. cit. However, the lowest electronic level above ground state is given as 107392.33 cm⁻¹ which is so high that the evaluated thermodynamic properties of Cs⁺(g) will not be affected if we disregard all of these higher levels for calculation. Therefore we do not use them. The H⁻H₂₉₈ value at 0°K is -1.481 kcal/mol.

Cesium Fluoride (CsF)

CsF

(Crystal)

GFW = 151.9034

T, °K	Cp*	$\frac{\text{gibbs/mol}}{S^\circ - (C^\circ - H^\circ_{298})/T}$	$\frac{\text{kcal/mol}}{H^\circ - H^\circ_{298}}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0						
100						
200						
298	19.420	21.100	21.100	0.000	-132.570	92.046
300	19.430	21.177	21.106	0.083	-132.568	91.867
400	19.480	21.267	21.106	1.267	-132.051	87.293
500	19.520	21.310	21.110	2.563	-132.034	84.702
600	19.560	21.337	21.114	3.843	-132.006	83.034
700	19.590	21.357	21.118	5.119	-132.006	81.359
800	19.610	21.372	21.122	6.395	-132.006	79.684
900	19.620	21.382	21.125	7.671	-132.006	78.009
1000	19.630	21.390	21.127	8.947	-132.006	76.334
1100	19.640	21.396	21.129	10.223	-132.006	74.659
1200	19.650	21.401	21.131	11.499	-132.006	72.984
1300	19.660	21.406	21.133	12.775	-132.006	71.309
1400	19.670	21.411	21.135	14.051	-132.006	69.634
1500	19.680	21.416	21.137	15.327	-132.006	67.959
1600	19.690	21.421	21.139	16.603	-132.006	66.284
1700	19.700	21.426	21.141	17.879	-132.006	64.609
1800	19.710	21.431	21.143	19.155	-132.006	62.934
1900	19.720	21.436	21.145	20.431	-132.006	61.259
2000	19.730	21.441	21.147	21.707	-132.006	59.584

CESIUM FLUORIDE (CsF)

(CRYSTAL)

GFW = 151.9034

 $\Delta H^\circ_f = \text{Unknown}$ $\Delta H^\circ_{298,15} = -132.57 \pm 0.5 \text{ kcal/mol}$ $\Delta H_m^\circ = 5.19 \text{ kcal/mol}$ $\Delta H^\circ_{298,15} (\text{to monomer}) = 47.37 \text{ kcal/mol}$ $S^\circ_{298,15} = [21.1 \pm 2] \text{ gibbs/mol}$ $T_m = 976^\circ\text{K}$

Heat of Formation

The enthalpy of solution (ΔH_{soln}) of CsF(c) in water at 298.15°K has been carefully determined with an adiabatic calorimeter by Somsen (1). Based on the reported value, $\Delta H_{\text{soln},298} = -8.62 \pm 0.04 \text{ kcal/mol}$ and $\Delta H^\circ_{298} = -61.69 (2)$ and -79.5 kcal/mol for Cs⁺ (in H₂O) and F⁻ (in H₂O), respectively, the heat of formation for CsF(c) is calculated to be -132.57 kcal/mol which is adopted.

The value, $\Delta H_{\text{soln},298} = -8.81 \pm 0.2 \text{ kcal/mol}$ for CsF(c), was reported by Parker (1), which is in agreement with the value measured by Somsen (1).

Heat Capacity and Entropy

The heat capacities of CsF(c) are estimated according to the method of Kristov (3), based on $H^\circ_{298} - H^\circ_{298} = 9.4 \text{ kcal/mol}$ reported by Dworin (3). The entropy (S°_{298}) is estimated such that the calculated and observed vapor pressures are in good agreement (see CsF(g) and Cs₂F₂(g) tables for details).

Melting Data

T_m and ΔH_m° are obtained from Bredig (7) and Dworin (3). Bukhalova (3) reported $T_m = 958^\circ\text{K}$, which is not adopted.

Heat of Sublimation

ΔH°_{298} is calculated as the difference between ΔH°_{298} for CsF(g) and CsF(c).

References

1. G. Somsen and L. Weeda, Rec. Trav. Chim. **83**, 810 (1964).
2. S. R. Gunn, J. Phys. Chem. **71**, 1386 (1967).
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-7, 1965.
5. G. A. Kristov, Izv. Vych. Uchebn. Zavedeni, SSR, Khim. i Khim. Techn. No. 5, 751, 1964.
6. A. S. Dworin, private communication, Oak Ridge National Laboratory, Dec. 1, 1964.
7. M. A. Bredig, H. R. Bronstein and W. T. Smith, Jr., J. Am. Chem. Soc. **77**, 1454 (1955).
8. A. S. Dworin and M. A. Bredig, J. Phys. Chem. **64**, 269 (1960).
9. G. A. Bukhalova and D. V. Sementsova, Russ. J. Inorg. Chem. (English Transl.) **10**, 1027 (1965).

T, °K	Cp	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
100							
200							
298	17.700	21.534	21.534	.000	- 129.983	- 123.114	90.245
300	17.700	21.644	21.535	.033	- 129.971	- 123.071	89.657
400	17.700	26.736	22.226	1.803	- 129.848	- 120.701	85.948
500	17.700	30.685	23.540	3.573	- 129.231	- 118.487	51.791
600	17.700	33.113	25.006	5.343	- 128.619	- 116.395	42.397
700	17.700	36.621	26.480	6.183	- 127.917	- 112.503	30.735
800	17.700	41.089	29.253	10.653	- 126.824	- 110.674	26.875
900	17.700	42.954	30.531	12.623	- 126.318	- 108.691	23.673
1000	17.700						
1100	17.700	44.641	31.739	13.193	- 124.490	- 104.708	20.803
1200	17.700	46.561	32.657	15.733	- 122.616	- 98.161	16.502
1300	17.700	48.558	34.076	16.503	- 139.025	- 94.986	14.428
1400	17.700	50.131	35.995	21.273	- 138.208	- 91.868	13.385
1500	17.700						
1600	17.700	51.273	36.871	23.043	- 137.394	- 88.806	12.130
1700	17.700	52.346	37.750	24.643	- 135.574	- 82.831	10.057
1800	17.700	53.420	38.629	26.353	- 134.772	- 79.910	9.192
1900	17.700	54.315	39.392	30.123	- 134.174	- 77.032	8.418
2000	17.700						
2100	17.700	56.086	40.499	31.693	- 133.382	- 74.196	7.722
2200	17.700	56.937	41.501	32.693	- 132.820	- 68.431	7.033
2300	17.700	57.850	42.640	37.203	- 131.053	- 65.900	6.521
2400	17.700	58.450	43.583	38.073	- 130.297	- 63.202	5.525
2500	17.700						
2600	17.700	59.687	44.186	40.743	- 129.554	- 60.532	5.048
2700	17.700	60.535	44.789	42.283	- 128.724	- 55.278	4.315
2800	17.700	61.135	45.392	44.653	- 127.415	- 52.688	3.971
2900	17.700	61.800	45.019	47.823	- 126.739	- 50.124	3.652
3000	17.700	62.400	46.456				

CESIUM FLUORIDE (CsF)

(LIQUID)

GFW = 151.9034

 $S^\circ_{298.15} = [21.534] \text{ gibbs/mol}$ $\Delta H^\circ_{298.15} = -129.983 \text{ kcal/mol}$ $\Delta H_m^\circ = 5.19 \text{ kcal/mol}$ $\Delta H_v^\circ = 27.6 \text{ kcal/mol of liquid}$ $T_m = 976^\circ\text{K}$ $T_b = 1504^\circ\text{K}$

Heat of Formation

 $\Delta H^\circ_{298}(l)$ is obtained from $\Delta H^\circ_{298}(c)$ by adding ΔH_m° and the difference between H°_{298} for crystal and liquid.

Heat Capacity and Entropy

Dorbin (1) measured the heat capacity of CsF(l) at the melting point to be 17.7 gibbs/mol which is adopted and assumed to be constant in the temperature range 298 - 3000°K. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See CsF(c) for details.

Vaporization Data

T_b is the temperature at which the calculated vapor pressures of CsF(g) and $\text{Cs}_2\text{F}_2(\text{g})$ equal one atmosphere. The vapor composition at T_m is calculated as CsF 80.3 per cent and Cs_2F_2 19.7 per cent. The heat required to vaporize one mole of liquid to the above vapor mixture at T_m is ΔH_v° .

T_b has been observed as 1524 and 1526°K by Wartenberg (1) and Ruff (2), respectively, which are in fair agreement with the calculated one, 1504°K.

References

1. H. von Wartenberg and H. Schulz, Z. Elektrochem. **27**, 568 (1921).
2. O. Ruff, G. Schmidt and S. Mugdan, Z. Anorg. Allgem. Chem. **123**, 83 (1922).

Cesium Fluoride (CsF)

CsF

(Ideal Gas) GFW = 151.9034

CESIUM FLUORIDE (CsF) (IDEAL GAS) GFW = 151.9034

T, °K Cp° S° - (G° - H°₂₉₈)/T H° - H°₂₉₈ kcal/mol ΔH° ΔG°

Log Kp

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

INFINITE

Ground State Configuration

1₂⁺S_{298.15} = 59.10 ± 0.01 gibbs/mol

Electronic Levels and Quantum Weights

E₁, cm⁻¹ g₁

0 1

ω_K = 353 ± 4 cm⁻¹ω_e = 1.23 cm⁻¹ω_e = 0.00105 cm⁻¹B_e = 0.18437 cm⁻¹

σ = 1

r_e = 2.345 Å

Heat of Formation

The vapor pressures of CsF(c) and CsF(g) were measured by the manometric method (A) by Wartenberg (1), Ruff (2) and Cantor (3); the torsion-fiber effusion method (B) by Pugh (4); and the Knudsen effusion method (C) by Scheer (5). Based on the reported total pressures, the corresponding partial pressures of CsF(g) and CsF₂(g) were evaluated using the adjusted heats of vaporization and Gibbs free energy functions such that the calculated and observed total pressures are in reasonable agreement, and the derived enthalpy changes by the second and third law methods are consistent. The results obtained are presented in the table below. The value of ΔH°₂₉₈ (CsF, g) is adopted as -82.5 ± 0.5 kcal/mol.The dissociation energy (D₀) of CsF(g) has been reported using the spectroscopic convergence limit as 5.65eV(130.3 kcal/mol) and 5.5eV(126.8 kcal/mol) by Herzberg (6) and Gaydon (7), respectively. Based on the above two D₀ values, and ΔH°_f = 18.68 and 18.36 for Cs(g) and F(g), we obtain the corresponding value for ΔH°_f (CsF, g) as -93.86 and -90.39 kcal/mol, which are not adopted.

Investigators Reaction* Method

2 A

2 A

2 A

1 B

1 C

*1 represents the reaction CsF(c) = CsF(g); 2, the reaction CsF(l) = CsF(g).

**Calculation based on the third law ΔH°₂₉₈ and ΔH°_f = -132.57 and -129.983 kcal/mol for CsF(c) and CsF(l), respectively.

Heat Capacity and Entropy

The ground state configuration was reported by Herzberg (6). The molecular constants are obtained from Honig (7), who observed the microwave spectra of CsF(g) at temperatures of about 700°K. Based on the J = 1 + 2 transition, the molecular constants are derived. The vibrational frequency (ω_e) has been reported, from different kinds of spectra, in the range 270 - 385 cm⁻¹ by many investigators, e.g., radiofrequency, infrared, ultraviolet, microwave, etc. The value of ω_e adopted was reported by Balkov (8), who also reviewed the ω_e values obtained by the earlier investigators.

References

1. H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921), 1391 - 1524°K, 6 points. Two data points at 1228 and 1319°K are not adopted for evaluation due to the inconsistency with the other data.

2. O. Ruff, G. Schmidt and S. Mugdan, Z. Anorg. Allgem. Chem. 123, 83 (1922), 1306 - 1528°K, 7 points.

3. S. Cantor and F. Blankenship, "Vapor Pressure of the Alkali Fluorides," Oak Ridge National Laboratory, Oak Ridge, Tennessee, September 1958, 1009 - 1380°K, 7 points calculated using the given vapor pressure equation.

4. A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 671 (1958), 753 - 856°K, 6 points.

5. M. D. Scheer and J. Fine, J. Chem. Phys. 36, 1647 (1962), 677 - 878°K, 32 points. Evaluation based on the reported data points.

6. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

7. A. Honig, H. Mandel, M. L. Stiche and C. H. Townes, Phys. Rev. 96, 629 (1954).

8. V. I. Balkov and K. P. Vasilievskii, Opt. Spectry. (USSR) (English Transl.) 22, 198 (1967).

9. A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.

June 30, 1968

CsF

CESIUM MONOXIDE (CsO) (IDEAL GAS) GFW = 146.9044

Ground State Configuration [2_π]

$\Delta H_f^\circ = [15.5 \pm 10] \text{ kcal/mol}$

$\Delta H_{298.15}^\circ = [61 \pm 1] \text{ gibbs/mol}$

$\Delta H_{298.15}^\circ = [15.0 \pm 10] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	$\frac{R_A}{h\nu}$	(4)
0		
$\omega_e = [280] \text{ cm}^{-1}$	$\omega_e x_e = [1.0] \text{ cm}^{-1}$	$\sigma = 1$
$B_e = [0.198] \text{ cm}^{-1}$	$\sigma_e = [0.001] \text{ cm}^{-1}$	$r_e = [2.40] \text{ \AA}$

Heat of Formation

The heat of formation is estimated from three calculated values. The methods of estimation are described as follows. Brewer and Margrave (1) suggested that the ΔH_f value for MO(g) from the gaseous ions can be taken as the mean of the corresponding ΔH_f values for the alkali fluoride and chlorides with a maximum uncertainty of 10 kcal/mol. Adopting $\Delta H_f^\circ = -131.1$ and -109.6 kcal/mol for the reaction $\text{Cs}^+(g) + \text{F}^-(g) = \text{CsF}(g)$ and $\text{Cs}^+(g) + \text{Cl}^-(g) = \text{CsCl}(g)$, respectively, we obtain $\Delta H_{298}^\circ = -120.4$ kcal/mol for $\text{Cs}^+(g) + \text{O}^-(g) = \text{CsO}(g)$ which leads to $\Delta H_{298}^\circ(\text{CsO}, g) = 12.0$ kcal/mol. The ΔH_{298}° values of the above species used for calculation are taken from the respective JANAF Thermochemical Tables.

Based on the assumption that $D(\text{Cs-O}) = 1/2[D(\text{Ca}_2) + D(\text{O}_2)]$, we derive $D_{298}(\text{Cs-O}) = 65.2$ kcal/mol and $\Delta H_{298}^\circ = 12.7$ kcal/mol for $\text{CsO}(g)$.

Adopting the Cs-O bond energy as half of the atomization energy of Cs_2O , we calculate $D(\text{Cs-O}) = 60 \pm 10$ kcal/mol and $\Delta H_{298}^\circ(\text{CsO}, g) = 17 \pm 10$ kcal/mol.

The heat of formation for $\text{CsO}(g)$ is tentatively selected as 15 ± 10 kcal/mol.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of the isolectronic molecule OH(g). ω_e is estimated from those of LiO(g), CaF(g), and CsCl(g). The bond distance is taken from that in CsOH(g) reported by Lide and Kuczkowski (2). $\omega_e x_e$ is estimated by comparison with those of the other alkali oxides. The values of B_e and σ_e are calculated from r_e , ω_e and $\omega_e x_e$ by the method suggested by Herzberg (3). The moment of inertia is $1.413 \times 10^{-38} \text{ g cm}^2$.

References

1. L. Brewer and J. L. Margrave, J. Phys. Chem. **59**, 421 (1955).
2. D. R. Lide, Jr. and R. L. Kuczkowski, J. Chem. Phys. **46**, 4768 (1967).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

Dec. 31, 1968

Cesium Monoxide (CsO)

GFW = 148.9044

T, °K	C_p°	$\frac{4R \ln S^\circ}{S^\circ} - (C_p^\circ - R^\circ)/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG_f°	Log Kp
0	7.000	INFINITE	-2.361	15.920	15.920	INFINITE
100	7.424	52.462	-1.841	15.920	15.920	12.806
200	7.824	61.439	-1.884	15.160	11.798	12.802
298	8.179	61.049	-0.000	15.000	10.171	7.456
300	8.1722	61.103	0.016	14.996	10.141	7.388
400	8.454	63.432	0.1393	14.836	8.723	4.766
500	8.627	65.616	0.2086	14.633	7.349	3.219
600	8.676	67.249	2.680	13.608	6.033	2.205
700	9.013	68.635	3.580	13.579	4.779	1.492
800	9.043	69.841	4.483	13.343	3.532	0.966
900	9.069	70.907	5.386	13.102	2.326	0.565
1000	9.093	71.864	6.290	3.224	1.162	0.285
1100	9.115	72.732	6.6160	7.207	2.482	0.493
1200	9.137	73.526	6.6119	3.236	3.001	0.547
1300	9.157	74.258	6.7309	9.034	3.522	0.592
1400	9.177	74.937	6.829	9.951	4.042	0.631
1500	9.196	75.571	10.869	3.276	4.565	0.665
1600	9.216	76.165	68.796	3.293	5.088	0.695
1700	9.236	76.724	69.246	3.311	5.612	0.722
1800	9.253	77.253	69.677	3.333	6.137	0.745
1900	9.272	77.753	70.089	3.358	6.665	0.767
2000	9.290	78.280	70.484	3.386	7.193	0.786
2100	9.307	78.843	70.863	3.424	7.723	0.804
2200	9.327	79.117	71.229	3.467	8.254	0.820
2300	9.345	79.532	71.581	3.516	8.788	0.835
2400	9.363	79.930	71.921	3.576	9.325	0.849
2500	9.381	80.312	72.249	3.647	9.863	0.862
2600	9.399	80.681	72.566	3.729	10.405	0.875
2700	9.417	81.036	72.873	3.825	10.951	0.886
2800	9.435	81.379	73.171	3.927	11.500	0.898
2900	9.453	81.710	73.460	4.065	12.054	0.908
3000	9.471	82.031	73.740	4.214	12.613	0.918
3100	9.489	82.342	74.012	4.383	13.177	0.929
3200	9.507	82.643	74.277	4.577	13.745	0.939
3300	9.525	82.936	74.535	4.797	14.320	0.948
3400	9.543	83.221	74.787	5.045	14.904	0.958
3500	9.561	83.498	75.032	5.325	15.494	0.967
3600	9.579	83.767	75.271	5.640	16.093	0.977
3700	9.597	84.030	75.504	5.992	16.702	0.987
3800	9.614	84.286	75.732	6.385	17.322	0.996
3900	9.632	84.536	75.954	6.822	17.950	1.006
4000	9.650	84.780	76.172	7.308	18.591	1.016
4100	9.668	85.019	76.385	7.845	19.245	1.026
4200	9.686	85.252	76.593	8.436	19.912	1.036
4300	9.703	85.480	76.797	9.083	20.596	1.047
4400	9.721	85.703	76.997	9.790	21.293	1.058
4500	9.739	85.922	77.193	10.557	22.008	1.069
4600	9.757	86.136	77.385	40.255	22.743	1.081
4700	9.775	86.346	77.573	12.280	23.494	1.092
4800	9.792	86.552	77.758	42.210	24.266	1.105
4900	9.810	86.754	77.940	14.236	25.055	1.118
5000	9.828	86.953	78.118	15.316	25.868	1.131
5100	9.846	87.147	78.293	45.136	26.705	1.144
5200	9.864	87.339	78.465	16.476	27.561	1.158
5300	9.881	87.527	78.634	16.921	28.445	1.173
5400	9.899	87.712	78.801	20.218	29.349	1.188
5500	9.917	87.893	78.965	49.109	30.281	1.203
5600	9.935	88.072	79.126	30.101	31.234	1.219
5700	9.952	88.248	79.284	51.051	32.214	1.235
5800	9.970	88.421	79.440	52.092	33.221	1.252
5900	9.988	88.592	79.594	53.089	34.249	1.269
6000	10.006	88.760	79.745	54.089	35.306	1.286

Cesium, Dimeric (Cs₂)

(Ideal Gas) GFW = 265.810

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	8.900	54.000	INFINITE	26.053	26.053	INFINITE
100	8.842	54.007	75.521	26.271	26.077	50.478
200	9.046	64.243	66.669	25.869	20.063	21.923
298	9.112	67.667	67.667	25.400	17.301	12.682
300	9.114	67.823	67.823	25.386	17.251	12.567
400	9.176	70.558	69.225	23.779	14.957	8.172
500	9.237	72.608	66.904	23.202	12.818	5.603
600	9.291	74.597	65.666	22.645	10.795	3.932
700	9.337	75.735	64.633	22.097	8.864	2.767
800	9.376	76.101	63.786	21.566	7.126	1.923
900	9.410	76.610	63.125	21.053	5.524	1.365
1000	9.436	77.102	62.557	20.569	5.138	1.123
1100	9.457	77.614	73.194	7.502	6.822	1.355
1200	9.475	78.152	81.465	11.704	8.507	1.548
1300	9.491	78.710	91.406	11.735	10.181	1.705
1400	9.505	79.286	103.021	11.761	11.843	1.835
1500	9.518	79.878	116.334	11.782	13.493	1.938
1600	9.530	80.484	131.352	11.792	15.135	2.017
1700	9.541	81.104	148.082	11.800	16.766	2.075
1800	9.551	81.736	166.532	11.806	18.388	2.118
1900	9.560	82.380	186.702	11.810	20.002	2.148
2000	9.568	83.036	208.602	11.812	21.608	2.168
2100	9.575	83.704	232.242	11.813	23.207	2.179
2200	9.581	84.384	257.632	11.814	24.799	2.182
2300	9.586	85.076	284.782	11.815	26.384	2.178
2400	9.590	85.780	313.712	11.815	27.962	2.168
2500	9.593	86.496	344.442	11.815	29.534	2.152
2600	9.595	87.224	376.982	11.815	31.100	2.131
2700	9.596	87.964	411.352	11.815	32.662	2.106
2800	9.597	88.716	447.572	11.815	34.220	2.078
2900	9.597	89.480	485.662	11.815	35.774	2.048
3000	9.597	90.256	525.642	11.815	37.324	2.016
3100	9.597	91.044	567.542	11.815	38.870	1.982
3200	9.597	91.844	611.382	11.815	40.412	1.947
3300	9.597	92.656	657.192	11.815	41.950	1.911
3400	9.597	93.480	704.992	11.815	43.484	1.874
3500	9.597	94.316	754.822	11.815	45.014	1.836
3600	9.597	95.164	806.712	11.815	46.540	1.797
3700	9.597	96.024	860.692	11.815	48.062	1.757
3800	9.597	96.896	916.802	11.815	49.580	1.716
3900	9.597	97.780	975.072	11.815	51.094	1.674
4000	9.597	98.676	1035.542	11.815	52.604	1.631
4100	9.597	99.584	1098.252	11.815	54.110	1.587
4200	9.597	100.504	1163.142	11.815	55.612	1.542
4300	9.597	101.436	1230.262	11.815	57.110	1.496
4400	9.597	102.380	1299.652	11.815	58.604	1.449
4500	9.597	103.336	1371.352	11.815	60.094	1.401
4600	9.597	104.304	1445.402	11.815	61.580	1.352
4700	9.597	105.284	1521.852	11.815	63.062	1.302
4800	9.597	106.276	1600.752	11.815	64.540	1.251
4900	9.597	107.280	1682.142	11.815	66.014	1.199
5000	9.597	108.296	1766.072	11.815	67.484	1.146
5100	9.597	109.324	1852.502	11.815	68.950	1.092
5200	9.597	110.364	1941.482	11.815	70.412	1.037
5300	9.597	111.416	2033.072	11.815	71.870	0.981
5400	9.597	112.480	2127.332	11.815	73.324	0.924
5500	9.597	113.556	2224.222	11.815	74.774	0.866
5600	9.597	114.644	2323.802	11.815	76.220	0.807
5700	9.597	115.744	2426.132	11.815	77.662	0.747
5800	9.597	116.856	2531.282	11.815	79.100	0.686
5900	9.597	117.980	2639.312	11.815	80.534	0.624
6000	9.597	119.116	2750.292	11.815	81.964	0.561

June 30, 1968

CESIUM, DIMERIC (Cs₂)

(IDEAL GAS)

GFW = 265.810

Ground State Configuration 1²S_gS_{298.15} = [67.67] gibbs/molΔHf°_{298.15} = 25.40 ± 1.0 kcal/mol

GFW = 265.810

ΔHf°_{298.15} = 25.40 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

State	E _i , cm ⁻¹	g _i
1 _g ⁺	0	1
1 _g ⁺	9000	1
1 _u ⁺	13043.87	2
1 _u ⁺	16086.03	[1]
1 _u ⁺	16175.80	[2]

ω_eX_e = 0.04005 cm⁻¹

σ = 2

B_e = [0.01263] cm⁻¹r_e = [4.48] Å

Heat of Formation

For internal consistency, the vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details).For internal consistency, the vapor pressures determined at temperatures 900-1600°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol.The ΔH₀(Cs-Cs) was reported as 0.45 eV or 10.30 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.The vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details).For internal consistency, the vapor pressures determined at temperatures 900-1600°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol.The ΔH₀(Cs-Cs) was reported as 0.45 eV or 10.30 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.The vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details).For internal consistency, the vapor pressures determined at temperatures 900-1600°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol.The ΔH₀(Cs-Cs) was reported as 0.45 eV or 10.30 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.The vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details).For internal consistency, the vapor pressures determined at temperatures 900-1600°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol.The ΔH₀(Cs-Cs) was reported as 0.45 eV or 10.30 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.The vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details).For internal consistency, the vapor pressures determined at temperatures 900-1600°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol.The ΔH₀(Cs-Cs) was reported as 0.45 eV or 10.30 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.The vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details).For internal consistency, the vapor pressures determined at temperatures 900-1600°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol.The ΔH₀(Cs-Cs) was reported as 0.45 eV or 10.30 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.The vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details).For internal consistency, the vapor pressures determined at temperatures 900-1600°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol.The ΔH₀(Cs-Cs) was reported as 0.45 eV or 10.30 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.The vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details).For internal consistency, the vapor pressures determined at temperatures 900-1600°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol.The ΔH₀(Cs-Cs) was reported as 0.45 eV or 10.30 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.The vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details).For internal consistency, the vapor pressures determined at temperatures 900-1600°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol.The ΔH₀(Cs-Cs) was reported as 0.45 eV or 10.30 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.The vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details).For internal consistency, the vapor pressures determined at temperatures 900-1600°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol.The ΔH₀(Cs-Cs) was reported as 0.45 eV or 10.30 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights, ω_e and ω_x are obtained from Herzberg (3). The electronic states are estimated by comparison with those for K₂(g) given by (3). The bond distance r_e is calculated from ω_e based on the method suggested by Guggenheimer (4). The values of B_e and ω_e are calculated (3). The moment of inertia is 2.2145 × 10⁻³⁷ g cm².

References

1. J. P. Stone, C. T. Ewing, J. R. Spann, E. W. Steinkuller, D. D. Williams, and R. R. Miller, J. Chem. Eng. Data 11, 309 (1966).

2. F. Tepper, J. Zelenak, F. Roehlich and V. May, "Thermophysical and Transport Properties of Liquid Metals," NSR 64-116, Third Quarterly Progress Rept. July - Sept. 1964, NSA Research Corp., Callery, Pennsylvania, October 19, 1964.

3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

4. K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).

5. A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.

Point Group [D_{2h}]
S_{298.15}^o = (84 ± 2) gibbs/mol
Ground State Quantum Weight = 11
S_{298.15}^o = -211.55 ± 2.0 kcal/mol
ΔH_F^o = -212.74 ± 2.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
(200) (1)	(120) (1)
(110) (1)	(220) (1)
(210) (1)	(230) (1)

Bond Angle: Cs-F = (95°) A

Bond Distance: F-Cs-F = (85°)

Product of the Moments of Inertia: I_AI_BI_C = (3.126 × 10⁻¹¹²) g³ cm⁶

σ = {4}

Heat of Formation

Evidence from the velocity distribution in molecular beams (1) has shown that alkali halide vapors contain significant amounts of polymeric species. Using the same method Eisenstadt (2) determined the molecular composition of CsF vapor in the temperature range 838 - 919°K. Based on the reported equilibrium constants for the reaction (CsF)₂(g) = 2CsF(g), we evaluate the enthalpy change (ΔH_F^o) by the second and third law methods to be 40.53 ± 1.75 and 42.34 ± 0.26 kcal/mol, respectively. Employing ΔH_F^o₂₉₈ = 42.34 and ΔH_F^o₂₉₈(CsF, g) = -85.2 kcal/mol, we obtained ΔH_F^o₂₉₈ = -212.74 kcal/mol for Cs₂F₂(g), which is adopted.

Heat Capacity and Entropy

The Cs₂F₂ molecule is assumed to have a rhombic configuration of symmetry D_{2h} as Cs₂Cl₂(3). The Cs-F bond distance is taken as the same as that in CsF(g). The bond angles and vibrational frequencies are estimated by comparison with those of the other dimeric alkali halides (3, 4). The three principal moments of inertia are: I_A = 1.590 × 10⁻³⁸, I_B = 1.325 × 10⁻³⁷ and I_C = 1.484 × 10⁻³⁷ g cm².

References

1. R. C. Miller and P. Kusch, J. Chem. Phys. **25**, 860 (1956); *ibid.* **27**, 981 (1957).
2. M. Eisenstadt, G. M. Rothberg and P. Kusch, J. Chem. Phys. **29**, 1386 (1956).
3. J. Berkowitz, J. Chem. Phys. **29**, 1319 (1956).
4. J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960).

T, °K	Cp ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _F ^o	ΔG _F ^o	Log Kp
0	18.000	45.000	INFINITE	-3.606	-211.548	-211.548	INFINITE
100	18.230	76.707	85.004	1.440	-212.485	-211.046	231.356
200	18.463	84.179	84.179	.000	-212.740	-211.525	154.856
300	19.103	84.297	84.179	.035	-212.747	-211.249	153.894
400	19.430	84.644	84.933	1.864	-214.112	-209.392	134.525
500	19.586	84.198	86.386	3.916	-214.483	-208.569	115.525
600	19.672	97.777	97.979	5.979	-214.618	-208.342	75.889
700	19.725	100.814	99.601	7.849	-215.179	-207.234	64.701
800	19.759	103.450	91.171	6.223	-215.551	-206.076	56.297
900	19.782	105.779	92.667	11.601	-215.921	-204.866	49.785
1000	19.799	107.664	107.664	13.760	-216.475	-203.102	44.162
1100	19.812	109.752	95.424	15.760	-216.379	-197.331	39.206
1200	19.821	111.476	96.691	17.742	-216.288	-192.694	35.004
1300	19.829	113.063	97.890	19.725	-216.202	-188.064	31.616
1400	19.835	114.533	99.027	21.708	-216.122	-183.443	28.637
1500	19.839	115.901	100.107	23.691	-216.044	-178.924	26.035
1600	19.843	117.142	101.135	25.676	-216.972	-174.213	23.796
1700	19.847	118.385	102.114	27.660	-217.006	-169.404	21.804
1800	19.849	119.519	103.050	29.645	-217.847	-165.002	20.034
1900	19.852	120.593	103.945	31.630	-217.794	-160.399	18.450
2000	19.854	121.611	104.803	33.615	-217.752	-155.600	17.025
2100	19.855	122.560	105.627	35.601	-217.722	-151.205	15.736
2200	19.857	123.503	106.419	37.586	-217.708	-146.810	14.544
2300	19.858	124.386	107.181	39.572	-217.707	-142.013	13.484
2400	19.859	125.231	107.915	41.558	-217.727	-137.418	12.514
2500	19.860	126.042	108.624	43.544	-217.770	-133.022	11.611
2600	19.861	126.821	109.309	45.530	-217.837	-128.822	10.778
2700	19.862	127.570	109.972	47.516	-217.932	-124.819	10.006
2800	19.862	128.293	110.613	49.502	-218.056	-120.914	9.289
2900	19.863	128.990	111.235	51.486	-218.221	-117.394	8.601
3000	19.864	129.663	111.838	53.475	-218.423	-114.399	7.956
3100	19.864	130.314	112.424	55.461	-218.669	-110.159	7.414
3200	19.865	130.945	112.993	57.448	-218.965	-105.525	6.866
3300	19.865	131.556	113.546	59.434	-219.314	-99.882	6.350
3400	19.865	132.149	114.095	61.421	-219.720	-93.225	5.864
3500	19.866	132.725	114.605	63.407	-220.194	-86.355	5.405
3600	19.866	133.285	115.120	65.394	-220.738	-81.873	4.970
3700	19.866	133.829	115.618	67.380	-221.360	-77.173	4.558
3800	19.867	134.359	116.105	69.367	-222.065	-72.454	4.167
3900	19.867	134.875	116.579	71.354	-222.863	-67.720	3.795
4000	19.867	135.378	117.043	73.340	-223.759	-62.960	3.440
4100	19.867	135.869	117.494	75.327	-224.759	-58.180	3.101
4200	19.868	136.347	117.935	77.314	-225.871	-53.372	2.777
4300	19.868	136.815	118.373	79.301	-227.098	-48.536	2.467
4400	19.868	137.272	118.797	81.287	-228.448	-43.670	2.169
4500	19.868	137.718	119.213	83.274	-230.922	-38.774	1.893
4600	19.868	138.155	119.620	85.261	-234.524	-33.842	1.608
4700	19.868	138.582	120.019	87.248	-239.257	-28.872	1.343
4800	19.869	139.000	120.410	89.235	-245.119	-23.865	1.087
4900	19.869	139.410	120.793	91.221	-252.683	-18.818	.839
5000	19.869	139.812	121.170	93.208	-262.232	-13.730	.600
5100	19.869	140.205	121.539	95.195	-271.473	-8.601	.369
5200	19.869	140.591	121.902	97.182	-282.432	-3.421	.144
5300	19.869	140.969	122.258	99.169	-295.299	1.804	-.074
5400	19.869	141.341	122.608	101.156	-310.469	7.070	-.286
5500	19.869	141.705	122.952	103.143	-328.594	12.352	-.492
5600	19.869	142.063	123.290	105.130	-349.270	17.761	-.693
5700	19.869	142.415	123.622	107.117	-382.082	23.181	-.889
5800	19.869	142.761	123.945	109.104	-427.951	28.649	-1.080
5900	19.870	143.100	124.271	111.091	-487.669	34.163	-1.265
6000	19.870	143.434	124.596	113.078	-562.619	39.733	-1.447

June 30, 1968

GFW = 281.8094

(IDEAL GAS)

DICESIUM MONOXIDE (Cs₂O) $\Delta H_f^\circ = -20.6 \pm 10$ kcal/mol $\Delta H_f^\circ = -22.0 \pm 10$ kcal/molPoint Group C_{2v} $S_{298.15}^\circ = \{76 \pm 2\}$ gibbs/mol

Ground State Quantum Weight = [1]

Dicesium Monoxide (Cs₂O)
(Ideal Gas) GFW = 281.8094

T, °K	Cp°	S°	$-(G^\circ - H_{298}^\circ)/T$	H° - H ₂₉₈ °	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	3.331	20.606	20.606	INFINITE
100	10.503	62.790	87.229	2.444	21.091	22.674	49.554
200	18.236	71.586	91.516	1.822	21.572	23.156	68.304
298	23.238	75.958	95.998	1.000	22.000	23.216	104.855
300	13.245	76.079	75.998	1.024	22.010	25.238	18.386
400	13.521	79.933	76.521	1.365	23.549	25.905	14.154
500	13.657	82.986	77.518	2.724	24.053	26.436	11.555
600	13.732	85.484	78.680	4.094	24.545	26.985	9.764
700	13.779	87.584	79.770	5.470	25.038	27.212	8.496
800	13.809	89.426	80.864	6.849	25.538	27.491	7.510
900	13.830	91.054	81.908	8.231	26.041	27.703	6.727
1000	13.845	92.512	82.897	9.615	26.542	27.870	6.070
1100	13.856	93.832	83.832	11.000	27.039	27.998	5.543
1200	13.865	95.038	84.716	12.386	27.521	28.088	5.100
1300	13.872	96.148	85.553	13.773	28.006	28.145	4.727
1400	13.877	97.176	86.347	15.161	28.487	28.180	4.410
1500	13.881	98.134	87.101	16.548	28.969	28.200	4.140
1600	13.885	99.030	87.819	17.937	29.452	28.215	3.910
1700	13.888	99.872	88.504	19.325	29.936	28.225	3.710
1800	13.890	100.666	89.158	20.714	30.420	28.230	3.530
1900	13.892	101.417	89.783	22.103	30.904	28.235	3.370
2000	13.894	102.129	90.383	23.493	31.388	28.240	3.230
2100	13.895	102.807	90.958	24.882	31.872	28.245	3.110
2200	13.897	103.454	91.512	26.272	32.356	28.250	3.000
2300	13.898	104.071	92.045	27.661	32.840	28.255	2.900
2400	13.899	104.663	92.558	29.051	33.324	28.260	2.810
2500	13.900	105.230	93.054	30.441	33.808	28.265	2.730
2600	13.901	105.775	93.533	31.831	34.292	28.270	2.660
2700	13.901	106.300	93.996	33.221	34.776	28.275	2.600
2800	13.902	106.806	94.444	34.611	35.260	28.280	2.550
2900	13.902	107.293	94.879	36.002	35.744	28.285	2.510
3000	13.903	107.765	95.301	37.392	36.228	28.290	2.470
3100	13.903	108.221	95.710	38.782	36.712	28.295	2.440
3200	13.904	108.662	96.108	40.173	37.196	28.300	2.410
3300	13.904	109.090	96.495	41.563	37.680	28.305	2.380
3400	13.904	109.505	96.872	42.953	38.164	28.310	2.350
3500	13.905	109.908	97.238	44.344	38.648	28.315	2.320
3600	13.905	110.300	97.594	45.736	39.132	28.320	2.300
3700	13.905	110.681	97.944	47.125	39.616	28.325	2.280
3800	13.906	111.052	98.284	48.515	40.100	28.330	2.260
3900	13.906	111.413	98.616	49.906	40.584	28.335	2.240
4000	13.906	111.765	98.941	51.297	41.068	28.340	2.220
4100	13.906	112.108	99.258	52.687	41.552	28.345	2.200
4200	13.906	112.443	99.566	54.078	42.036	28.350	2.180
4300	13.907	112.771	99.871	55.469	42.520	28.355	2.160
4400	13.907	113.090	100.168	56.859	43.004	28.360	2.140
4500	13.907	113.403	100.458	58.250	43.488	28.365	2.120
4600	13.907	113.709	100.743	59.641	43.972	28.370	2.100
4700	13.907	114.008	101.022	61.031	44.456	28.375	2.080
4800	13.907	114.300	101.296	62.422	44.940	28.380	2.060
4900	13.907	114.587	101.564	63.813	45.424	28.385	2.040
5000	13.908	114.868	101.827	65.204	45.908	28.390	2.020
5100	13.908	115.144	102.086	66.594	46.392	28.395	2.000
5200	13.908	115.414	102.339	67.985	46.876	28.400	1.980
5300	13.908	115.679	102.589	69.376	47.360	28.405	1.960
5400	13.908	115.938	102.833	70.767	47.844	28.410	1.940
5500	13.908	116.194	103.074	72.157	48.328	28.415	1.920
5600	13.908	116.444	103.311	73.548	48.812	28.420	1.900
5700	13.908	116.690	103.543	74.939	49.296	28.425	1.880
5800	13.908	116.932	103.772	76.330	49.780	28.430	1.860
5900	13.908	117.170	103.997	77.721	50.264	28.435	1.840
6000	13.908	117.404	104.219	79.112	50.748	28.440	1.820

Dec. 31, 1968

Heat of Formation
The appearance potentials of CsOH and Cs₂O ions were investigated by Emel'yanov et al. (1), using the electron-impact method with a mass spectrometer fitted with a heated ion source and a Pt effusion chamber. The heat of atomization of Cs₂O was derived as 117 ± 9 kcal/mol. Based on this value we calculate the heat of formation (ΔH_f°) of Cs₂O to be -22 ± 10 kcal/mol, employing $\Delta H_f^\circ = 18.68$ and 58.99 kcal/mol for Cs(g) and O(g), respectively. Brewer and Mastick (2) calculated theoretically the stability of gaseous alkali oxides according to ionic models and gave the heats of formation from gaseous atoms for Cs₂O(g) as -74 kcal/mol. The ΔH_f° value is evaluated to be 71.2 kcal/mol which is not adopted.

Heat Capacity and Entropy

The molecular structure of Cs₂O(g) has been determined to be nonlinear by Büchler et al. (3), using electric-deflection method. The Cs-O bond distance is assumed to be the same as that in CsOH(g) reported by Lide and Kuczkowski (4). The bond angle is estimated by comparison with that in the H₂O molecule. Three vibrational frequencies are estimated from those for H₂O(g). The three principal moments of inertia are: $I_A = 5.350 \times 10^{-39}$, $I_B = 1.600 \times 10^{-37}$, and $I_C = 1.6535 \times 10^{-37}$ g cm².

References

1. A. M. Emel'yanov, A. V. Gusarov, L. N. Gorokhov, and N. A. Sadovnikova, Teor. Eksp. Khim. **3**, 276 (1967).
2. L. Brewer and D. F. Mastick, J. Am. Chem. Soc. **73**, 2045 (1951).
3. A. Büchler and J. L. Strauffer and W. Klemperer, J. Chem. Phys. **46**, 605 (1967).
4. D. R. Lide, Jr. and R. L. Kuczkowski, J. Chem. Phys. **46**, 4768 (1967).

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈ °	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	-	1.195	0.000	0.000	0.000
100	3.826	2.392	12.749	1.036	0.000	0.000	0.000
200	5.399	5.061	8.437	0.555	0.000	0.000	0.000
298	5.843	7.913	7.913	0.000	0.000	0.000	0.000
300	5.846	7.949	7.943	0.11	0.000	0.000	0.000
400	6.077	9.665	8.146	0.608	0.000	0.000	0.000
500	6.250	11.040	8.591	1.224	0.000	0.000	0.000
600	6.394	12.193	9.098	1.857	0.000	0.000	0.000
700	6.513	13.163	9.562	2.502	0.000	0.000	0.000
800	6.620	14.068	10.015	3.159	0.000	0.000	0.000
900	6.725	14.850	10.459	3.826	0.000	0.000	0.000
1000	6.822	15.564	11.060	4.504	0.000	0.000	0.000
1100	6.910	16.218	11.500	5.190	0.000	0.000	0.000
1200	7.008	17.387	12.318	6.250	0.000	0.000	0.000
1300	7.100	20.263	12.772	10.488	0.000	0.000	0.000
1400	7.500	20.780	13.288	11.238	0.000	0.000	0.000
1500	7.500	21.264	13.772	11.988	0.000	0.000	0.000
1600	7.500	22.148	14.654	13.488	0.000	0.000	0.000
1700	7.500	22.553	15.060	14.238	0.000	0.000	0.000
1800	7.500	22.938	15.444	14.988	0.000	0.000	0.000
1900	7.500	23.304	15.810	15.738	0.000	0.000	0.000
2000	7.500	23.984	16.491	17.238	0.000	0.000	0.000
2100	7.500	24.305	16.810	17.988	0.000	0.000	0.000
2200	7.500	24.612	17.116	18.738	0.000	0.000	0.000
2300	7.500	24.906	17.410	19.488	0.000	0.000	0.000
2400	7.500	25.462	17.965	20.988	0.000	0.000	0.000
2500	7.500	51.236	18.686	94.396	0.000	0.000	0.000
2600	6.010	51.438	19.774	94.991	0.000	0.000	0.000
2700	6.131	51.637	20.799	95.598	0.000	0.000	0.000
2800	6.250	52.028	22.486	96.849	0.000	0.000	0.000
2900	6.375	52.220	23.546	97.492	0.000	0.000	0.000
3000	6.496	52.410	24.368	98.148	0.000	0.000	0.000
3100	6.732	52.598	25.149	98.815	0.000	0.000	0.000
3200	6.866	52.964	26.894	100.184	0.000	0.000	0.000
3300	6.959	53.150	27.282	100.885	0.000	0.000	0.000
3400	7.059	53.330	27.931	101.596	0.000	0.000	0.000
3500	7.251	53.508	28.553	102.316	0.000	0.000	0.000
3600	7.329	53.684	29.149	103.046	0.000	0.000	0.000
3700	7.498	54.029	30.272	104.530	0.000	0.000	0.000
3800	7.568	54.198	30.802	105.283	0.000	0.000	0.000
3900	7.633	54.365	31.312	106.043	0.000	0.000	0.000
4000	7.692	54.530	31.805	107.582	0.000	0.000	0.000
4100	7.797	54.853	32.739	108.359	0.000	0.000	0.000
4200	7.842	55.011	33.183	109.141	0.000	0.000	0.000
4300	7.884	55.167	33.612	109.927	0.000	0.000	0.000
4400	7.955	55.270	34.026	111.512	0.000	0.000	0.000
4500	7.987	55.620	34.822	112.309	0.000	0.000	0.000
4600	8.016	55.767	35.202	113.109	0.000	0.000	0.000
4700	8.043	55.912	35.570	113.912	0.000	0.000	0.000
4800	8.099	56.054	35.929	114.717	0.000	0.000	0.000
4900	8.118	56.334	36.616	116.336	0.000	0.000	0.000
5000	8.142	56.470	36.945	117.149	0.000	0.000	0.000

Dec. 31, 1965

AT. WT. = 63.54

(REFERENCE STATE)

0 to 1356.6°K. Crystal
1356.6 to 2848°K. Liquid
2848 to 6000°K. Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

COPPER (Cu)

Cu

Copper (Cu)
(Crystal)

At. Wt. = 63.54

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	INFINITE	- 1.195	.000	.000	INFINITE
100	3.826	12.749	- 1.036	.000	.000	.001
200	5.399	8.437	.000	.000	.000	.000
298	5.843	7.913	.000	.000	.000	.000
300	5.846	7.949	.011	.000	.000	.000
400	6.077	9.665	8.146	.000	.000	.000
500	6.250	11.040	8.591	.000	.000	.000
600	6.394	12.193	9.098	.000	.000	.000
700	6.516	13.188	9.613	.000	.000	.000
800	6.620	14.064	10.116	.000	.000	.000
900	6.725	14.850	10.599	.000	.000	.000
1000	6.822	15.564	11.060	.000	.000	.000
1100	6.910	16.218	11.500	.000	.000	.000
1200	6.998	16.823	11.918	.000	.000	.000
1300	7.086	17.387	12.318	.000	.000	.000
1400	7.174	17.915	12.699	.000	.000	.000
1500	7.262	18.413	13.063	.000	.000	.000
1600	7.350	18.885	13.413	.000	.000	.000
1700	7.438	19.333	13.748	.000	.000	.000
1800	7.526	19.761	14.070	.000	.000	.000
1900	7.614	20.170	14.380	.000	.000	.000
2000	7.702	20.563	14.680	.000	.000	.000

(CRYSTAL)

COPPER (Cu)

AT. WT. = 63.54

$$\Delta H_f^0 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 298.15 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 3.17 \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^0 298.15 = 81 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 7.913 \pm 0.04 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1356.6^\circ \text{K.}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The low temperature specific heat of copper has been measured by several workers and generally there is good agreement. The selected values lie close to the determinations of J. A. Kok and W. H. Keason (1.2-20°K), Physics 3, 1035 (1936); D. L. Martin (20-300°K), Can. J. Phys. 39, 17 (1960); C. B. Satterthwaite, R. S. Craig and W. E. Wallace, J. Am. Chem. Soc. 76, 232 (1954), and S. M. Dookerby, Can. J. Research 2, 84 (1933) and 15L, 59 (1937). Several other workers have reported values of C_p slightly higher than the adopted values especially W. P. Glaue and P. P. Meads, J. Am. Chem. Soc. 63, 1897 (1941), however these measurements were not used for reasons discussed by Martin. The heat capacity above room temperature has been determined directly by several workers, the values of R. E. Pawel and E. E. Stanbury, J. Phys. Chem. Solids 26, 607 (1965) join well with the low temperature data and are adopted. These values lie within 1% of the values adopted by R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley "Selected Values of Thermodynamic Properties of Metals and Alloys", John Wiley and Sons, Inc., New York, 1963. Several determinations of the solid enthalpy are also in good agreement with selected heat capacity curve. For references to these determinations refer to Hultgren et al. loc. cit.

Melting Data.

The melting point of copper is well established and the recent determination of W. Heyne, Exptl. Tech. Physik. 12, 87 (1964) is adopted. The heat of fusion was obtained from the calculated enthalpy of the solid at the melting point and the liquid enthalpy measurements of P. Just, A. Meuthen and R. Durrer, Forsch. Geb. Ingenieurw. VDI-Forsch. 204 (1918). The liquid enthalpies of I. B. Fieldhouse, J. C. Hedge, J. I. Lang and T. E. Waterman, ASTIA Doc. No. A. D. 150954 are somewhat higher than the adopted values.

Sublimation Data.

See Cu(g) for details.

Cu

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈)/T	ΔF [‡] kcal. mole ⁻¹	ΔH [‡] kcal. mole ⁻¹	Log K _r
0					
100					
200					
298					
300	7.500	8.663	8.663	2.224	1.466
400	7.500	8.709	8.663	2.227	1.456
500	7.500	10.867	8.657	2.227	1.456
600	7.500	12.951	8.653	2.514	1.771
700	7.500	13.908	10.135	2.631	1.602
800	7.500	15.064	10.759	2.736	1.444
900	7.500	16.066	11.361	2.859	1.277
1000	7.500	16.842	11.934	2.984	1.117
1100	7.500	17.739	12.475	3.048	1.117
1200	7.500	18.454	12.987	3.102	1.066
1300	7.500	19.107	13.470	3.148	1.022
1400	7.500	19.707	13.927	3.186	1.000
1500	7.500	20.263	14.360	3.218	1.000
1600	7.500	20.780	14.771	3.244	1.000
1700	7.500	21.264	15.162	3.264	1.000
1800	7.500	21.719	15.534	3.279	1.000
1900	7.500	22.148	15.890	3.289	1.000
2000	7.500	22.558	16.230	3.294	1.000
2100	7.500	22.938	16.556	3.294	1.000
2200	7.500	23.304	16.869	3.294	1.000
2300	7.500	23.653	17.169	3.294	1.000
2400	7.500	24.005	17.458	3.294	1.000
2500	7.500	24.351	17.737	3.294	1.000
2600	7.500	24.696	18.006	3.294	1.000
2700	7.500	25.041	18.266	3.294	1.000
2800	7.500	25.461	18.517	3.294	1.000
2900	7.500	25.861	18.760	3.294	1.000
3000	7.500	26.225	19.224	3.294	1.000
3100	7.500	26.225	19.446	3.294	1.000
3200	7.500	26.463	19.662	3.294	1.000
3300	7.500	26.694	19.871	3.294	1.000
3400	7.500	26.918	20.075	3.294	1.000
3500	7.500	27.135	20.274	3.294	1.000
3600	7.500	27.346	20.467	3.294	1.000
3700	7.500	27.552	20.656	3.294	1.000
3800	7.500	27.752	20.840	3.294	1.000
3900	7.500	27.947	21.020	3.294	1.000
4000	7.500	28.136	21.195	3.294	1.000

Dec. 31, 1965

AT. WT. = 63.54

(LIQUID)

COPPER (Cu)

$$\Delta H_f^\circ 298.15 = 9.683 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^\circ = 3.17 \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^\circ = 72.743 \text{ kcal. mole}^{-1}$$

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH_m° and the difference between $H_{1356.6}^\circ - H_{298}^\circ$ for (c) and (l).

Heat Capacity and Entropy.

The heat capacity was calculated from the enthalpy data of P. Kist, A. Weithen and R. Durrer, Forsch. Geb. Ingenieurw. VDI-Forsch. 204 (1916). The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See crystal table for details.

Vaporization Data.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

Copper Unipositive Ion (Cu⁺)
(Ideal Gas) At. Wt. = 63.53945

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	4.968	38.367	38.367	•000	260.668	250.101	- 183.320		
100	4.968	38.397	38.367	•009	260.675	250.035	- 182.142		
200	4.968	38.427	38.367	•506	261.072	249.636	- 134.636		
300	4.968	38.457	38.367	1.003	261.450	249.224	- 106.089		
400	4.968	38.487	38.367	1.500	261.811	238.944	- 87.031		
500	4.968	38.517	38.367	1.996	262.158	235.105	- 73.400		
600	4.968	38.547	38.367	2.493	262.495	231.217	- 63.162		
700	4.968	38.577	38.367	2.990	262.822	227.288	- 55.190		
800	4.968	38.607	38.367	3.487	263.138	223.322	- 48.805		
900	4.968	38.637	38.367	3.984	263.446	219.327	- 43.574		
1000	4.968	38.667	38.367	4.481	263.744	215.302	- 39.210		
1100	4.968	38.697	38.367	4.977	264.032	211.254	- 35.513		
1200	4.968	38.727	38.367	5.474	264.318	207.186	- 32.357		
1300	4.968	38.757	38.367	5.971	264.600	203.100	- 29.638		
1400	4.968	38.787	38.367	6.468	264.876	199.000	- 27.257		
1500	4.968	38.817	38.367	6.965	265.148	194.874	- 25.154		
1600	4.968	38.847	38.367	7.461	265.416	190.724	- 23.283		
1700	4.968	38.877	38.367	7.958	265.680	186.559	- 21.608		
1800	4.968	38.907	38.367	8.455	265.940	182.382	- 20.048		
1900	4.968	38.937	38.367	8.952	266.200	178.193	- 18.731		
2000	4.968	38.967	38.367	9.449	266.456	174.000	- 17.488		
2100	4.968	38.997	38.367	9.946	266.710	170.000	- 16.351		
2200	4.968	39.027	38.367	10.443	266.960	166.108	- 15.308		
2300	4.968	39.057	38.367	10.940	267.210	162.347	- 14.347		
2400	4.968	39.087	38.367	11.437	267.460	158.686	- 13.460		
2500	4.968	39.117	38.367	11.934	267.710	155.135	- 12.638		
2600	4.968	39.147	38.367	12.431	267.960	151.686	- 11.873		
2700	4.968	39.177	38.367	12.928	268.210	148.347	- 11.261		
2800	4.968	39.207	38.367	13.425	268.460	145.100	- 10.777		
2900	4.968	39.237	38.367	13.922	268.710	141.946	- 10.325		
3000	4.968	39.267	38.367	14.419	268.960	138.886	- 9.899		
3100	4.968	39.297	38.367	14.916	269.210	135.924	- 9.499		
3200	4.968	39.327	38.367	15.413	269.460	133.060	- 9.121		
3300	4.968	39.357	38.367	15.910	269.710	130.296	- 8.764		
3400	4.968	39.387	38.367	16.407	269.960	127.631	- 8.427		
3500	4.968	39.417	38.367	16.904	270.210	125.066	- 8.107		
3600	4.968	39.447	38.367	17.401	270.460	122.601	- 7.803		
3700	4.968	39.477	38.367	17.898	270.710	120.236	- 7.515		
3800	4.968	39.507	38.367	18.395	270.960	117.972	- 7.240		
3900	4.968	39.537	38.367	18.892	271.210	115.807	- 7.000		
4000	4.968	39.567	38.367	19.389	271.460	113.742	- 6.789		
4100	4.968	39.597	38.367	19.886	271.710	111.777	- 6.604		
4200	4.968	39.627	38.367	20.383	271.960	109.912	- 6.442		
4300	4.968	39.657	38.367	20.880	272.210	108.147	- 6.299		
4400	4.968	39.687	38.367	21.377	272.460	106.482	- 6.174		
4500	4.968	39.717	38.367	21.874	272.710	104.917	- 6.064		
4600	4.968	39.747	38.367	22.371	272.960	103.452	- 5.979		
4700	4.968	39.777	38.367	22.868	273.210	102.087	- 5.915		
4800	4.968	39.807	38.367	23.365	273.460	100.822	- 5.863		
4900	4.968	39.837	38.367	23.862	273.710	99.657	- 5.821		
5000	4.968	39.867	38.367	24.359	273.960	98.592	- 5.789		
5100	4.968	39.897	38.367	24.856	274.210	97.627	- 5.764		
5200	4.968	39.927	38.367	25.353	274.460	96.762	- 5.746		
5300	4.968	39.957	38.367	25.850	274.710	95.997	- 5.733		
5400	4.968	39.987	38.367	26.347	274.960	95.332	- 5.724		
5500	4.968	40.017	38.367	26.844	275.210	94.767	- 5.719		
5600	4.968	40.047	38.367	27.341	275.460	94.302	- 5.717		
5700	4.968	40.077	38.367	27.838	275.710	93.937	- 5.716		
5800	4.968	40.107	38.367	28.335	275.960	93.672	- 5.716		
5900	4.968	40.137	38.367	28.832	276.210	93.507	- 5.716		
6000	4.968	40.167	38.367	29.329	276.460	93.442	- 5.716		

Dec. 31, 1965

COPPER UNIPosITIVE ION (Cu⁺) (IDEAL GAS) AT. WT. = 63.53945

Ground State Configuration ¹S₀
ΔH_f⁰ 0 = 258.9 ± 0.5 kcal. mole⁻¹
ΔH_f⁰ 298.15 = 260.668 ± 0.5 kcal. mole⁻¹

Electronic Levels and Quantum Weight			
E _i , cm. ⁻¹	g _i	E _i , cm. ⁻¹	g _i
0.0	1	66894.7	39
21928.6	7	72085.4	42
22847.0	5	85388.8	5
23988.3	3	88505.7	9
26264.5	5	95565.7	9

Heat of Formation.

The heat of formation was obtained from the dissociation limit of Cu(g) which was given as 62317.2 cm.⁻¹ (or 178.187 kcal. mole⁻¹) by C. E. Moore "Atomic Energy Levels", Nat. Bur. Stds. Circ. 467, Washington 1952. This value applies to 0°K. the enthalpy of Cu, Cu⁺ and e⁻ between 298°K. and zero are all 1.481 kcal. mole⁻¹, thus at 298°K. the dissociation energy is 179.668 kcal. mole⁻¹. The heat of formation was then obtained from the reaction Cu(g) → Cu⁺ + e⁻ as ΔH_f⁰ 298.15 = 260.668 ± 0.5 kcal. mole⁻¹, the uncertainty is that due to Cu(g).

Heat Capacity and Entropy.

The ground state configuration and higher electronic levels were taken from C. E. Moore, loc. cit. Levels above 100,000 cm.⁻¹ were not included since they do not affect the thermodynamic function, levels above 30,000 cm.⁻¹ were averaged.

Cu⁺

Copper Monofluoride (CuF)

CuF

(Crystal) GFW = 82.5384

T, °K	Cp ^o	gibbs/mol S ^o - (G ^o - H ^o)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0						
100						
200						
298	10.720	15.500	0.000	- 46.000	- 41.040	30.083
300	10.790	15.567	0.020	- 45.998	- 41.010	29.975
400	12.890	16.577	1.218	- 45.782	- 39.374	21.513
500	14.820	17.587	2.594	- 45.461	- 37.608	16.526
600	16.350	18.556	3.969	- 45.100	- 36.311	13.226
700	17.700	19.480	5.423	- 44.716	- 34.875	10.889
800	18.920	20.364	6.904	- 44.325	- 33.497	9.151
900	20.050	21.205	8.404	- 43.930	- 32.167	7.811
1000	21.150	22.017	9.915	- 43.540	- 30.881	6.740
1100	22.220	22.798	11.432	- 43.155	- 29.634	5.988
1200	23.270	23.551	12.952	- 42.770	- 28.422	5.176
1300	24.300	24.276	14.475	- 42.411	- 27.240	4.579
1400	25.310	24.981	16.000	- 42.088	- 26.085	4.056
1500	26.300	25.669	17.525	- 41.764	- 24.961	3.587

COPPER MONOFLUORIDE (CuF)

(CRYSTAL)

GFW = 82.5384

 $\Delta H_f^o = \text{Unknown}$ $\Delta H_f^o_{298.15} = [-46 \pm 10] \text{ kcal/mol}$ $\Delta H_m^o = \text{Unknown}$ $\Delta H_m^o_{298.15} = [58] \text{ kcal/mol}$ $S^o_{298.15} = [15.5 \pm 0.5] \text{ gibbs/mol}$ $T_m = \text{Unknown}$ Heat of Formation.

The heat of formation ($\Delta H_f^o_{298.15}$) for CuF(c) is not available from literature at the present time. The lattice energy (U_o) for CuF(c) has been calculated to be 209, 213 and 232 kcal/mol, based on the assumption of ionic bonding in CuF(c), by Pauling, Zachariasen and Ebert and Kottinek, respectively (see T. C. Maddington, Trans. Faraday Soc. 55, 1531 (1959) for details). The corresponding enthalpy change for the reaction $\text{CuF(c)} = \text{Cu}^+(g) + \text{F}^-(g)$ was evaluated as 210.18, 214.18 and 233.18 kcal/mol. Using $\Delta H_f^o_{298.15} = 280.67 \text{ kcal/mol}$ for $\text{Cu}^+(g)$ and -62.2 kcal/mol for $\text{F}^-(g)$, the values of $\Delta H_f^o_{298.15}$ (CuF, c) were calculated to be -11.7, -15.7 and -34.7 kcal/mol. However, based on $\Delta H_f^o_{298.15}(\text{CuF, g}) = 12 \pm 9 \text{ kcal/mol}$ which was measured, the values of $\Delta H_f^o_{298.15}$ would be 23.7, 27.7 and 46.7 kcal/mol which seem to be too small. By comparison with those for KF(c) and HgF(c), the value of $\Delta H_f^o_{298.15}$ was estimated as 58 kcal/mol. From this $\Delta H_f^o_{298.15}$ value and $\Delta H_f^o_{298.15}$ (CuF, g), the heat of formation for CuF(c) was derived.

Heat Capacity and Entropy.

The heat capacities, 298.15-1000°K, and $S^o_{298.15}$ were estimated by comparison with those for CuCl(c), NaCl(c) and NaF(c). The Cp values above 1000°K were obtained by graphical extrapolation.

Heat of Sublimation.

The value of $\Delta H^o_{298.15}$ was estimated by comparison with those for KF(c) and HgF(c).

COPPER MONOFLUORIDE (CuF)

(IDEAL GAS)

OFW = 82.5384

Ground State Configuration $1\Sigma^+$
 $\Delta H_f^\circ = 12 \pm 9 \text{ kcal/mol}$
 $S_{298.15}^\circ = 54.11 \text{ gibbs/mol}$
 $\Delta H_f^\circ = 12 \pm 9 \text{ kcal/mol}$
 $\Delta H_f^\circ = 12 \pm 9 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$$\frac{\epsilon_i, \text{cm}^{-1}}{0} \frac{g_i}{1}$$

$$\omega_e x_e = 3.941 \text{ cm}^{-1}$$

$$\alpha_e = 0.004586 \text{ cm}^{-1}$$

$$r_e = 1.743 \text{ \AA}$$

Heat of Formation

Based on spectroscopic data, the dissociation energy (D_0°) of CuF (g) was selected as $3.0 \pm 1.0 \text{ eV}$ by A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953. Using $\Delta H_f^\circ = 18.36$ and 80.71 kcal/mol for F(g) and Cu(g), respectively, the value of ΔH_f° for CuF (g) was calculated to be $30 \pm 23 \text{ kcal/mol}$.

Values of the dissociation energy for CuF(g) have been derived by R. A. Kent, J. D. McDonald, and J. L. Margrave, J. Phys. Chem. **70**, 874 (1966), as 3.63 ± 0.2 to $4.1 \pm 0.5 \text{ eV}$, based on mass spectrometric studies of CuF₂ sublimation from a Knudsen cell, the appearance potential of CuF⁺ ion from CuF₂ in both reducing and nonreducing systems, and a theoretical calculation assuming an ionic model like that used by E. S. Rittner, J. Chem. Phys. **19**, 1030 (1951). Until further data are available, a value $D(\text{CuF}) = 3.8 \pm 0.5 \text{ eV}$ was recommended. Using this dissociation energy for CuF (g), the heat of formation (298.15°K) for CuF(g) was evaluated to be $12 \pm 9 \text{ kcal/mol}$ which is adopted here.

Heat Capacity and Entropy

The values of ground state configuration, ω_e , $\omega_e x_e$, α_e , r_e , ϵ_i , g_i were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950, and corrected to the average isotopic species.

T, °K	Cp°, gibbs/mol	S°, gibbs/mol	-(G°-H° ₂₉₈)/T, cal/mol	H°-H° ₂₉₈ , kcal/mol	ΔG°, kcal/mol	Log Kp
0	6.000	INFINITE	-	2.171	12.070	INFINITE
100	6.070	6.070	-	2.171	12.070	INFINITE
200	7.466	51.030	54.823	759	7.634	2.110
298	7.983	54.110	54.823	759	5.449	3.994
300	7.992	54.154	54.109	0.015	11.997	3.940
400	8.342	56.509	56.427	0.853	11.833	3.237
500	8.553	58.390	58.030	1.079	11.659	2.484
600	8.693	59.968	59.436	2.541	11.473	1.985
700	8.786	61.316	60.436	3.416	11.277	1.651
800	8.855	62.494	61.121	4.298	11.069	1.388
900	8.907	63.540	61.776	5.186	10.852	1.170
1000	8.948	64.491	62.400	6.079	10.624	0.981
1100	8.983	65.335	62.994	6.976	10.389	0.810
1200	9.013	66.118	63.555	7.875	10.144	0.650
1300	9.039	66.840	64.088	8.778	9.891	0.500
1400	9.063	67.511	64.595	9.683	9.645	0.360
1500	9.084	68.137	65.077	10.590	9.417	0.230
1600	9.105	68.724	65.537	11.500	9.199	0.110
1700	9.124	69.277	65.976	12.411	8.981	0.000
1800	9.143	69.799	66.396	13.325	8.764	-0.110
1900	9.161	70.294	66.799	14.241	8.550	-0.220
2000	9.179	70.764	67.185	15.157	8.340	-0.330
2100	9.197	71.212	67.557	16.076	8.134	-0.440
2200	9.216	71.640	67.915	16.996	7.931	-0.550
2300	9.235	72.051	68.260	17.919	7.733	-0.660
2400	9.253	72.446	68.594	18.844	7.538	-0.770
2500	9.270	72.822	68.914	19.770	7.346	-0.880
2600	9.303	73.187	69.225	20.699	7.157	-0.990
2700	9.330	73.538	69.527	21.631	6.972	-1.100
2800	9.359	73.878	69.819	22.565	6.791	-1.210
2900	9.387	74.207	70.103	23.503	6.613	-1.320
3000	9.420	74.526	70.378	24.443	6.439	-1.430
3100	9.465	74.836	70.646	25.388	6.269	-1.540
3200	9.507	75.137	70.907	26.337	6.102	-1.650
3300	9.552	75.430	71.161	27.289	5.939	-1.760
3400	9.602	75.716	71.408	28.247	5.779	-1.870
3500	9.653	75.993	71.648	29.210	5.622	-1.980
3600	9.712	76.268	71.885	30.178	5.467	-2.090
3700	9.773	76.535	72.115	31.153	5.314	-2.200
3800	9.837	76.796	72.340	32.133	5.162	-2.310
3900	9.905	77.053	72.560	33.120	5.011	-2.420
4000	9.976	77.304	72.776	34.114	4.862	-2.530
4100	10.050	77.552	72.987	35.115	4.715	-2.640
4200	10.128	77.795	73.194	36.124	4.570	-2.750
4300	10.207	78.034	73.396	37.141	4.427	-2.860
4400	10.289	78.270	73.595	38.166	4.285	-2.970
4500	10.374	78.502	73.791	39.199	4.144	-3.080
4600	10.460	78.731	73.983	40.241	4.004	-3.190
4700	10.547	78.957	74.171	41.291	3.865	-3.300
4800	10.636	79.180	74.357	42.350	3.727	-3.410
4900	10.726	79.400	74.539	43.418	3.590	-3.520
5000	10.816	79.617	74.716	44.495	3.454	-3.630
5100	10.906	79.832	74.895	45.581	3.319	-3.740
5200	10.997	80.045	75.069	46.677	3.185	-3.850
5300	11.087	80.255	75.240	47.781	3.052	-3.960
5400	11.177	80.463	75.409	48.894	2.920	-4.070
5500	11.266	80.669	75.576	50.016	2.788	-4.180
5600	11.354	80.873	75.740	51.147	2.657	-4.290
5700	11.440	81.075	75.902	52.287	2.527	-4.400
5800	11.525	81.275	76.062	53.435	2.397	-4.510
5900	11.609	81.472	76.219	54.592	2.268	-4.620
6000	11.690	81.668	76.375	55.757	2.138	-4.730

June 30, 1966

Copper Difluoride (CuF₂)

(Crystal)

GFW = 101.5368

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
298	16.770	16.400	16.400	0.000	-131.200	-119.286	87.439
300	16.780	16.504	16.400	1.031	-131.194	-119.213	86.846
400	17.460	21.424	17.067	1.743	-130.849	-115.270	82.980
500	18.140	25.394	18.447	3.523	-130.492	-111.416	78.700
600	18.800	28.760	19.809	5.371	-130.109	-107.636	74.207
700	19.410	31.704	21.302	7.281	-129.695	-103.922	69.446
800	19.980	34.334	22.770	9.251	-129.248	-100.272	64.393
900	20.490	36.718	24.189	11.275	-128.767	-96.679	59.077
1000	20.960	38.900	25.553	13.348	-128.257	-93.140	53.556
1100	21.300	40.914	26.859	15.460	-127.723	-89.655	47.813
1200	21.580	42.780	28.109	17.605	-127.171	-86.218	41.702
1300	21.750	44.514	29.305	19.772	-126.611	-82.827	35.244
1400	21.860	46.130	30.450	21.953	-126.035	-79.478	28.561
1500	21.918	47.641	31.546	24.142	-125.442	-76.166	21.649
1600	21.960	49.057	32.597	26.336	-124.836	-72.890	14.580
1700	21.987	50.389	33.604	28.534	-124.218	-69.648	7.352
1800	22.000	51.646	34.572	30.733	-123.584	-66.432	0.000
1900	22.000	52.835	35.502	32.933	-122.935	-63.242	-7.131
2000	22.000	53.964	36.397	35.133	-122.272	-60.076	-14.265

CuF₂

(CRYSTAL)

COPPER DIFLUORIDE (CuF₂)

GFW = 101.5368

$\Delta H_f^\circ = \text{Unknown}$
 $\Delta H_f^\circ_{298.15} = -131.2 \pm 0.8 \text{ kcal/mol}$
 $\Delta H_m^\circ = [9.4] \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = 62.5 \pm 0.6 \text{ kcal/mol}$

$S^\circ_{298.15} = [16.4] \text{ gibbs/mol}$
 $T_m = 1043^\circ\text{K}$

Heat of Formation.

The chemical equilibrium for the reaction (1) $\text{CuF}_2(\text{c}) + \text{H}_2(\text{g}) = \text{Cu}(\text{c}) + 2\text{HF}(\text{g})$ has been studied by K. Jellinek and A. Rudat, Z. anorg. allgem. Chem. 175, 281 (1928). The equilibrium gas phase composition was found to be HF 4.3% and H₂ 95.7%, at 423°K. From this data the enthalpy change ($\Delta H^\circ_{298.15}$) of the reaction was evaluated. The equilibrium for the reaction (2) $\text{CuF}_2(\text{c}) + \text{H}_2\text{O}(\text{g}) = \text{CuO}(\text{c}) + 2\text{HF}(\text{g})$ was investigated by L. Domange, Compt. rend. 200, 239 (1935). Based on the equilibrium data reported, the $\Delta H^\circ_{298.15}$ value for the reaction was derived. The results obtained are presented as follows.

Reaction	Temperature, °K	Second Law Value	Third Law Value	Drift	$\Delta H^\circ_{298.15}$ kcal/mol
(1)	423	22.38	22.15	—	-152.0
(2)	473.15-723.15	23.06 ± 1.33	22.15	-1.67 ± 1.96	-131.2

Using the third law values for $\Delta H^\circ_{298.15}$, the corresponding $\Delta H^\circ_{298.15}$ (CuF₂, c) values were calculated. The adopted heat of formation for CuF₂(c) is $-131.2 \pm 0.8 \text{ kcal/mol}$.

Heat Capacity and Entropy.

The heat capacities, $S^\circ_{298.15}$ and $S^\circ_{298.15}$ were estimated by comparison with those for CuCl₂(c), CaF₂(c) and CaCl₂(c), respectively. The Cp values above 1000°K were obtained by graphical extrapolation.

Melting Data.

T_m was reported by H. M. Haendler, L. H. Towle, E. F. Bennett and M. L. Patterson, Jr., J. Am. Chem. Soc. 76, 2178 (1954). T_m for CuF₂(c) in HF(g) or H₂(g) was found to be $950 \pm 5^\circ\text{C}$ or $785 \pm 10^\circ\text{C}$, respectively, by H. von Wartenberg, Z. anorg. allgem. Chem. 241, 381 (1939). Heat of melting was estimated by comparison with those for other related compounds.

Heat of Sublimation.

See CuF₂(g) table for details.

T, °K	C _p ^o	gibbs/mol S ^o - (C ^o - H ²⁹⁸)/T	H ^o - H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	22.500	20.584	0.000	- 124.300	- 113.633	83.295
300	22.500	20.723	20.584	- 124.283	- 113.568	82.734
400	22.500	27.196	2.582	- 124.265	- 113.500	80.172
500	22.500	32.217	4.582	- 124.253	- 113.489	76.730
600	22.500	36.319	6.792	- 121.788	- 103.851	37.828
700	22.500	39.787	9.042	- 121.034	- 100.920	31.509
800	22.500	42.792	11.262	- 120.307	- 98.099	25.790
900	22.500	45.442	13.496	- 119.600	- 95.269	20.129
1000	22.500	47.821	15.752	- 118.824	- 92.439	14.653
1100	22.500	49.957	18.042	- 118.241	- 90.121	17.905
1200	22.500	51.815	20.262	- 117.584	- 87.584	15.953
1300	22.500	53.716	22.542	- 116.941	- 85.120	14.310
1400	22.500	55.593	24.896	- 116.308	- 82.734	12.953
1500	22.500	57.408	27.402	- 115.697	- 80.404	11.653
1600	22.500	59.198	30.292	- 115.122	- 78.121	10.473
1700	22.500	60.952	33.582	- 114.582	- 75.883	9.424
1800	22.500	62.658	37.262	- 114.072	- 73.686	8.486
1900	22.500	64.323	41.323	- 113.593	- 71.529	7.659
2000	22.500	65.948	45.763	- 113.143	- 69.409	6.939

OPW = 101.5368

(LIQUID)

ΔH_{f298.15}^o = [-124.30] kcal/mol

ΔH_m^o = [9.4] kcal/mol

ΔH_v^o = [43.98] kcal/mol

S_{298.15}^o = [20.584] gibbs/mol

T_m = 1043°K

T_b = [1722]°K

Heat of Formation.

The heat of formation (ΔH_{f298.15}^o) was obtained from ΔH_{f298.15}^o (CuF₂, c) by adding ΔH_m^o and the difference between H₁₀₄₃^o-H_{298.15}^o for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated based on an assumption that the average heat capacity for CuF₂(l) is 7.5 gibbs/atom. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See CuF₂(c) table for details.

Vaporization Data.

T_b is the temperature at which the free energy change for the reaction CuF₂(l) = CuF₂(g) becomes zero. The difference between ΔH_f^o for liquid and gas at T_b is ΔH_v^o.

Copper Difluoride (CuF₂)
(Ideal Gas)

OPW = 101.5368

T, °K	Cp ^a	gibbs/mol S ^b - (C ^a - H ³⁰⁰)/T	H ³⁰⁰ - H ³⁰⁰ ΔH ^c	ΔG ^d	Log Kp
0	∞	INFINITE	- 2.920	- 68.315	INFINITE
100	8.999	49.386	2.160	- 68.409	150.884
200	11.016	56.302	1.151	- 68.581	76.055
298	12.340	60.966	∞	- 68.700	51.365
300	12.340	61.062	∞	- 68.702	51.055
400	13.199	64.723	1.904	- 68.788	38.955
500	13.709	67.727	2.652	- 68.863	31.014
600	14.029	70.257	3.324	- 68.940	25.995
700	14.280	72.437	3.954	- 69.022	22.405
800	14.488	74.289	4.546	- 69.113	19.110
900	14.654	75.809	5.094	- 69.213	17.110
1000	14.792	77.079	5.604	- 69.323	15.829
1100	14.904	78.090	6.075	- 69.441	14.550
1200	15.000	78.954	6.516	- 69.569	13.400
1300	15.082	79.684	6.926	- 69.706	12.360
1400	15.151	80.293	7.304	- 69.850	11.410
1500	15.208	80.784	7.650	- 69.999	10.570
1600	15.254	81.161	7.974	- 70.152	9.820
1700	15.291	81.431	8.278	- 70.308	9.150
1800	15.319	81.603	8.563	- 70.466	8.553
1900	15.339	81.687	8.829	- 70.624	8.017
2000	15.352	81.692	9.076	- 70.781	7.530
2100	15.359	81.618	9.304	- 70.937	7.091
2200	15.361	81.562	9.514	- 71.091	6.699
2300	15.359	81.523	9.700	- 71.242	6.323
2400	15.353	81.494	9.863	- 71.390	5.961
2500	15.344	81.472	10.004	- 71.534	5.612
2600	15.332	81.456	10.126	- 71.674	5.274
2700	15.318	81.444	10.231	- 71.809	4.947
2800	15.302	81.434	10.321	- 71.939	4.632
2900	15.284	81.426	10.396	- 72.064	4.326
3000	15.264	81.419	10.456	- 72.184	4.029
3100	15.242	81.413	10.501	- 72.299	3.741
3200	15.218	81.407	10.531	- 72.409	3.461
3300	15.193	81.401	10.547	- 72.514	3.191
3400	15.167	81.395	10.559	- 72.614	2.931
3500	15.140	81.388	10.566	- 72.709	2.681
3600	15.112	81.380	10.569	- 72.800	2.441
3700	15.083	81.372	10.568	- 72.886	2.211
3800	15.053	81.363	10.563	- 72.968	1.991
3900	15.022	81.353	10.554	- 73.046	1.781
4000	14.990	81.343	10.541	- 73.120	1.581
4100	14.957	81.332	10.524	- 73.190	1.391
4200	14.923	81.320	10.504	- 73.256	1.211
4300	14.888	81.307	10.480	- 73.318	1.041
4400	14.852	81.293	10.453	- 73.376	0.881
4500	14.815	81.278	10.423	- 73.429	0.731
4600	14.778	81.261	10.390	- 73.477	0.591
4700	14.739	81.243	10.354	- 73.520	0.461
4800	14.699	81.223	10.315	- 73.558	0.341
4900	14.658	81.201	10.273	- 73.591	0.231
5000	14.615	81.177	10.228	- 73.619	0.131
5100	14.571	81.151	10.180	- 73.642	0.041
5200	14.526	81.123	10.129	- 73.660	- 0.049
5300	14.480	81.093	10.075	- 73.674	- 0.159
5400	14.433	81.061	10.018	- 73.684	- 0.279
5500	14.385	81.027	9.958	- 73.690	- 0.409
5600	14.336	80.991	9.894	- 73.692	- 0.549
5700	14.286	80.953	9.826	- 73.690	- 0.699
5800	14.235	80.913	9.754	- 73.685	- 0.859
5900	14.183	80.871	9.678	- 73.676	- 1.019
6000	14.130	80.827	9.598	- 73.663	- 1.179

June 30, 1966

COPPER DIFLUORIDE (CuF₂)

OPW = 101.5368

(IDEAL GAS)

Point Group D_{∞h}

ΔH_f⁰ = -68.3 ± 1.0 kcal/mol

ΔH_f^{298.15} = -68.7 ± 1.0 kcal/mol

S_{298.15} = [60.97] gibbs/mol

Electronic Levels and Quantum Weights

ε _i , cm ⁻¹	g _i
0	2
[9000] [4]	
[18000] [4]	

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
[608] (1)
[205] (2)
768 (1)

Bond Distance: Cu-F = [1.72] Å

Bond Angle: F-Cu-F = [180]°

Rotational Constant: B₀ = [0.14996] cm⁻¹

σ = 2

Heat of Formation

The vapor pressures of CuF₂(c), at temperatures from 897 to 1026°K, have been determined by R. A. Kent, J. D. McDonald and J. L. Margrave, J. Phys. Chem. 70, 874 (1966). Based on these data, the heat of sublimation (ΔH_{sub}^{298.15}) of CuF₂(c) was derived to be 62.45 ± 0.5 and 62.50 kcal/mol by the second and third law method, respectively. From the values of ΔH_{sub}^{298.15} and ΔH_f^{298.15} for CuF₂(c), the heat of formation (ΔH_f^{298.15}) for CuF₂(g) was evaluated.

Heat Capacity and Entropy

The molecular structure, bond distance and angle were estimated by L. Brewer, O. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The ground state electronic configuration, 2Σ_g⁺, was obtained from A. Büchler, J. L. Stauffer and W. Klemperer, Intern. J. Mass Spectrom. Ion Processes, 10, 6, Apr. 30, 1964, Arthur D. Little, Inc., Cambridge, Mass. The other electronic levels and quantum weights were assumed from those for CuCl₂(g) reported by J. T. Hougen, G. E. Leroy and T. C. James, J. Chem. Phys. 33, 1670 (1961). The vibrational frequency, ν₃, was determined by P. H. Kasa, E. B. Whipple and M. Weltner, Jr., J. Chem. Phys. 44, 2581 (1966). The other two frequencies, ν₁ and ν₂, were calculated by Valence Force Treatment described by O. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is I = 1.66649 X 10⁻³⁸ g cm².

Copper Dihydroxide (Cu(OH)₂)
(Crystal) GFW = 97.55474

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
298	22.750	25.900	25.900	0.000	-107.640	- 89.088	65.303
300	22.760	26.041	25.900	0.062	-107.635	- 88.973	64.817
400	23.780	32.728	26.805	24.369	-107.310	- 82.800	45.240
500	24.800	38.124	28.548	4.768	-106.927	- 76.715	33.532
600	25.820	42.756	30.541	7.329	-106.484	- 70.713	25.757
700	26.840	46.647	32.581	12.762	-105.976	- 64.790	20.228
800	27.860	50.047	34.616	17.622	-105.414	- 58.940	15.012
900	28.200	53.735	36.538	15.477	-104.815	- 53.172	10.374
1000	28.600	56.729	38.610	18.318	-104.197	- 47.468	8.310
1100	28.860	59.467	40.202	21.162	-103.574	- 41.824	6.600
1200	29.130	61.937	41.916	24.069	-102.956	- 36.239	5.290
1300	29.410	64.315	43.815	26.989	-102.343	- 30.711	4.263
1400	29.170	66.475	45.110	29.912	-101.735	- 25.111	3.490
1500	29.200	68.489	46.602	32.830	-101.132	- 19.427	2.831

June 30, 1966

COPPER DIHYDROXIDE (Cu(OH)₂)

(CRYSTAL)

OPW = 97.55474

CuH₂O₂

ΔHf° = Unknown

ΔHf°_{298.15} = -107.64 ± 2.0 kcal/mol

S°_{298.15} = [25.9] gibbs/mol

Td = 433°K

Heat of Formation.

The enthalpy change (ΔHf°₄₃₃) for the reaction Cu(OH)₂(c) = CuO(c) + H₂O(g) has been determined by L. V. Py, Bull. soc. chim. France, No. 3, 545 (1964). Based on the reported value, ΔHf°₄₃₃ = 12 kcal/mol, the heat of formation (ΔHf°_{298.15}) for Cu(OH)₂(c) was derived as -107.64 kcal/mol, using ΔHf°_{298.15} = -37.250 and -57.798 kcal/mol for CuO(c) and H₂O(g), respectively, which was adopted here.

The free energy change (ΔG°_{298.15}) of the reaction Cu(OH)₂(c) = Cu⁺⁺(aq) + 2 OH⁻(aq) was evaluated to be 26.36 and 26.26 kcal/mol, based on the solubility product for Cu(OH)₂(c) reported by (1) E. S. Oenelina, Zh. prikl. Khim. 37, 1358 (1964) and (2) N. P. Zhuk, Zh. Fiz. Khim. 28, 1523 (1954), respectively. Using values of S°_{298.15} and ΔHf°_{298.15} for Cu⁺⁺(aq) and OH⁻(aq) from "Selective Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952, and NBS Technical Note 270-1, 1955, by D. D. Wagman and co-workers, the corresponding enthalpy change ΔHf°_{298.15} and heat of formation (ΔHf°_{298.15}) for Cu(OH)₂(c) were derived. The results obtained are presented as follows.

Chemical Reaction	ΔHf° _{298.15} kcal/mol	Reference
Cu(OH) ₂ (c) = Cu ⁺⁺ (aq) + 2 OH ⁻ (aq)	10.06	(1)
Cu(OH) ₂ (c) = Cu ⁺⁺ (aq) + 2 OH ⁻ (aq)	9.97	(2)
CuO(c) + H ₂ O(l) = Cu(OH) ₂ (c)	-1.9	(3)
CuO(c) + H ₂ O(l) = Cu(OH) ₂ (c)	0.3	(4)

The heats of solution of CuO(c) and Cu(OH)₂(c) in HNO₃(aq.) have been determined by (3) de Forcrand, Compt. rend. 157, 441 (1913) to be -16.38 and -14.46 kcal/mol, respectively. From these data the enthalpy change for the reaction CuO(c) + H₂O(l) = Cu(OH)₂(c) was derived as -1.9 kcal/mol. For the same reaction, the enthalpy change was reported to be 0.3 kcal/mol by (4) P. Sabatier, Compt. rend. 125, 301 (1897). Based on ΔHf°_{298.15} = -37.25 and -68.315 kcal/mol for CuO(c) and H₂O(l), respectively, the heat of formation for Cu(OH)₂(c) was evaluated. The results obtained are presented in the above table.

Heat Capacity and Entropy.

The heat capacities, 298.15-700°K, were estimated by comparison with those for CuO(c), CaO(c) and Ca(OH)₂(c). The Cp values above 700°K were obtained by graphical extrapolation. S°_{298.15} was estimated such that the derived ΔGf° (Cu(OH)₂, c) = ΔGf° (CuO, c) + ΔGf° (H₂O, g) at 433°K.

Decomposition Temperature.

Td is the temperature at which the Gibbs energy change for the reaction Cu(OH)₂(c) = CuO(c) + H₂O(g) equals zero.

CuH₂O₂

Copper Monoxide (CuO)

CuO

(Crystal) GFW = 79.5394

COPPER MONOXIDE (CuO)

(CRYSTAL)

QFM = 79.5394

T, °K	Cp*	$\frac{S^0}{J}$	$-(G^0 - H^0_{298})/T$	$H^0 - H^0_{298}$	ΔH^0	ΔG^0	Log Kp
0	3.000	0.000	INFINITE	-1.695	-36.713	-36.713	INFINITE
100	3.945	2.335	17.732	-1.695	-37.028	-37.028	INFINITE
200	8.321	6.460	11.058	-1.920	-37.272	-37.272	INFINITE
298	10.066	10.183	10.183	0.000	-37.250	-30.622	22.446
300	10.094	10.245	10.183	0.019	-37.249	-30.581	22.278
400	10.404	10.565	10.565	1.091	-37.129	-28.374	15.503
500	11.560	15.016	11.406	2.254	-36.958	-26.204	11.434
600	12.500	18.145	12.348	3.478	-36.734	-24.076	8.770
700	12.980	20.108	13.319	4.752	-36.494	-21.984	6.864
800	13.430	21.871	14.280	6.073	-36.229	-19.930	5.445
900	13.850	23.468	15.144	7.446	-35.948	-17.909	4.349
1000	14.310	24.962	16.115	8.867	-35.621	-15.923	3.460
1100	14.750	26.347	16.983	10.300	-35.273	-13.970	2.776
1200	15.190	27.649	17.818	11.797	-34.896	-12.050	2.195
1300	15.630	28.887	18.622	13.318	-34.498	-10.161	1.708
1400	16.070	30.070	19.397	14.853	-34.077	-8.266	1.281
1500	16.510	31.180	20.146	16.352	-33.639	-6.417	0.896
1600	16.950	32.250	20.869	18.225	-33.185	-4.612	0.563
1700	17.390	33.301	21.570	19.942	-32.719	-2.925	0.273
1800	17.820	34.307	22.250	21.703	-32.242	-1.460	0.019
1900	18.250	35.270	22.900	23.506	-31.750	-0.204	-0.170
2000	18.710	36.231	23.493	25.357	-31.250	0.600	-0.401

$S^0_{298,15} = 10.18 \pm 0.1$ gibbs/mol
 $T_d = 1395^\circ K$

Heat of Formation.
 The more consistent data relative to the heat of formation are reviewed below. The selected value of -37.25 kcal/mol was derived from $\Delta H^0_{298} = -40.7$ kcal/mol for $Cu_2O(c)$ and $\Delta H^0_{298} = 33.80$ kcal/mol for $2CuO(c) = Cu_2O(c) + O_2$. Four different sets of oxygen dissociation pressure measurements yield heats of reaction in close agreement with each other and with the aqueous calorimetry of Thomsen. Thomsen's data may be reduced to the heat of reduction of $CuO(c)$ by combining heats of reaction for $CuO + H_2SO_4$, $Fe + H_2SO_4$, and $Fe + CuSO_4(aq)$. Direct calorimetric measurement of the heat of reduction by von Wartenberg and Werth yields $\Delta H^0_{298} = -36.04 \pm 0.2$ when corrected for incomplete condensation of water. Direct measurement is difficult and this value may correspond to incomplete reduction. The value of -33.02 reported by Wöhler and Jochum, Z. physik. Chem. 167, 169 (1933), is unreasonable. Equilibrium constants derived from Balascent and Chiche yield -37.6 kcal/mol by third law analysis, but a serious entropy error is present. This is no doubt due to uncertainties in the activity of Cu in Cu-Au alloys. Other data have been reviewed by Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931).

Author	Method	Reaction**	Temp.	No. of Points	ΔH^0_{298} (kcal/mol)	Drift (kcal/mol)
1. Thomsen (1883)	Aqueous Calorimetry	A	291	—	-31.15	—
2. Wartenberg et al. (1932)	Calorimetry	A	295	—	-30.27 $\pm$ 0.2	—
3. Balascent (1955)	Equilibrium Data	B	1011-1156	32	68.2 $\pm$ 0.7	75.18 6.4 $\pm$ 0.7 -37.59
4. Aasvåg (1955)	Kp	C	1047-1342	11	33.28 $\pm$ 0.15	33.81 0.4 $\pm$ 0.1 -37.25
5. Becker (1927)	Kp	C	1193-1293	6	33.84 $\pm$ 0.27	33.80 0.0 $\pm$ 0.2 -37.25
6. Roberts et al. (1921)	Kp	C	1189-1358	20	33.96 $\pm$ 0.07	33.76 -0.1 $\pm$ 0.1 -37.22
7. Foote et al. (1908)	Kp	C	1223-1323	7	33.19 $\pm$ 0.17	33.74 0.4 $\pm$ 0.1 -37.22
8. Combined 4,5,6,7	Kp	C	1047-1358	45	33.70 $\pm$ 0.10	33.77 0.04 $\pm$ 0.09 -37.24

*Based on third law where possible.

**Reaction A: $CuO(c) + H_2 = Cu(c) + H_2O(l)$ B: $2CuO(c) = 2Cu(c) + O_2$ C: $2CuO(c) = Cu_2O(c) + 0.5 O_2$

1. J. Thomsen, "Thermochemische Untersuchungen," vol. I, III, Barth, Leipzig, 1883.
2. H. von Wartenberg and H. Werth, Z. elektrochem. 38, 51 (1932).
3. D. Balascent, Compt. rend. 240, 760 (1955); 1864 (1955); P. Chiche, Ann. chim. 1, 361 (1952).
4. P. Aasvåg, Ann. chim. (Paris) 12, 637 (1955).
5. F. Becker, Dissertation, Darmstadt, 1927; cf. Wöhler and Jochum, Z. physik. Chem. 167A, 169 (1933).
6. H. S. Roberts and P. H. Smyth, J. Am. Chem. Soc. 43, 1061 (1921); 42, 2582 (1920).
7. H. W. Foote and E. K. Smith, J. Am. Chem. Soc. 30, 1344 (1908).

Heat Capacity and Entropy.

Low temperature values are based on data (15-297°K) from J. Hu and H. L. Johnston, J. Am. Chem. Soc. 75, 2471 (1953). Earlier data from R. W. Miller (71-302°K), J. Am. Chem. Soc. 51, 215 (1929), are in satisfactory agreement, while those of K. Clusius and P. Harteck (30-200°K), Z. physik. Chem. 134, 243 (1928), are higher by several percent. A small anomaly in the heat capacity is observed in the region 210-230°K. Magnetic measurements of M. O'Keefe and F. S. Stone, Phys. Chem. Solids 23, 261 (1962), and neutron diffraction studies of B. N. Brockhouse, Phys. Rev. 94, 781 (1954), suggest that this is a Néel point associated with antiferromagnetism. The entropy was obtained from the heat capacities based on $S^0_{15} = 0.016$ eu.

High temperature values are based on specific heats (373-1273°K) obtained from a dynamic method by D. M. Chizhikov and A. S. Khirik, Tr. Inst. Met. im. A. A. Baikova, Akad. Nauk SSSR, No. 12, 79 (1963); cf. Chem. Abs. 59, 5860 b (1963). Enthalpy data (523-1253°K) of Wöhler and Jochum, loc. cit., lead to a value for S^0_{1200} lower by about 0.25 eu, but this is inconsistent with the equilibrium data for $2CuO = Cu_2O + 0.5 O_2$.

Temperature of Decomposition.

T_d is calculated as the temperature at which ΔF equals zero for $2CuO(c) = Cu_2O(c) + 0.5 O_2(g)$.

CuO

June 30, 1966

Copper Monoxide (CuO)

(Ideal Gas)

GFW = 79.5394

Symmetry Number = 1

 $S_{298.15}^{\circ} = 56.07 \pm 0.1$ gibbs/mol $\Delta H_f^{\circ} = 58.8 \pm 8$ kcal/mol $\Delta H_f^{\circ}{}_{298.15} = 58.9 \pm 8$ kcal/mol

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	7.090	47.222	-	2.333	58.800	58.800	INFINITE
100	7.245	47.223	56.333	1.422	59.005	59.005	-121.681
200	7.400	47.224	56.333	1.424	59.073	59.073	-59.208
298	7.522	47.225	56.072	1.424	59.000	59.000	-36.005
300	7.526	47.226	56.072	1.424	58.998	58.998	-37.734
400	7.689	47.227	56.008	1.427	58.907	58.907	-27.019
500	7.791	47.228	55.949	1.432	58.760	58.760	-20.506
600	7.862	47.229	55.771	1.434	58.572	58.572	-16.326
700	7.921	47.230	55.498	1.434	58.267	58.267	-13.282
800	7.962	47.231	55.204	1.434	57.867	57.867	-11.004
900	8.000	47.232	54.896	1.434	57.389	57.389	-9.330
1000	8.026	47.233	54.576	1.434	56.841	56.841	-8.061
1100	8.051	47.234	54.246	1.434	56.234	56.234	-7.061
1200	8.074	47.235	53.906	1.434	55.572	55.572	-6.281
1300	8.096	47.236	53.558	1.434	54.858	54.858	-5.681
1400	8.117	47.237	53.202	1.434	54.096	54.096	-5.201
1500	8.137	47.238	52.838	1.434	53.290	53.290	-4.811
1600	8.156	47.239	52.466	1.434	52.444	52.444	-4.481
1700	8.174	47.240	52.086	1.434	51.562	51.562	-4.201
1800	8.191	47.241	51.698	1.434	50.638	50.638	-3.961
1900	8.207	47.242	51.302	1.434	49.676	49.676	-3.751
2000	8.222	47.243	50.898	1.434	48.678	48.678	-3.561
2100	8.236	47.244	50.486	1.434	47.646	47.646	-3.381
2200	8.249	47.245	50.066	1.434	46.582	46.582	-3.211
2300	8.261	47.246	49.638	1.434	45.488	45.488	-3.051
2400	8.272	47.247	49.202	1.434	44.366	44.366	-2.901
2500	8.282	47.248	48.758	1.434	43.218	43.218	-2.761
2600	8.291	47.249	48.306	1.434	42.046	42.046	-2.631
2700	8.299	47.250	47.846	1.434	40.852	40.852	-2.511
2800	8.306	47.251	47.378	1.434	39.638	39.638	-2.401
2900	8.312	47.252	46.902	1.434	38.406	38.406	-2.301
3000	8.317	47.253	46.418	1.434	37.158	37.158	-2.211
3100	8.321	47.254	45.926	1.434	35.896	35.896	-2.131
3200	8.324	47.255	45.426	1.434	34.622	34.622	-2.061
3300	8.326	47.256	44.918	1.434	33.338	33.338	-2.001
3400	8.328	47.257	44.402	1.434	32.046	32.046	-1.941
3500	8.329	47.258	43.878	1.434	30.746	30.746	-1.891
3600	8.329	47.259	43.346	1.434	29.438	29.438	-1.841
3700	8.328	47.260	42.806	1.434	28.124	28.124	-1.791
3800	8.326	47.261	42.258	1.434	26.806	26.806	-1.741
3900	8.323	47.262	41.702	1.434	25.484	25.484	-1.691
4000	8.319	47.263	41.138	1.434	24.158	24.158	-1.641
4100	8.314	47.264	40.566	1.434	22.828	22.828	-1.591
4200	8.308	47.265	39.986	1.434	21.494	21.494	-1.541
4300	8.301	47.266	39.398	1.434	20.156	20.156	-1.491
4400	8.293	47.267	38.802	1.434	18.814	18.814	-1.441
4500	8.284	47.268	38.198	1.434	17.468	17.468	-1.391
4600	8.274	47.269	37.586	1.434	16.118	16.118	-1.341
4700	8.263	47.270	36.966	1.434	14.764	14.764	-1.291
4800	8.251	47.271	36.338	1.434	13.406	13.406	-1.241
4900	8.238	47.272	35.702	1.434	12.044	12.044	-1.191
5000	8.224	47.273	35.058	1.434	10.678	10.678	-1.141
5100	8.209	47.274	34.406	1.434	9.308	9.308	-1.091
5200	8.193	47.275	33.746	1.434	7.934	7.934	-1.041
5300	8.176	47.276	33.078	1.434	6.556	6.556	-0.991
5400	8.158	47.277	32.402	1.434	5.174	5.174	-0.941
5500	8.139	47.278	31.718	1.434	3.788	3.788	-0.891
5600	8.119	47.279	31.026	1.434	2.398	2.398	-0.841
5700	8.098	47.280	30.326	1.434	1.004	1.004	-0.791
5800	8.076	47.281	29.618	1.434	-0.394	-0.394	-0.741
5900	8.053	47.282	28.902	1.434	-1.786	-1.786	-0.691
6000	8.029	47.283	28.178	1.434	-3.172	-3.172	-0.641

Sept. 30, 1966; June 30, 1970

Electronic Levels and Molecular Constants									
State	E_e , cm ⁻¹	E_e , cm ⁻¹	E_e , cm ⁻¹	E_e , cm ⁻¹	E_e , cm ⁻¹	E_e , cm ⁻¹	E_e , cm ⁻¹	E_e , cm ⁻¹	E_e , cm ⁻¹
X ² Π	0	2	1.726	0.4446	[0.0034]	632			[3.5]
A ² Π	269	2			[0.0040]	633			4.5
B ² Σ	4460	2			[0.0052]	637			6.5
C ² Π	4735	2			[0.0046]	610			[5.0]

Heat of Formation

The heat of formation is calculated from that of the crystal, $\Delta H_{298}^{\circ} = 95.1$ kcal/mol, which was obtained by 3rd law analysis of the sublimation pressure at 1773°K reported by Mack et al. (1). They employed a transpiration method and analysed for copper (in minute amounts) by its catalytic effect on the oxidation rate of sodium sulfite. The resulting pressure is only 100 times the predicted pressure of Cu(g) over CuO(c). These pressures were reported but not used in the range 873-1173°K, since these yield a much smaller value for the heat of vaporization and imply a high dissociation energy.

Some estimates of D_0° CuO obtained by different methods are given below. These estimates along with a correlation of D_0° values for MnO, FeO, NiO and ZnO favor $D_0^{\circ} = 82 \pm 10$, close to the value adopted.

Method	ΔH_{298}° , kcal/mol	D_0° , kcal/mol	ΔH_{298}° , kcal/mol
Mack et al. (1) Transpiration	95.1	80.8	58.9
Arithmetic mean of D_0° for O ₂ and Cu ₂		82	57.7
Geometric mean of D_0° for O ₂ and Cu ₂		73	66.7
Linear Birge-Sponer extrapolation of A ² Π state		76±12	63.7±12

Heat Capacity and Entropy

The visible spectrum of CuO has been extensively investigated, but only very recently has significant progress been made in its analysis. Antic-Jovanovic et al. (2) were able to obtain a vibrational analysis of the major band system by use of ⁶³isotope studies. Shirk and Bass (3) recently reported absorption and fluorescence spectra in inert-gas matrices which allows assignment of the ground state and the first two excited states. They have strong evidence for the lower state of the blue system being the ground state and also for the second system, which corresponds to the red-orange system, originating in the upper state of the blue system. Thus, it is probable that the B state is Σ and the X and A states are both Σ Π with very similar molecular constants, which serves to confuse the analysis of the spectra. It also appears likely that the 4187Å band analysed by Lagerqvist and Uhler (4) is a Σ Π transition terminating in the ground state; thus we adopt their rotational constants for the X and C states. The vibrational frequencies and anharmonicities for the A and B states were from Antic-Jovanovic (2), as well as the vibrational interval for the ground state. The anharmonicity for the ground state was chosen so as to provide a reasonable Birge-Sponer extrapolation of the dissociation energy. The values of the q_e were estimated from the Morse potential function relations. The rotational constants were assumed to be nearly constant. The values of the splitting in the electronic levels in the X and A states are from Antic-Jovanovic (2), and are roughly confirmed by Shirk and Bass (3).

The thermodynamic functions were calculated by summing over the individual partition functions for the separate states.

References

1. E. Mack, G. O. Osterhof and H. M. Kramer, J. Amer. Chem. Soc. **45**, 617 (1923).
2. A. Antic-Jovanovic, D. S. Pesic and A. G. Gaydon, Proc. Roy. Soc. (London) **307A**, 399 (1968).
3. J. S. Shirk and A. M. Bass, J. Chem. Phys. **52**, 1894 (1970).
4. A. Lagerqvist and U. Uhler, Z. Naturforsch. **22b**, 551 (1967).

Copper Sulfate (CuSO₄)

(Crystal) GFW = 159.6016

CuO₄S

T, K	Cp	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log Kp
0	0.000	0.000	INFINITE	4.030	-181.662	INFINITE
100	10.449	7.808	3.561	3.555	-181.662	382.166
200	18.405	17.726	28.119	2.078	-181.662	181.931
298	23.630	26.112	26.112	0.000	-181.662	115.788
300	23.730	26.259	26.113	0.044	-181.662	114.956
400	27.470	33.617	27.693	2.611	-181.662	81.422
500	30.400	40.076	29.055	5.510	-181.662	61.243
600	32.590	45.820	31.479	8.664	-181.662	47.792
700	34.100	50.806	33.816	12.005	-181.662	38.188
800	35.100	55.081	36.043	15.428	-181.662	29.393
900	35.700	58.811	38.243	18.932	-181.662	21.458
1000	36.100	62.049	40.454	22.605	-181.662	14.458
1100	37.300	67.178	43.180	26.398	-181.662	8.439
1200	38.200	71.485	45.316	30.352	-181.662	3.568
1300	38.700	75.049	46.937	34.438	-181.662	0.547
1400	38.900	77.836	48.137	37.708	-181.662	0.247
1500	39.010	79.914	51.227	41.680	-181.662	0.527
1600	39.370	81.543	53.044	45.599	-181.662	4.768
1700	39.700	82.820	54.791	49.553	-181.662	3.223
1800	40.050	83.822	56.487	53.542	-181.662	1.943
1900	40.370	84.594	58.098	57.562	-181.662	0.943
2000	40.690	85.072	59.665	61.615	-181.662	0.445

COPPER SULFATE (CuSO₄)

(CRYSTAL)

GFW = 159.6016

ΔHf°₀ = -181.66 ± 0.2 kcal/molΔHf°_{298.15} = -184.03 ± 0.2 kcal/molS°_{298.15} = 26.11 ± 0.1 gibbs/mol

Td = 1078°K

Heat of Formation.

The heat of solution (ΔH_{298.15}) of CuO(c) in sulfuric acid to form CuSO₄(c) has been measured by L. H. Adami and E. G. King, U. S. Bur. Mines RI 6617, 1965. From the reported value, ΔH_f° = -5.61 ± 0.09 kcal/mol for the reaction CuO(c) + H₂SO₄(7.068 H₂O) = CuSO₄(c) + H₂O(l), the heat of formation (ΔH_f°_{298.15} for CuSO₄(c) was evaluated as -184.03 kcal/mol, using ΔH_f°_{298.15} = -37.25, -209.49 and -68.315 kcal/mol for CuO(c), H₂SO₄(7.068 H₂O) and H₂O(l), respectively. See Fe₂(SO₄)₃(c) table for the sources of the last two ΔH_f°_{298.15} values.

The equilibrium pressures for the following chemical reactions: (A) 2CuSO₄(c) = CuO·CuSO₄(c) + SO₃(g), (B) 3Cu(c) + CuSO₄(c) = 2Cu₂O(c) + SO₂(g), and (C) 4CuSO₄(c) + Cu₂O(c) = 3Cu₂O·CuSO₄(c) + SO₂(g), were determined by several investigators. For reaction (A), the partial pressures of SO₃(g) at different temperatures were calculated from the measured total pressures exerted by SO₃(g), SO₂(g) and O₂(g) produced by the reaction SO₃(g) = SO₂(g) + 1/2 O₂(g). From these vapor pressure data, the corresponding enthalpy changes (ΔH_f°_{298.15}) for the three reactions were evaluated by the second and third law methods. The results obtained are presented in the following table. The value of ΔH_f°_{298.15} (CuSO₄, c) adopted was -184.03 ± 0.2 kcal/mol.

Investigator	Reaction	Temperature, °K	Second Law Value	Third Law Value	Drift	ΔHf° _{298.15} kcal/mol
Wöhler, et al. (1)	(A)	819.15-1004.15	25.90±3.60	47.45	22±4	-181.87
Reinders and Goudrian (2)	(A)	953.15-1053.15	56.54±0.77	51.96	-4.55±0.79	-184.13
(C)	(C)	825.15- 921.15	42.84±1.38	42.34	-0.55±1.57	-184.42
Ingraham (3)	(A)	880.15-1071.75	51.59±0.41	51.75	0.07±0.43	-184.02
Randall et al. (4)	(B)	525.1 - 608.1	31.71±0.76	32.27	0.84±1.30	-184.62

(1) L. Wöhler, W. Plüddemann and P. Wöhler, Ber. Daut. Chem. Gesell. 41, 703 (1908).

(2) W. Reinders and F. Goudrian, Z. anorg. allgem. Chem. 126, 85 (1923).

(3) T. R. Ingraham, Trans. Met. Soc. AIME, 233, 259 (1965).

(4) M. Randall, R. F. Nielsen and G. H. West, Ind. Eng. Chem. 23, 388 (1931). In this report, the high temperature equilibrium reactions of copper were critically reviewed.

Heat Capacity and Entropy.

The low temperature heat capacities, 52.67-296.29°K, were obtained from W. W. Weller, U. S. Bur. Mines RI 6669, 1965. The high temperature heat capacities were measured by H. Schottky, Z. phys. Chem. 54, 415 (1908), 282°K; R. Ewald, Ann. Physik., 44, 1215 (1914), 275-373°K; A. N. Krestovnikov and E. J. Peigine, J. Gen. Chem. USSR, 6, 1481 (1936), 288-873°K; and D. M. Chizhikov and A. S. Khirik, Tr. Inst. Met. Im. A. A. Baikova, Akad. Nauk SSSR, No. 12 79-84 (1963), 373-1273°K. The heat capacities below 51°K were obtained from J. W. Stout, J. Chem. Phys. 2, 285 (1941). In that paper, the Cp values, 15-58°K, were plotted as function of temperature and the Cp curve shows a maximum at 34.8°K. In an attempt to evaluate the entropy due to the anomalous portion of the curve, a "normal" heat capacity curve was drawn. The entropy above the normal Cp curve is reported to be 0.48 eu, rather than a magnetic entropy of Rln2 = 1.377 eu. Apparently the magnetic entropy increases gradually above 40°K so that it is not feasible to separate the heat capacity due to magnetic effects from that of the crystal lattice.

The Cp values above 298.15°K were extrapolated smoothly by comparison with those for MnSO₄(c) (see FeSO₄(c) table for details). The adopted Cp values are close to the average of the reported Cp values.

The value of S°_{298.15} was derived using the low temperature Cp data reported by W. W. Weller, loc. cit., based on S°₀ = 2.851 eu evaluated from Cp data determined by J. W. Stout, loc. cit.

Decomposition Temperature.

Td is the temperature at which the total pressure of the gaseous decomposition products equals one atmosphere. It was obtained by graphical extrapolation of the decomposition pressures for CuSO₄(c), determined by T. R. Ingraham, loc. cit.

CuO₄S

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	+0.000	INFINITE	-	2.373	116.017	116.017	INFINITE
100	7.640	48.700	65.302	-1.660	116.412	-244.820	-244.820
200	8.471	54.304	58.538	-8.67	116.263	107.667	-117.653
298	8.744	57.745	57.745	+0.000	116.000	103.502	-175.869
300	8.747	57.799	57.745	+0.016	115.996	103.424	-175.344
400	8.868	60.334	58.090	+8.69	115.682	104.260	-164.244
500	8.935	62.321	58.745	+1.788	115.340	95.220	-41.620
600	8.981	63.954	59.481	2.684	114.970	91.229	-33.230
700	9.014	65.267	60.150	3.484	114.580	87.234	-27.759
800	9.034	66.347	60.756	4.287	114.169	83.234	-23.759
900	9.050	67.164	61.222	5.392	113.740	79.234	-19.334
1000	9.062	68.570	62.270	6.301	113.293	75.851	-16.577
1100	9.113	69.438	62.883	7.211	112.831	72.129	-14.331
1200	9.144	70.463	63.463	8.123	112.351	68.448	-12.466
1300	9.158	71.590	64.048	9.035	111.851	64.764	-10.987
1400	9.173	72.764	64.533	9.944	111.334	61.078	-9.587
1500	9.192	72.276	65.028	10.872	104.396	58.322	-8.498
1600	9.211	72.870	65.500	11.792	103.816	55.269	-7.549
1700	9.227	73.590	65.950	12.714	103.238	52.253	-6.718
1800	9.240	74.357	66.382	13.632	102.658	49.282	-5.952
1900	9.265	74.458	66.793	14.564	102.088	46.319	-5.328
2000	9.284	74.933	67.188	15.491	101.515	43.401	-4.743
2100	9.302	75.387	67.567	16.420	100.944	40.508	-4.216
2200	9.318	75.820	67.935	17.351	100.375	37.645	-3.740
2300	9.338	76.235	68.285	18.282	99.806	34.816	-3.313
2400	9.357	76.632	68.624	19.219	99.243	31.990	-2.913
2500	9.376	77.015	68.952	20.156	98.680	29.202	-2.553
2600	9.395	77.383	69.270	21.094	98.118	26.434	-2.222
2700	9.414	77.738	69.577	22.035	97.559	23.687	-1.917
2800	9.432	78.081	69.875	22.978	96.998	20.964	-1.637
2900	9.455	78.412	70.163	23.922	96.434	18.275	-1.375
3000	9.477	78.733	70.443	24.866	95.868	15.631	-1.129
3100	9.500	79.044	70.716	25.817	95.300	13.034	-0.894
3200	9.523	79.346	70.981	26.768	94.732	10.481	-0.674
3300	9.546	79.640	71.240	27.720	94.164	7.972	-0.472
3400	9.573	79.925	71.490	28.678	93.596	5.505	-0.287
3500	9.600	80.203	71.735	29.636	93.028	3.080	-0.121
3600	9.628	80.473	71.974	30.598	92.460	0.695	0.021
3700	9.657	80.738	72.207	31.562	91.892	-1.740	0.160
3800	9.687	81.000	72.435	32.528	91.324	-4.165	0.299
3900	9.719	81.248	72.658	33.497	90.756	-6.590	0.438
4000	9.752	81.494	72.876	34.471	90.188	-9.015	0.577
4100	9.786	81.735	73.089	35.450	89.620	-11.440	0.716
4200	9.822	81.971	73.298	36.430	89.052	-13.865	0.855
4300	9.857	82.203	73.502	37.412	88.484	-16.290	0.994
4400	9.897	82.430	73.702	38.397	87.916	-18.715	1.133
4500	9.936	82.653	73.899	39.384	87.348	-21.140	1.272
4600	9.976	82.872	74.091	40.389	86.780	-23.565	1.411
4700	10.017	83.087	74.281	41.389	86.212	-25.990	1.550
4800	10.058	83.298	74.466	42.391	85.644	-28.415	1.689
4900	10.103	83.509	74.646	43.391	85.076	-30.840	1.828
5000	10.147	83.711	74.828	44.413	84.508	-33.265	1.967
5100	10.191	83.912	75.004	45.430	83.940	-35.690	2.106
5200	10.237	84.110	75.177	46.452	83.372	-38.115	2.245
5300	10.287	84.306	75.348	47.478	82.804	-40.540	2.384
5400	10.339	84.498	75.518	48.500	82.236	-42.965	2.523
5500	10.376	84.688	75.680	49.543	81.668	-45.390	2.662
5600	10.423	84.876	75.843	50.583	81.100	-47.815	2.801
5700	10.471	85.061	76.003	51.628	80.532	-50.240	2.940
5800	10.520	85.243	76.161	52.678	79.964	-52.665	3.079
5900	10.567	85.423	76.318	53.732	79.396	-55.090	3.218
6000	10.615	85.601	76.469	54.791	78.828	-57.515	3.357

Sept. 30, 1966

Round State Configuration [$1^1 \Sigma^+$] $\Delta H_f^\circ = 116.0 \text{ kcal/mol}$ $S_{298.15} = 57.74 \text{ gibbs/mol}$ $\Delta H_f^\circ = 116.0 \pm 3 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

 $\epsilon_1, \text{ cm}^{-1}$ g_1

0

20433

21758

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

[1]

Heat of Formation

The heat of formation was calculated from that of Cu(g) using $\Delta H_f^\circ = 46.0 \text{ kcal/mol}$ for $\text{Cu}_2(\text{g}) \rightarrow 2 \text{ Cu(g)}$ obtained by third law analysis of the mass spectrometric data of Ackerman et al. Earlier studies of mass spectra and of the electronic band spectra yield values in reasonable agreement as shown below. The selected ΔH_f° corresponds to $D_0 = 1.97 \text{ eV}$ compared with the linear Birge-Sponer extrapolation of 2.1 eV.

Source	Method	Range °K	2nd law	3rd law	Drift eu	ΔH_f° kcal/mol
1. Ackerman et al. (1950)	Mass Spect.	1549-1709	47.8 ± 2.6	45.99	-1.0 ± 1.6	116.0
2. Schiessel (1957)	Mass Spect.	1575-1720	50.3 ± 3.7	46.76	-2.1 ± 2.3	115.0
3. Drowart et al. (1956)	Mass Spect.	1440-1560	-	46.5	-	115.5
4. Klemen et al. (1954)	Band Spectra	-	-	49	-	113

1. M. Ackerman, P. E. Stafford and J. Drowart, J. Chem. Phys. **33**, 1784 (1960). Dimer-monomer pressure ratio obtained from intensity ratio using factor 0.705.

2. P. Schiessel, J. Chem. Phys. **26**, 1276 (1957). Point at 1730°K omitted. Dimer-monomer pressure ratio obtained from intensity ratio using factor 0.598.

3. J. Drowart and R. E. Honig, J. Chem. Phys. **25**, 581 (1956).

4. B. Klemen and S. Lindqvist, Arkiv Fysik **9**, 333 (1954).

Heat Capacity and Entropy

Molecular constants, except for $\omega_e x_e$, were taken from the rotational analysis of bands of the B-X system given by D. N. Travia and R. P. Barrow, Proc. Chem. Soc. (London), **44** (1962). The value for $\omega_e x_e$ was obtained from the earlier study of Klemen and Lindqvist, loc. cit., who showed by means of the vibrational isotope effect that the emitter was Cu_2 . The spectroscopic characters of the ground and excited states are uncertain, but Travia and Barrow indicate that the transition is probably $1^1\Sigma_u^+ - 1^1\Sigma_g^+$ for the B-X system. Vibrational and rotational constants were adjusted for 30.91% ^{65}Cu .

Copper Monoxide (Cu₂O)

(Crystal) GFW = 143.0794

Cu₂O

T, °K	Cp ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c kcal/mol	ΔG ^d	Log K ^e
0	.000	.000	INFINITE	3.037	-40.309	-40.309	INFINITE
100	9.506	8.902	34.082	2.518	-40.455	-38.798	84.792
200	12.493	16.598	23.537	1.388	-40.635	-37.069	40.507
298	13.159	22.213	.000	.000	-40.700	-35.259	25.691
300	15.230	22.307	.028	.028	-40.700	-35.266	25.691
400	16.560	26.893	22.829	1.626	-40.652	-33.459	18.281
500	17.410	30.687	24.032	3.327	-40.548	-31.671	13.843
600	18.040	33.919	25.417	5.101	-40.418	-29.909	10.894
700	18.620	36.743	26.838	6.934	-40.268	-28.167	8.794
800	19.220	39.269	28.237	8.826	-40.085	-26.454	7.227
900	19.850	41.568	29.592	10.779	-39.873	-24.760	6.013
1000	20.520	43.694	30.897	12.797	-39.624	-23.094	5.047
1100	21.220	45.683	32.152	14.884	-39.329	-21.468	4.263
1200	21.920	47.559	33.358	17.061	-38.988	-19.886	3.614
1300	22.620	49.341	34.520	19.268	-38.597	-18.265	3.071
1400	23.320	51.043	35.640	21.565	-38.154	-16.514	2.578
1500	24.020	52.676	36.721	23.932	-37.667	-14.729	2.117
1600	24.720	54.242	37.762	26.268	-37.136	-12.904	1.689
1700	25.420	55.768	38.782	28.676	-36.562	-11.040	1.289
1800	26.120	57.241	39.767	31.143	-35.948	-9.144	.914
1900	26.820	58.672	40.725	33.100	-35.294	-7.214	.558
2000	27.520	60.066	41.657	35.817	-34.593	-5.253	.219
2100	28.220	61.425	42.566	38.606	-33.846	-3.270	.000
2200	28.920	62.754	43.454	41.461	-33.054	-1.272	.000
2300	29.620	64.055	44.321	44.388	-32.219	.822	.000
2400	30.320	65.331	45.170	47.385	-31.343	1.728	.000
2500	31.020	66.582	46.002	50.452	-30.426	2.602	.000

DI-COPPER MONOXIDE (Cu₂O)

(CRYSTAL)

GFW = 143.0794

ΔH_f^o = -40.31 kcal/mol
 ΔH_f^{298.15} = -40.7 ± 0.5 kcal/mol
 ΔH_m^o = 13.58 ± 2 kcal/mol
 T_m = 1509°K
 S_{298.15}^o = 22.21 ± 0.08 gibbs/mol

Heat of Formation.

Summarized below are the more consistent results for the heat of formation. The selected value of -40.7 kcal/mol is based on data from Thomsen and from Ishakawa and Kimura. More recent equilibrium data yield essentially the same average for ΔH_f but the separate values scatter by about ±0.7 kcal/mol and significant entropy errors are apparent.

Thomsen obtained values of -40.80, -40.87 and -41.51 from aqueous calorimetry using three different paths. He favored the first path which may be recalculated by combination of the heats of reaction of Cu₂O + H₂SO₄, Fe + H₂SO₄ and Fe + CuSO₄(aq) to yield the heat of reduction of Cu₂O with H₂. Direct measurements of the heat of reduction reported by L. Wöhler and N. Jochum, Z. physik. Chem. 167A, 169 (1933), appear to be unreliable since they lead to -43.0 for the heat of formation. The cell data of Ishakawa and Kimura show very little drift and are in excellent agreement with Thomsen.

Author	Method	Reaction**	Temp. (°K)	No. of Points	ΔH _f ²⁹⁸ (kcal/mol)	Drift (eu)	ΔH _f ²⁹⁸ (kcal/mol)
1. Thomsen (1883)	Aqueous Calorimetry	A	291	—	-27.61	—	-40.70
2. Hill et al. (1958)	Fused salt Emf	B	987	1	-41.38	—	-41.38
3. Kluckhohn et al. (1957)	Emf vs. Fe/Fe ₂ O ₃	B	1073-1323	4	-43.03±0.56	2.1±0.5	-40.42
	Emf vs. Fe ₂ O ₃ /Fe ₃ O ₄	B	1073-1323	4	-44.14±0.10	3.1±0.1	-40.36
4. Balesdent (1955)	Equilibrium data	C	1011-1156	28	36.03±1.1	41.20	4.7±1.0
5. Mskolkin (1942)	Aqueous Emf	D	288-308	3	29.4±0.7	28.30	-4.0±2.5
6. Maier (1929)	Aqueous Emf	D	298-318	7	29.94±0.4	28.07	-6.2±1.3
7. Ishakawa et al. (1927)	Aqueous Emf	D	273-318	5	27.42±0.04	27.63	0.7±0.1
							-40.69

*Based on 3rd law values wherever possible.

**Reaction A: Cu₂O(c) + H₂ = 2Cu + H₂O(l), B: 2Cu + 0.5 O₂ = Cu₂O(c)

C: Cu₂O(c) = 2Cu + 0.5 O₂, D: 2Cu + H₂O(l) = Cu₂O(c) + H₂.

- J. Thomsen, "Thermochemische Untersuchungen," vol. III, Barth, Leipzig, 1883.
- D. G. Hill, B. Porter and A. S. Gillespie, Jr., J. Electrochem. Soc. 105, 408 (1958).
- K. Kluckhohn, C. Wagner, J. Electrochem. Soc. 104, 379 (1957).
- D. Balesdent, Compt. rend. 240, 760 (1955); 1884 (1955).
- I. A. Mskolkin, J. Phys. Chem. (U.S.S.R.) 16, 13 (1942); cf. Chem. Abs. 37, 2641 (1943).
- C. O. Maier, J. Am. Chem. Soc. 51, 194 (1929).
- F. Ishakawa and G. Kimura, "Sexagint, Yikichi Oseka," pp. 255-69, Chem. Inst. Kyoto Imp. Univ., Kyoto, Japan, 1927; cf. Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931).

Heat Capacity and Entropy.

Low temperature values are based on data from L. V. Oregon (2.8-21°K), J. Phys. Chem. 66, 1645 (1962) and from J. Hu and H. L. Johnston (15-300°K), J. Am. Chem. Soc. 73, 4550 (1951). Earlier data by R. W. Miller (76-291°K), J. Am. Chem. Soc. 51, 215 (1929) are in satisfactory agreement. The entropy was obtained from the heat capacities based on S_{2.8}^o = 0.0015 eu.

High temperature values were obtained from specific heats (373-1273°K) determined with a dynamic method by D. M. Chizhikov and A. S. Knirik, Tr. Inst. Met. im A. A. Baikova, Akad. Nauk SSSR, No. 12, 79 (1963); cf. Chem. Abs. 59, 79 (1963). Enthalpy data (543-1223°K) from Wöhler and Jochum, loc. cit., yield for S₁₀₀₀^o a value about 0.4 eu higher, but this is inconsistent with extensive equilibrium data for 2CuO(c) = Cu₂O(c) + 0.5 O₂ (see CuO(c)).

Melting Data.

For details see Cu₂O(l).

Cu₂O

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K ^e
0							
100							
200							
298	24.000	22.901	22.901	0.000	- 32.029	- 26.893	19.669
300	24.000	23.069	22.901	0.064	- 32.013	- 26.801	19.525
400	24.000	29.954	23.843	2.444	- 31.163	- 25.194	13.765
500	24.000	35.309	25.620	4.844	- 30.360	- 23.794	10.400
600	24.000	39.685	27.611	7.244	- 29.604	- 22.554	8.215
700	24.000	43.385	29.607	12.644	- 28.883	- 21.435	6.092
800	24.000	46.416	31.667	14.444	- 27.537	- 19.487	4.732
900	24.000	49.416	33.667	16.844	- 26.906	- 18.627	4.071
1000	24.000	51.945	35.100	19.244	- 26.298	- 17.828	3.542
1100	24.000	54.232	36.737	21.644	- 25.714	- 17.086	3.112
1200	24.000	56.321	38.284	24.044	- 25.150	- 16.400	2.682
1300	24.000	58.140	40.000	26.444	- 24.605	- 15.671	2.252
1400	24.000	60.020	41.131	28.844	- 24.078	- 14.931	1.822
1500	24.000	61.676	42.446	31.244	- 23.514	- 14.146	1.392
1600	24.000	63.225	43.697	33.644	- 22.952	- 13.390	0.962
1700	24.000	64.680	44.889	36.044	- 22.393	- 12.561	0.532
1800	24.000	66.049	46.115	38.444	- 21.835	- 11.695	0.102
1900	24.000	67.349	47.315	40.844	- 21.285	- 10.785	- 0.328
2000	24.000	68.580	48.458	43.244	- 20.745	- 9.843	- 0.858
2100	24.000	69.751	49.559	45.644	- 20.215	- 8.873	- 1.388
2200	24.000	70.868	50.620	48.044	- 19.690	- 7.873	- 1.918
2300	24.000	71.936	51.658	50.444	- 19.170	- 6.843	- 2.448
2400	24.000	72.956	52.678	52.844	- 18.655	- 5.783	- 2.978
2500	24.000	73.936	53.698	55.244	- 18.145	- 4.693	- 3.508
2600	24.000	74.877	54.629	57.644	- 17.640	- 3.540	- 4.038
2700	24.000	75.783	55.433	60.044	- 17.140	- 2.350	- 4.568
2800	24.000	76.658	56.215	62.444	- 16.645	- 1.115	- 5.098
2900	24.000	77.498	56.965	64.844	- 16.155	- 0.894	- 5.628
3000	24.000	78.312	57.697	67.244	- 15.670	- 0.672	- 6.158

June 30, 1966

$S_{298.15}^{\circ} = 22.901$ gibbs/mol
 $T_m = 1509^{\circ}\text{K}$

Heat of Formation.
 The heat of formation was calculated from that of the crystal by adding ΔH_m° and the difference between $(H_{1509}^{\circ}-H_{298}^{\circ})$ for the crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated on the basis of 8 gibbs per g atom, giving a value of 24 gibbs/mol which is essentially the same as that of the crystal at the melting point. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

T_m is the value recommended by S. J. Schneider, NBS Monograph 88, U. S. Govt. Printing Office, Washington, D.C., October, 1963, based on pressure-temperature-composition studies of H. S. Roberts and P. H. Smyth, J. Am. Chem. Soc. 43, 1061 (1921). The heat of melting was selected as 13.58 kcal/mol, corresponding to $\Delta S_m^{\circ} = 3$ eu per g atom. A value of 13.4 kcal/mol has been derived from the Cu₂O-CuCl phase diagram by K. K. Kelley, USNM Bulletin 393, U. S. Govt. Printing Office, Washington, 1936. Another value may be obtained from oxygen dissociation pressures for the system Cu₂O(l)-CuO(c) determined by Roberts and Smyth, loc. cit. Equilibrium constants may be obtained for the reaction $2\text{CuO}(c) = \text{Cu}_2\text{O}(l) + 0.5 \text{O}_2$ by assuming the activity of Cu₂O in the melt to be equal to its mole fraction. Based on the mole fractions given by Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931), the equilibrium data yield $\Delta H_m^{\circ} = 15.8 \pm 0.8$ kcal/mol by second law analysis of all points or 12.9 ± 1.6 by omission of 4 points at high pressure and low mole fraction. These results appear to be consistent with the selected value within the approximations involved.

Copper Oxide Sulfate ($\text{CuO} \cdot \text{CuSO}_4$)
(Crystal) $\Delta H_f^\circ = 239.141$

T, K	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°	Log Kp
0							
100							
200							
298	33.710	37.450	5.000	-221.400	-139.490	138.327	
300							
350	37.820	37.820	4.562	-221.102	-139.432	137.824	
400	38.820	38.201	4.175	-220.752	-139.365	137.365	
450	39.820	38.524	3.824	-220.452	-139.298	136.906	
500	40.820	38.847	3.500	-220.152	-139.231	136.447	
550	41.820	39.170	3.196	-219.852	-139.164	135.988	
600	42.820	39.493	2.912	-219.552	-139.097	135.529	
650	43.820	39.816	2.647	-219.252	-139.030	135.070	
700	44.820	40.139	2.400	-218.952	-138.963	134.611	
750	45.820	40.462	2.171	-218.652	-138.896	134.152	
800	46.820	40.785	1.958	-218.352	-138.829	133.693	
850	47.820	41.108	1.761	-218.052	-138.762	133.234	
900	48.820	41.431	1.579	-217.752	-138.695	132.775	
950	49.820	41.754	1.412	-217.452	-138.628	132.316	
1000	50.820	42.077	1.259	-217.152	-138.561	131.857	
1050	51.820	42.400	1.119	-216.852	-138.494	131.398	
1100	52.820	42.723	0.991	-216.552	-138.427	130.939	
1150	53.820	43.046	0.875	-216.252	-138.360	130.480	
1200	54.820	43.369	0.771	-215.952	-138.293	130.021	
1250	55.820	43.692	0.678	-215.652	-138.226	129.562	
1300	56.820	44.015	0.595	-215.352	-138.159	129.103	
1350	57.820	44.338	0.522	-215.052	-138.092	128.644	
1400	58.820	44.661	0.459	-214.752	-138.025	128.185	
1450	59.820	44.984	0.405	-214.452	-137.958	127.726	
1500	60.820	45.307	0.359	-214.152	-137.891	127.267	

Cu_2O_5

Copper Oxide Sulfate ($\text{CuO} \cdot \text{CuSO}_4$) (Crystal)

$\Delta H_f^\circ = 239.141$

$\Delta H_f^\circ = 239.141$

$\Delta H_f^\circ = 239.141$

$\Delta H_f^\circ = 239.141$

$\Delta H_f^\circ = 239.141$

Heat of Formation.

The equilibrium pressures for the following reactions: (A) $\text{CuO} \cdot \text{CuSO}_4(s) = 2\text{CuO}(c) + \text{SO}_2(g)$ and $\text{SO}_2(g) = \text{SO}_3(g)$, (B) $\text{CuO} \cdot \text{CuSO}_4(s) = \text{Cu}_2\text{O}(c) + \text{SO}_2(g)$, and (C) $\text{CuO} \cdot \text{CuSO}_4(s) = \text{Cu}_2\text{O}(c) + \text{SO}_3(g)$, were determined by (1) A. H. Reid and P. G. H. Reid, *J. Res. Natl. Bur. Stand., Sect. A*, **68**, 125 (1964), and (2) E. B. Beaton, *Trans. Faraday Soc.*, **58**, 155 (1962). Using the reported vapor pressures, the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented as follows.

Reference	Reaction	Temperature, °K	Second Law Value	Third Law Value	Unit	ΔH_f° , kcal/mol
(1)	A	1015 - 1035	43.03 ± 2.63	52.43	-0.7 ± 2.4	-221.5
(2)	B	527 - 1027	41.72 ± 3.42	42.43	0.6 ± 3.4	-221.7
(2)	A**	298 - 1153	50.52 ± 0.16	52.67	1.6 ± 0.2	-221.7

* Based on the third law value for ΔH_f° of SO_2 .

** Partial pressures were calculated from JANAF values for the $\text{SO}_2 - \text{SO}_3$ equilibrium. The value of ΔH_f° of $\text{CuO} \cdot \text{CuSO}_4$ adopted is -221.7 ± 0.3 kcal/mol.

Heat Capacity and Entropy.

The heat capacities were calculated as the sum of those for $\text{CuO}(c)$ and $\text{CuSO}_4(c)$. The value of S_{298}° was estimated by comparison with those for $\text{CuO}(c)$ and $\text{CuSO}_4(c)$, and adjusted so that, using the derived free energy functions, the second and third law values for ΔH_f° agree reasonably.

Decomposition Temperature.

T_d is the temperature at which the total pressure of the gaseous decomposition products of reaction (A) equals one atmosphere. It was obtained by graphical extrapolation of the decomposition pressures for $\text{CuO} \cdot \text{CuSO}_4(c)$, determined by E. B. Beaton, loc. cit.

Fluorine, Monatomic (F)

(Ideal Gas) Mol. wt. = 18.9984

Ground State Configuration $2p_{3/2}$ $\Delta H_f^0 = 18.36 \pm 0.40 \text{ kcal. mole}^{-1}$ $S_{298.15}^0 = 37.917 \text{ cal. deg}^{-1} \text{ mole}^{-1}$ $\Delta H_f^0 = 18.86 \pm 0.40 \text{ kcal. mole}^{-1}$

T, °K.	C _p	S°	$-(F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	0.000	INFINITE	18.357	18.357	INFINITE
100	5.068	32.116	42.710	18.508	17.331	-37.875
200	5.003	35.746	39.415	18.684	16.089	-17.580
298	5.037	37.917	37.017	18.860	14.777	-10.832
300	5.036	37.951	37.017	18.863	14.752	-10.746
400	5.361	39.505	38.129	19.018	13.358	-7.298
500	5.282	40.693	38.528	19.147	11.927	-5.213
600	5.218	41.650	38.871	19.286	10.472	-3.814
700	5.163	42.430	39.176	19.431	9.003	-2.953
800	5.113	43.078	39.437	19.574	7.517	-2.405
900	5.065	43.614	40.037	19.724	6.023	-1.662
1000	5.083	44.077	40.615	19.872	4.522	-0.988
1100	5.066	44.461	40.970	19.933	3.013	-0.599
1200	5.042	44.710	41.305	19.991	1.500	-0.314
1300	5.013	44.924	41.610	20.046	0.000	-0.000
1400	5.032	45.078	41.818	20.097	-1.500	-0.240
1500	5.025	45.185	42.001	20.144	-3.005	-0.447
1600	5.018	45.249	42.169	20.186	-4.594	-0.627
1700	5.003	45.274	42.317	20.223	-6.126	-0.788
1800	5.005	45.251	42.449	20.256	-7.600	-0.931
1900	5.001	45.177	42.561	20.284	-9.017	-1.058
2000	5.001	45.051	42.651	20.307	-10.373	-1.173
2100	4.999	44.874	42.719	20.326	-11.673	-1.277
2200	4.996	44.644	42.761	20.341	-12.916	-1.371
2300	4.992	44.364	42.779	20.352	-14.104	-1.454
2400	4.987	44.034	42.774	20.359	-15.239	-1.528
2500	4.980	43.654	42.756	20.362	-16.321	-1.593
2600	4.988	43.224	42.724	20.360	-17.351	-1.648
2700	4.987	42.744	42.679	20.356	-18.329	-1.694
2800	4.985	42.214	42.624	20.350	-19.256	-1.731
2900	4.984	41.634	42.559	20.342	-20.131	-1.758
3000	4.983	41.004	42.484	20.332	-20.954	-1.777
3100	4.982	40.324	42.399	20.320	-21.724	-1.786
3200	4.982	39.594	42.304	20.306	-22.444	-1.786
3300	4.980	38.814	42.199	20.290	-23.114	-1.777
3400	4.980	37.984	42.084	20.272	-23.734	-1.758
3500	4.980	37.104	41.959	20.252	-24.304	-1.729
3600	4.977	36.174	41.824	20.230	-24.824	-1.690
3700	4.978	35.194	41.679	20.206	-25.294	-1.641
3800	4.977	34.164	41.524	20.180	-25.714	-1.582
3900	4.977	33.084	41.359	20.152	-26.084	-1.513
4000	4.977	31.954	41.184	20.122	-26.404	-1.434
4100	4.977	30.774	40.999	20.090	-26.674	-1.345
4200	4.976	29.544	40.804	20.056	-26.894	-1.246
4300	4.975	28.264	40.599	20.020	-27.064	-1.137
4400	4.975	26.934	40.374	19.982	-27.184	-1.018
4500	4.975	25.554	40.129	19.933	-27.254	-0.889
4600	4.975	24.124	39.864	19.872	-27.284	-0.750
4700	4.975	22.644	39.579	19.800	-27.274	-0.591
4800	4.974	21.114	39.274	19.719	-27.224	-0.412
4900	4.974	19.534	38.959	19.629	-27.144	-0.223
5000	4.974	17.904	38.634	19.530	-27.034	-0.024
5100	4.974	16.224	38.299	19.421	-26.894	0.175
5200	4.973	14.594	37.954	19.299	-26.724	0.374
5300	4.973	12.914	37.599	19.164	-26.524	0.573
5400	4.973	11.184	37.234	19.019	-26.294	0.772
5500	4.973	9.404	36.859	18.864	-26.034	0.971
5600	4.973	7.574	36.474	18.699	-25.744	1.170
5700	4.973	5.694	36.079	18.524	-25.424	1.369
5800	4.972	3.764	35.674	18.339	-25.074	1.568
5900	4.972	1.784	35.259	18.144	-24.694	1.767
6000	4.972	-0.184	34.834	17.939	-24.284	1.966

Dec. 31, 1960; June 30, 1961; Sept. 30, 1965

Electronic Levels and Quantum Weight

E_1 , cm ⁻¹	E_2	E_3	E_4	E_5	E_6
0	4	116,597.23	14	120,346.36	80
404	2	117,465.68	22	132,786.07	16
103,327.14	18	116,827.73	10	135,531.81	22
115,918.7	6	123,118.7	12	134,978.71	88

Heat of Formation.

The dissociation energy (D_0) of fluorine has been discussed by numerous investigators for many years. Until about fifteen years ago, high values of $D_0(F_2)$, about 65 kcal. mole⁻¹, were widely accepted. These values were obtained from extrapolations of the spectroscopic data for the halogens, e.g. $D_0 = 63.3$ kcal. mole⁻¹ was reported by H. V. Martenbergs, O. Sprenger and J. Taylor, *Z. physik. Chem., Bodenstein-Pentland*, 61 (1931). However, mean-while many indirect determinations as well as estimation have been carried out, which yield appreciably lower values. In 1950 the available data were examined critically by M. O. Evans, E. Warhurst and E. Whittle, *J. Chem. Soc.* 1524 (1950) and shown to support a value, $D_0(F_2) = 37 \pm 8$ kcal. mole⁻¹. The indirect determinations include (1) the thermal conductivity measurements by E. U. Franck and E. Wicke, *Z. Elektrochem.* 55, 643 (1951); (2) the explosion method by K. Fritz, *Disser.*, Göttingen, 1952; (3) estimation by use of the relations between D_0 and the vibrational frequencies by A. Bucken and E. Wicke, *Naturwiss.*, 37, 233 (1950); and (4) spectroscopic data on the dissociation energy of diatomic fluorides. Recently more direct methods have been used to determine $D_0(F_2)$. They gave similar values. The D_0 values reported by the previous investigators have been reviewed by L. Haar and C. W. Beckett, National Bureau of Standards Report 1435 (1952), and E. Wicke and H. Fritz, *Z. Elektrochem.* 57, 9 (1953).

The low bond dissociation energy of $F_2(g)$ has been attributed to the repulsion between the unshared electrons on the bound fluorine atoms by K. S. Pitzer, *J. Am. Chem. Soc.* 70, 2140 (1948), or to the absence in fluorine of strengthening of the bond by hybridization of the p- or d- orbitals as may take place in the higher halogens by R. S. Mulliken, *J. Am. Chem. Soc.* 77, 884 (1955). M. O. Brown, *Trans. Faraday Soc.* 55, 9 (1959) suggests that the observed low D_0 value results from the large energy required to promote the p atoms to the valence state from which the bond may be formed.

The equilibrium pressures for the reaction $F_2(g) \rightarrow 2F(g)$ have been measured by several investigators. Using the reported equilibrium constants, the dissociation energy, $D_{298.15}$, was evaluated by both the second and third law methods. The results obtained are presented as follows.

Temperature, °K.	$D_{298.15}$, kcal. mole ⁻¹	Reference
759 - 1115	36.91 ± 0.41	1
810 - 960	36.7 ± 18.2	2
723 - 820	41.8 ± 0.2	3
	36.0	4

1. R. N. Doescher, *J. Chem. Phys.* 20, 330 (1952).2. F. M. Ollies and J. L. Margrave, *J. Chem. Phys.* 21, 381 (1953).3. H. Wicke, *J. Phys. Chem.* 59, 389 (1954).

4. M. Farber, et al. "Study of Rocket Engine Exhaust Products", Thirteenth Quarterly Report, June 1 - Oct. 31, 1964, Westmont Corporation, Pasadena, California.

By use of H_2 - F_2 mixture explosion method, $D_0(F_2)$ was reported as 37 ± 2 kcal. mole⁻¹ by E. Wicke and H. Fritz, loc. cit. K. L. Wray and D. F. Hornis, *J. Chem. Phys.* 24, 1271 (1956), using shock wave method, obtained $D_0 = 31.0 \pm 4.3$ kcal. mole⁻¹. The continuous absorption electronic spectrum of $F_2(g)$ and the Raman displacement for the $0 \rightarrow 1$ vibrational transition have been used by A. L. O. Rees, *J. Chem. Phys.* 26, 1567 (1957) to compute the potential energy curve for the repulsive Π_u state dissociating to two normal $F(g)$. This curve is consistent with the value, $D_0 = 37.1 \pm 0.85$ kcal. mole⁻¹. The absorption spectrum of $F_2(g)$ has been observed in the vacuum UV region by R. P. Iczkowski and J. L. Margrave, *J. Chem. Phys.* 30, 403 (1959). From a progression of bands at 8744, the value, $D_0 = 37.5 \pm 2$ kcal. mole⁻¹ is deduced.

The P_2 dissociation energy is selected as 37.72 ± 0.60 kcal. mole⁻¹, yielding $\Delta H_f^0 298.15(P, g) = 18.86 \pm 0.40$ kcal. mole⁻¹.

Heat Capacity and Entropy.

The ground state configuration, electronic levels and quantum weights were taken from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Fluorine Uninegative Ion (F⁻)
(Ideal Gas) Mol. wt. = 18.99895

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F ⁻ -H ₂₉₈ °)/T	H ⁻ -H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0								
100	4.968	34.768	34.768	.000	- 62.200	- 63.857		46.806
200	4.968	34.768	34.768	.009	- 62.207	- 63.867		46.524
298	4.968	34.768	34.768	.036	- 62.592	- 64.363		35.164
300	4.968	34.768	34.768	.036	- 62.592	- 64.363		35.164
400	4.968	34.768	34.768	.036	- 62.592	- 64.363		28.305
500	4.968	34.768	34.768	.036	- 62.592	- 64.363		23.702
600	4.968	34.768	34.768	.036	- 62.592	- 64.363		20.391
700	4.968	34.768	34.768	.036	- 62.592	- 64.363		17.606
800	4.968	34.768	34.768	.036	- 62.592	- 64.363		15.095
900	4.968	34.768	34.768	.036	- 62.592	- 64.363		12.812
1000	4.968	34.768	34.768	.036	- 62.592	- 64.363		10.703
1100	4.968	34.768	34.768	.036	- 62.592	- 64.363		8.826
1200	4.968	34.768	34.768	.036	- 62.592	- 64.363		7.179
1300	4.968	34.768	34.768	.036	- 62.592	- 64.363		5.764
1400	4.968	34.768	34.768	.036	- 62.592	- 64.363		4.529
1500	4.968	34.768	34.768	.036	- 62.592	- 64.363		3.436
1600	4.968	34.768	34.768	.036	- 62.592	- 64.363		2.467
1700	4.968	34.768	34.768	.036	- 62.592	- 64.363		1.606
1800	4.968	34.768	34.768	.036	- 62.592	- 64.363		0.826
1900	4.968	34.768	34.768	.036	- 62.592	- 64.363		0.119
2000	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 0.521
2100	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 1.152
2200	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 1.750
2300	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 2.314
2400	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 2.839
2500	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 3.322
2600	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 3.768
2700	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 4.179
2800	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 4.557
2900	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 4.896
3000	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 5.199
3100	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 5.466
3200	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 5.698
3300	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 5.894
3400	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.053
3500	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.182
3600	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.280
3700	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.348
3800	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.387
3900	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.400
4000	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.388
4100	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.352
4200	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.293
4300	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.203
4400	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 6.083
4500	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 5.934
4600	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 5.757
4700	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 5.553
4800	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 5.322
4900	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 5.065
5000	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 4.784
5100	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 4.480
5200	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 4.156
5300	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 3.815
5400	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 3.460
5500	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 3.085
5600	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 2.693
5700	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 2.278
5800	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 1.843
5900	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 1.390
6000	4.968	34.768	34.768	.036	- 62.592	- 64.363		- 0.920

June 30, 1965

F⁻

FLUORINE UNINEGATIVE ION (F⁻) (IDEAL GAS)

MOL. WT. = 18.99895

Ground State Configuration 1S₀
S_{298.15}⁰ = 34.768 cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ = -81.1 ± .5 kcal/mole
ΔH_f⁰ 298.15 = -62.2 ± .5 kcal/mole

Electronic Levels and Quantum Weight
C₁, cm.⁻¹ g₁
0.00 1

Heat of Formation.

The heat of formation was calculated from the equation: P(g) + e⁻ → F⁻(g) with the JANAP auxiliary value for P(g) using the measured electron affinity = 3.446 e.v. (79.511 kcal/mole) obtained from R. S. Berry and C. W. Reinmann, J. Chem. Phys. 39, 1540 (1963). Other calculated values for the electron affinity are: 3.37 reported by E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964); 3.08 e.v. E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, 133, A1274 (1964); 3.50 e.v. B. Edlen, J. Chem. Phys. 33, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Neon. The electronic levels above 1 X 10⁵ cm.⁻¹ were omitted because their contribution is negligible below 6000°K. The H⁺-H₂₉₈ value at 0°K. is -1.481 kcal/mole.

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	6.978	49.406	2.167	11.363	11.363	11.363	11.363	INFINITE
200	7.421	54.350	1.572	11.608	8.849	8.849	-19.337	-19.337
298	7.650	57.417	∞.000	11.552	6.097	6.097	-6.662	-6.662
300	7.659	57.417	∞.000	11.400	3.450	3.450	-2.559	-2.559
300	7.959	57.467	∞.015	11.397	3.400	3.400	-2.477	-2.477
400	8.306	59.808	57.735	11.200	.764	.764	-4.17	-4.17
500	8.518	61.686	58.113	1.672	10.964	-	1.819	.795
600	8.652	63.252	59.035	2.531	10.477	-	4.349	1.594
700	8.753	64.553	60.017	3.401	10.333	-	6.827	2.791
800	8.807	65.765	60.417	4.278	9.909	-	9.252	2.527
900	8.854	66.805	61.070	5.161	9.378	-	11.616	2.821
1000	8.891	67.740	61.691	6.049	8.666	-	13.913	3.061
1100	8.921	68.589	62.280	6.930	7.736	-	16.122	3.293
1200	8.946	69.364	62.839	7.813	6.703	-	18.266	3.524
1300	8.967	70.083	63.369	8.728	5.639	-	20.355	3.752
1400	8.985	70.748	63.872	9.626	4.544	-	22.416	3.979
1500	9.002	71.369	64.352	10.525	3.450	-	24.450	4.206
1600	9.017	71.950	64.809	11.426	2.365	-	26.455	4.433
1700	9.030	72.493	65.237	12.332	1.280	-	28.430	4.660
1800	9.043	73.014	65.642	13.243	0.195	-	30.375	4.887
1900	9.055	73.503	66.022	14.157	-	-	32.290	5.114
2000	9.067	73.968	66.446	15.043	-	-	34.175	5.341
2100	9.078	74.410	66.815	15.900	-	-	36.030	5.568
2200	9.088	74.810	67.125	16.738	-	-	37.855	5.795
2300	9.099	75.237	67.412	17.568	-	-	39.650	6.022
2400	9.108	75.624	67.684	18.378	-	-	41.415	6.249
2500	9.118	75.996	68.161	19.500	-	-	43.150	6.476
2600	9.128	76.354	68.469	20.502	-	-	44.855	6.703
2700	9.136	76.696	68.707	21.485	-	-	46.530	6.930
2800	9.144	77.031	69.057	22.450	-	-	48.175	7.157
2900	9.151	77.352	69.345	23.395	-	-	49.790	7.384
3000	9.164	77.663	69.659	24.161	-	-	51.375	7.611
3100	9.173	77.964	69.874	25.077	-	-	52.930	7.838
3200	9.181	78.256	70.091	25.912	-	-	54.455	8.065
3300	9.190	78.538	70.332	26.674	-	-	55.950	8.292
3400	9.199	78.812	70.626	27.463	-	-	57.415	8.519
3500	9.208	79.079	70.864	28.254	-	-	58.850	8.746
3600	9.216	79.338	71.095	29.075	-	-	60.255	8.973
3700	9.224	79.587	71.325	30.020	-	-	61.630	9.200
3800	9.233	79.837	71.576	30.940	-	-	62.975	9.427
3900	9.241	80.077	71.758	32.443	-	-	64.290	9.654
4000	9.250	80.311	71.669	33.368	-	-	65.575	9.881
4100	9.258	80.540	72.175	34.293	-	-	66.830	10.108
4200	9.266	80.769	72.576	35.120	-	-	68.055	10.335
4300	9.274	80.991	72.977	35.940	-	-	69.250	10.562
4400	9.283	81.214	73.376	36.760	-	-	70.415	10.789
4500	9.291	81.403	73.768	37.074	-	-	71.550	11.016
4600	9.299	81.607	73.144	38.933	-	-	72.665	11.243
4700	9.307	81.803	73.526	40.795	-	-	73.750	11.470
4800	9.315	82.003	73.906	42.660	-	-	74.815	11.697
4900	9.323	82.196	73.690	41.726	-	-	75.860	11.924
5000	9.332	82.384	73.852	42.659	-	-	76.885	12.151
5100	9.340	82.569	74.021	43.592	-	-	77.890	12.378
5200	9.348	82.750	74.186	44.527	-	-	78.875	12.605
5300	9.356	82.926	74.346	45.460	-	-	79.840	12.832
5400	9.364	83.103	74.511	46.398	-	-	80.785	13.059
5500	9.372	83.275	74.669	47.335	-	-	81.710	13.286
5600	9.380	83.444	74.824	48.272	-	-	82.615	13.513
5700	9.388	83.610	74.977	49.210	-	-	83.500	13.740
5800	9.396	83.776	75.125	50.140	-	-	84.365	13.967
5900	9.404	83.934	75.275	51.090	-	-	85.210	14.194
6000	9.412	84.093	75.421	52.010	-	-	86.035	14.421

Sept. 30, 1965

Ground State Configuration $[6\Sigma]$ $S_{298.15}^0 = [57.4] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^0 = [11.4 \pm 5.0] \text{ kcal. mole}^{-1}$ $\Delta H_f^0 298.15 = [11.4 \pm 5.0] \text{ kcal. mole}$

Electronic Levels and Quantum Weight

ϵ , cm ⁻¹	g_i
0	[6]

 $\omega_e x_e = [2.7] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$ $\sigma^- = 1$ $\omega_e = [0.3670] \text{ cm.}^{-1}$ $r_e = [1.8] \text{ \AA}$ $\alpha_e = [0.0017] \text{ cm.}^{-1}$

Hydrogen Fluoride (HF)

(Ideal Gas)

GFW = 20.00637

HYDROGEN FLUORIDE (HF)

(IDEAL GAS)

GFW = 20.00637

Ground State Configuration $1s^2$ $\Delta H_f^\circ = -55.13 \pm 0.2 \text{ kcal/mol}$ $S_{298.15} = 41.508 \text{ gibbs/mol}$ $\Delta H_f^\circ(298.15) = -65.14 \pm 0.2 \text{ kcal/mol}$

T, °K	Cp°	gibbs/mol $S^\circ - (G^\circ - H^\circ_{298})/T$	cal/mol ΔH_f°	Log Kp
0	+0.00	INFINITE	-	INFINITE
100	6.962	33.492	- 65.128	142.747
200	6.962	38.725	- 65.130	141.947
298	6.964	41.508	- 65.135	46.116
300	6.964	41.508	- 65.141	46.116
400	6.967	43.555	- 65.176	35.955
500	6.972	45.110	- 65.232	28.431
600	6.986	46.382	- 65.300	24.076
700	7.015	47.461	- 65.377	20.676
800	7.063	48.400	- 65.459	18.124
900	7.129	49.236	- 65.544	16.135
1000	7.210	49.991	- 65.628	14.543
1100	7.303	50.683	- 65.712	13.238
1200	7.402	51.322	- 65.792	12.189
1300	7.504	51.919	- 65.870	11.227
1400	7.606	52.479	- 65.945	10.436
1500	7.705	53.007	- 66.016	9.749
1600	7.800	53.507	- 66.089	9.147
1700	7.891	53.983	- 66.157	8.616
1800	7.977	54.436	- 66.223	8.143
1900	8.058	54.870	- 66.287	7.720
2000	8.133	55.285	- 66.348	7.339
2100	8.204	55.683	- 66.408	6.993
2200	8.270	56.067	- 66.467	6.679
2300	8.331	56.436	- 66.524	6.392
2400	8.389	56.791	- 66.580	6.126
2500	8.442	57.135	- 66.637	5.886
2600	8.493	57.467	- 66.691	5.661
2700	8.540	57.789	- 66.746	5.454
2800	8.584	58.100	- 66.800	5.261
2900	8.625	58.402	- 66.853	5.081
3000	8.664	58.695	- 66.907	4.913
3100	8.701	58.980	- 66.960	4.756
3200	8.736	59.256	- 67.014	4.608
3300	8.768	59.526	- 67.067	4.469
3400	8.800	59.788	- 67.121	4.339
3500	8.829	60.043	- 67.176	4.215
3600	8.857	60.293	- 67.231	4.099
3700	8.884	60.536	- 67.287	3.988
3800	8.910	60.773	- 67.343	3.884
3900	8.934	61.005	- 67.402	3.784
4000	8.958	61.231	- 67.460	3.690
4100	8.981	61.453	- 67.520	3.600
4200	9.002	61.669	- 67.580	3.514
4300	9.023	61.881	- 67.642	3.432
4400	9.043	62.089	- 67.705	3.354
4500	9.063	62.292	- 67.769	3.279
4600	9.082	62.492	- 67.834	3.208
4700	9.100	62.687	- 67.901	3.139
4800	9.118	62.879	- 67.968	3.073
4900	9.135	63.067	- 68.037	3.010
5000	9.152	63.252	- 68.107	2.950
5100	9.168	63.433	- 68.176	2.891
5200	9.184	63.612	- 68.251	2.835
5300	9.200	63.787	- 68.324	2.781
5400	9.215	63.959	- 68.400	2.729
5500	9.230	64.128	- 68.476	2.678
5600	9.244	64.295	- 68.555	2.630
5700	9.259	64.458	- 68.634	2.583
5800	9.272	64.619	- 68.715	2.537
5900	9.286	64.778	- 68.797	2.493
6000	9.300	64.934	- 68.880	2.451

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Dec. 31, 1968

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	1

 $\omega_e X_e = 4138.37 \text{ cm}^{-1}$ $\sigma = 1$ $\omega_e = 89.88 \text{ cm}^{-1}$ $r_e = 0.9168 \text{ \AA}$ $B_e = 20.9557 \text{ cm}^{-1}$

Heat of Formation

The selected value is obtained from a least squares, simultaneous solution (1) for the heats of formation of HF(g), HF(50 H₂O) and five closely related fluorides. Other results, based on 23 selected observations relating the 7 variables, are as follows in kcal/mol: HF(50 H₂O), -76.78 ± 0.1; NaF(c), -137.52 ± 0.2; BF₃(g), -271.42 ± 0.4; CF₄(g), -221.04 ± 0.3; NF₃(g), -31.43 ± 0.3; and C₂F₄ (polymer), -138.2 ± 0.7. The ± values are approximate estimates of the overall uncertainty including systematic error. Further details of the simultaneous solution are given in (1).

The values given above require the use of certain auxiliary data; e.g., the value for NaF(c) presumes $\Delta H_f^\circ(\text{NaF(c)}) = 0.23 \pm 0.01$ and $\Delta H_f^\circ(\text{NaF(aq)}) = -57.47 \pm 0.04$ kcal/mol. Use of these auxiliary data leads to $\Delta H_f^\circ(298.15) = -79.82$ kcal/mol for HF(50 H₂O) and F⁻(50 H₂O); however, values for HF(n H₂O) should be obtained from that of HF(50 H₂O) by use of $\Delta H_f^\circ(\text{HF(n H}_2\text{O)}) - \Delta H_f^\circ(\text{HF(50 H}_2\text{O)}) = (n - 50) \Delta H_f^\circ(\text{HF})$. This procedure should be reliable except in dilute solutions (n > 1000) where the equilibria HF + H⁺ + F⁻ + HF⁺ + HF⁻ yield an overall ΔH of about 3 kcal/mol. Parker (2) used thermodynamic data for these equilibria in order to calculate ϕ_L for the dilute solutions, but recent data (3-5) suggest that minor changes in the calculations may be desirable. For this reason the simultaneous solution includes $\phi_L(50) = 3184 \pm 300$ cal/mol (2) as an "observation" rather than as a fixed value. The result of the simultaneous solution is smaller by only 150 cal/mol, suggesting that $\phi_L(50)$ does not contain a major inconsistency.

Heat Capacity and Entropy

The ground state configuration is that deduced from UV spectra by Johns and Barrow (8). The excited state near 85000 cm⁻¹ is omitted since its contribution to the thermodynamic functions is negligible. High-resolution studies of the vibration-rotation spectrum were reported by Hann et al. (7) and subsequently confirmed by others (9, 10). The analysis of Webb and Rao (2) is adopted for this table.

References

- Quarterly Technical Report No. 4 under Contract F04611-67-C-0009, Dow Chemical Co. Report No. T-0009-4Q-68, Jan. 1969.
- V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965. Heat of Dilution.
- A. J. Ellis, J. Chem. Soc. 1963, 4300 (1963). Aqueous ionic equilibria.
- L. G. Silen and A. E. Martell, "Stability Constants," Special Publication No. 17, pp. 256-7, The Chemical Society, London, 1964; H. N. Farnham and F. J. C. Rossotti, J. Inorg. Nucl. Chem. 26, 1959 (1964). Aqueous ionic equilibria.
- J. D. Cox and D. Harrop, Trans. Faraday Soc. 61, 1328 (1965). Heat of dilution.
- J. W. C. Johns and R. F. Barrow, Proc. Roy. Soc. A251, 504 (1959). UV spectra.
- D. E. Mann, B. A. Thrush, D. R. Lide, J. J. Ball and M. Acquista, J. Chem. Phys. 39, 470 (1961). Vibration-rotation spectra.
- A. A. Mason and A. H. Nielsen, J. Opt. Soc. Amer. 57, 1464 (1967); W. G. Rothschild, ibid. 54, 20 (1964). Rotation spectra.
- D. U. Webb and K. N. Rao, J. Mol. Spectrosc. 28, 121 (1958); E. S. Fishburne and K. N. Rao, ibid. 19, 290 (1966); V. E. Nevich and S. A. Stankevich, Dokl. Akad. Nauk SSSR 170 (6), 1376 (1966). Vibration-rotation spectra.

MOL. WT. = 36.00577

(IDEAL GAS)

HYPOFLUOROUS ACID (HFO)

T, °K. C_p^o S^o - (F^o - H₂₉₈^o)/T ΔH_f^o ΔF_f^o Log K_p

Point Group C_s
 $\Delta H_f^o = [53.954] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta F_f^o = [-31 \pm 10] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\lambda, \text{ cm.}^{-1}$
 [1500] (1)
 [1065] (1)
 [3645] (1)

Bond Distances: H-O = [0.96] Å O-F = [1.41] Å
 Bond Angle: H-O-F = [104]°
 Product of the Moments of Inertia: $I_A I_B I_C = [1.2926 \times 10^{-117}] \text{ g.}^3 \text{ cm.}^6$
 $\sigma^- = 1$

Heat of Formation.

The value of ΔH_f^o 298.15 for HFO(g) was calculated based on an estimated value for the heat of atomization 1.e. $\Delta H_f^o = 161.6 \text{ kcal. mole}^{-1}$ for the reaction $\text{HFO(g)} = \text{H(g)} + \text{F(g)} + \text{O(g)}$. The ΔH_f^o value was assumed to be the sum of the F-O and H-O bond energies which were obtained from the corresponding bond energies in F₂O(g) and H₂O(g) molecules.

Heat Capacity and Entropy.

The H-O and F-O bond distances were assumed to be the same as those in the H₂O(g) and F₂O(g) molecules. The vibrational frequencies and H-O-F bond angle were estimated by comparison with the corresponding values for H₂O(g), F₂O(g) and Cl₂O(g). The three principal moments of inertia are $I_A = 0.1332 \times 10^{-39}$, $I_B = 3.0366 \times 10^{-39}$ and $I_C = 3.1699 \times 10^{-39} \text{ g. cm.}^2$

Dec. 31, 1960; Sept. 30, 1965

Fluorosilane (H₃SiF)

(Ideal Gas) Mol. Wt. = 50.114

INTERIM TABLE

T, °K.	C _p	S° - (F° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0	∞	∞	∞	∞	∞	∞
100	6.971	57.035	2,617	102,770	102,770	INFINITE
200	6.971	57.035	5,822	103,535	102,473	223.993
298	11.313	57.035	9,900	105,000	101,170	110.548
300	11.379	57.105	9,921	105,014	99,471	72.461
400	13.730	60.711	1,280	105,691	97,517	53.278
500	15.651	63,888	2,752	106,219	95,411	41.702
600	17.213	66,985	4,398	106,612	93,210	33.950
700	18.579	69,981	6,161	106,881	90,825	28.225
800	19.763	72,940	8,091	107,082	88,641	24,225
900	20.844	75,837	10,092	107,201	86,350	20,968
1000	21.873	78,629	12,174	107,263	84,030	18,364
1100	22.858	81,371	14,323	107,282	81,706	16,233
1200	23.795	84,074	16,527	107,265	79,382	14,583
1300	24.698	86,749	18,777	107,224	77,059	12,958
1400	25.565	89,391	21,066	107,166	74,739	11,667
1500	26.397	91,999	23,398	107,097	72,425	10,552
1600	27.197	94,571	25,738	107,023	70,118	9,577
1700	27.965	97,104	28,076	106,935	67,813	8,723
1800	28.707	99,601	30,506	106,832	65,509	7,953
1900	29.429	102,063	32,919	106,715	63,209	7,264
2000	30.130	104,494	35,346	106,585	60,911	6,641
2100	30.811	106,893	37,788	106,437	58,615	6,084
2200	31.472	109,259	40,254	106,282	56,321	5,594
2300	32.114	111,594	42,744	106,117	54,028	5,161
2400	32,737	113,907	45,177	105,942	51,735	4,783
2500	33,342	116,196	47,658	105,757	49,442	4,458
2600	33,929	118,463	50,187	105,562	47,149	4,183
2700	34,500	120,707	52,764	105,357	44,856	3,958
2800	35,056	122,928	55,393	105,142	42,563	3,783
2900	35,598	125,126	58,076	104,917	40,270	3,648
3000	36,127	127,301	60,812	104,682	37,977	3,553
3100	36,643	129,453	63,599	104,437	35,684	3,498
3200	37,146	131,584	66,436	104,182	33,391	3,473
3300	37,636	133,694	69,323	103,917	31,098	3,478
3400	38,112	135,783	72,260	103,642	28,805	3,503
3500	38,574	137,851	75,247	103,357	26,512	3,548
3600	39,022	139,897	78,284	103,062	24,219	3,613
3700	39,456	141,921	81,371	102,757	21,926	3,698
3800	39,876	143,924	84,508	102,442	19,633	3,803
3900	40,282	145,905	87,694	102,117	17,340	3,928
4000	40,674	147,864	90,929	101,782	15,047	4,073
4100	41,052	149,801	94,212	101,437	12,754	4,238
4200	41,416	151,716	97,544	101,082	10,461	4,423
4300	41,766	153,609	100,925	100,717	8,168	4,628
4400	42,102	155,481	104,356	100,342	5,875	4,853
4500	42,424	157,332	107,837	99,957	3,582	5,098
4600	42,732	159,163	111,368	99,562	1,289	5,363
4700	43,026	160,974	114,939	99,157	-1,014	5,648
4800	43,306	162,765	118,550	98,742	-3,311	5,953
4900	43,572	164,536	122,211	98,317	-5,608	6,278
5000	43,824	166,287	125,922	97,882	-7,905	6,623
5100	44,062	168,018	129,683	97,437	-10,202	6,988
5200	44,286	169,729	133,494	96,982	-12,499	7,373
5300	44,496	171,420	137,355	96,517	-14,796	7,778
5400	44,692	173,091	141,266	96,042	-17,093	8,193
5500	44,874	174,742	145,227	95,557	-19,390	8,628
5600	45,042	176,373	149,238	95,062	-21,687	9,083
5700	45,196	177,984	153,299	94,557	-23,984	9,558
5800	45,336	179,575	157,410	94,042	-26,281	10,053
5900	45,462	181,146	161,571	93,517	-28,578	10,568
6000	45,574	182,697	165,782	92,982	-30,875	11,103

December 31, 1980.

FH₃Si

Fluorosilane (H₃SiF)

Mol. Wt. = 50.114

ΔH_f 298.15 = [-105 ± 15] kcal. mole⁻¹

S_{298.15} = 57.04 ± 2 cal. deg.⁻¹ mole⁻¹

Point group C_{3v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies	
ω _{cm⁻¹}	
2706 (1)	
990 (1)	
872 (1)	
2196 (2)	
943.4(2)	
729.1(2)	

Moments of Inertia: I_A = 0.9784 X 10⁻³⁹ g. cm.² I_B = 5.8578 X 10⁻³⁹ g. cm.² I_C = 5.8578 X 10⁻³⁹ g. cm.² σ = 3

Heat of Formation. ΔH_f 298.15 was estimated in C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were found in Henderson and Scheffee, op. cit. Moments of Inertia were calculated using the constants found in C. Newman, J. K. O'Leane, S. R. Polo, and M. K. Wilson, J. Chem. Phys. 25, 855 (1956).

FH₃Si

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 219.61

MERCUROUS FLUORIDE (HgF)

(IDEAL GAS)

MOL. WT. = 219.61

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	7.925	51.935	2.226	1.762	1.762	1.762	1.762	INFINITE
200	7.925	51.935	1.762	1.762	1.762	1.762	1.762	INFINITE
298	8.242	59.338	1.700	1.700	1.700	1.700	1.700	3.190
300	8.249	59.349	1.696	1.696	1.696	1.696	1.696	3.193
400	8.570	61.416	1.485	1.485	1.485	1.485	1.485	3.302
500	8.731	63.747	1.175	1.175	1.175	1.175	1.175	3.347
600	8.839	65.349	0.604	0.604	0.604	0.604	0.604	3.363
700	8.905	66.716	3.491	14.095	14.095	14.095	14.095	2.874
800	8.956	67.909	6.229	14.132	14.132	14.132	14.132	2.323
900	9.001	68.967	8.097	14.166	14.166	14.166	14.166	1.894
1000	9.036	69.917	8.373	14.194	14.194	14.194	14.194	1.549
1100	9.067	70.780	8.435	7.090	14.243	14.243	14.243	1.267
1200	9.095	71.570	7.998	7.998	14.280	14.280	14.280	1.031
1300	9.121	72.294	6.546	6.546	14.318	14.318	14.318	0.830
1400	9.145	72.976	6.560	9.822	14.354	14.354	14.354	0.658
1500	9.166	73.607	6.449	10.738	14.391	14.391	14.391	0.508
1600	9.184	74.200	6.415	11.655	14.428	14.428	14.428	0.377
1700	9.210	74.758	6.360	12.575	14.464	14.464	14.464	0.261
1800	9.231	75.285	6.286	13.497	14.500	14.500	14.500	0.158
1900	9.251	75.784	6.194	14.421	14.534	14.534	14.534	0.065
2000	9.270	76.259	6.085	15.348	14.568	14.568	14.568	0.019
2100	9.290	76.712	6.062	16.276	14.602	14.602	14.602	0.094
2200	9.309	77.145	6.032	17.205	14.636	14.636	14.636	0.163
2300	9.328	77.559	6.073	18.137	14.668	14.668	14.668	0.227
2400	9.346	77.956	6.010	19.071	14.700	14.700	14.700	0.285
2500	9.365	78.338	6.035	20.006	14.732	14.732	14.732	0.338
2600	9.383	78.706	6.050	20.944	14.763	14.763	14.763	0.388
2700	9.401	79.060	6.055	21.883	14.793	14.793	14.793	0.434
2800	9.420	79.402	6.051	22.824	14.822	14.822	14.822	0.477
2900	9.438	79.733	6.038	23.767	14.850	14.850	14.850	0.517
3000	9.456	80.054	6.016	24.712	14.879	14.879	14.879	0.554
3100	9.474	80.364	6.007	25.658	14.907	14.907	14.907	0.589
3200	9.492	80.665	6.000	26.604	14.934	14.934	14.934	0.622
3300	9.510	80.957	6.007	27.557	14.961	14.961	14.961	0.653
3400	9.527	81.241	6.007	28.508	14.985	14.985	14.985	0.682
3500	9.545	81.510	6.010	29.462	15.011	15.011	15.011	0.710
3600	9.563	81.787	6.017	30.417	15.035	15.035	15.035	0.736
3700	9.581	82.049	6.030	31.375	15.058	15.058	15.058	0.760
3800	9.598	82.305	6.043	32.334	15.081	15.081	15.081	0.784
3900	9.616	82.555	6.058	33.294	15.104	15.104	15.104	0.806
4000	9.634	82.796	6.074	34.257	15.126	15.126	15.126	0.827
4100	9.651	83.036	6.090	35.221	15.147	15.147	15.147	0.847
4200	9.669	83.269	6.103	36.187	15.167	15.167	15.167	0.867
4300	9.687	83.497	6.116	37.155	15.187	15.187	15.187	0.885
4400	9.704	83.720	6.129	38.124	15.206	15.206	15.206	0.903
4500	9.722	83.938	6.142	39.096	15.224	15.224	15.224	0.919
4600	9.739	84.152	6.155	40.069	15.243	15.243	15.243	0.935
4700	9.757	84.362	6.169	41.044	15.261	15.261	15.261	0.951
4800	9.775	84.567	6.183	42.020	15.278	15.278	15.278	0.966
4900	9.792	84.769	6.196	42.999	15.294	15.294	15.294	0.980
5000	9.810	84.967	6.211	43.979	15.310	15.310	15.310	0.994
5100	9.827	85.161	6.226	44.940	15.327	15.327	15.327	1.007
5200	9.845	85.352	6.241	45.904	15.343	15.343	15.343	1.020
5300	9.862	85.540	6.256	46.869	15.359	15.359	15.359	1.032
5400	9.880	85.725	6.271	47.834	15.374	15.374	15.374	1.043
5500	9.897	85.906	6.286	48.795	15.389	15.389	15.389	1.055
5600	9.915	86.084	6.301	49.754	15.405	15.405	15.405	1.066
5700	9.932	86.260	6.316	50.714	15.420	15.420	15.420	1.076
5800	9.950	86.433	6.331	51.674	15.436	15.436	15.436	1.086
5900	9.967	86.603	6.346	52.634	15.451	15.451	15.451	1.096
6000	9.985	86.771	6.361	53.594	15.466	15.466	15.466	1.106

December 31, 1961

S°_{298.15} = 59.338 cal deg⁻¹ mole⁻¹ΔH°_f 298.15 = 0.7 ± 12.0 kcal mole⁻¹

Electronic Levels and Multiplicities

$$\frac{E_e, \text{cm}^{-1}}{0} \quad \frac{g_e}{2}$$
ω_e = 490.8 cm⁻¹ ω_ex_e = 4.05 cm⁻¹ σ = 1B_e = [0.2732] cm⁻¹ α_e = [0.0026] cm⁻¹ r_e = [1.89] Å

Heat of Formation

A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, London 1953, gives 32 ± 12 kcal for the heat of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants from G. Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York 1950. Rotational constants were estimated using equation III, 123 p. 108, G. Herzberg (loc. cit.). Bond length estimated by comparison of the mercurous halides with thallium and cesium halides.

Iodine Monofluoride (IF)

(Ideal Gas) Mol. wt. = 145.9028

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H ₂₉₈ °)/T H°-H ₂₉₈ °	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	.000	INFINITE	- 2.176	- 22.192	INFINITE
100	6.983	48.396	- 22.192	- 22.192	53.071
200	7.473	53.359	- 22.209	- 26.277	28.713
298	8.021	58.451	- 22.249	- 28.611	20.611
300	8.030	58.501	- 22.652	- 28.153	20.408
400	8.384	58.864	- 24.801	- 29.885	16.328
500	8.601	60.760	- 30.116	- 30.650	13.397
600	8.743	62.341	- 30.113	- 30.767	11.293
700	8.841	63.696	- 30.108	- 30.865	10.293
800	8.915	64.882	- 30.104	- 30.973	9.461
900	8.973	65.936	- 30.099	- 31.083	8.754
1000	9.020	66.883	- 30.095	- 31.192	8.117
1100	9.061	67.745	- 30.090	- 31.302	7.539
1200	9.097	68.535	- 30.085	- 31.412	7.019
1300	9.130	69.265	- 30.080	- 31.523	6.549
1400	9.160	69.942	- 30.075	- 31.634	6.128
1500	9.188	70.575	- 30.069	- 31.745	5.754
1600	9.215	71.169	- 30.064	- 31.857	5.425
1700	9.241	71.729	- 30.058	- 31.970	5.130
1800	9.266	72.258	- 30.052	- 32.084	4.869
1900	9.290	72.759	- 30.046	- 32.195	4.638
2000	9.313	73.236	- 30.039	- 32.309	4.425
2100	9.336	73.691	- 30.032	- 32.423	4.234
2200	9.359	74.126	- 30.025	- 32.538	4.062
2300	9.381	74.543	- 30.018	- 32.652	3.907
2400	9.403	74.942	- 30.011	- 32.765	3.768
2500	9.425	75.327	- 30.003	- 32.883	3.642
2600	9.447	75.697	- 29.994	- 32.994	3.527
2700	9.468	76.054	- 29.986	- 33.113	3.423
2800	9.490	76.398	- 29.977	- 33.227	3.329
2900	9.511	76.732	- 29.968	- 33.344	3.243
3000	9.532	77.055	- 29.960	- 33.464	3.167
3100	9.553	77.367	- 29.950	- 33.577	3.097
3200	9.574	77.671	- 29.940	- 33.695	3.031
3300	9.595	77.966	- 29.930	- 33.812	2.969
3400	9.616	78.253	- 29.920	- 33.932	2.911
3500	9.636	78.532	- 29.909	- 34.048	2.857
3600	9.657	78.804	- 29.898	- 34.167	2.805
3700	9.678	79.068	- 29.887	- 34.284	2.754
3800	9.698	79.327	- 29.875	- 34.404	2.704
3900	9.719	79.579	- 29.863	- 34.524	2.655
4000	9.739	79.825	- 29.851	- 34.643	2.607
4100	9.760	80.066	- 29.839	- 34.763	2.560
4200	9.780	80.301	- 29.826	- 34.881	2.514
4300	9.801	80.532	- 29.812	- 35.005	2.469
4400	9.821	80.757	- 29.798	- 35.124	2.425
4500	9.842	80.978	- 29.786	- 35.245	2.382
4600	9.862	81.195	- 29.772	- 35.368	2.340
4700	9.882	81.407	- 29.758	- 35.489	2.299
4800	9.903	81.615	- 29.743	- 35.609	2.259
4900	9.923	81.820	- 29.728	- 35.733	2.219
5000	9.943	82.021	- 29.713	- 35.858	2.179
5100	9.964	82.218	- 29.698	- 35.983	2.139
5200	9.984	82.411	- 29.682	- 36.102	2.099
5300	10.004	82.602	- 29.666	- 36.227	2.059
5400	10.025	82.789	- 29.650	- 36.351	2.019
5500	10.045	82.973	- 29.633	- 36.475	1.979
5600	10.065	83.154	- 29.616	- 36.600	1.939
5700	10.085	83.332	- 29.599	- 36.721	1.899
5800	10.106	83.508	- 29.581	- 36.846	1.859
5900	10.126	83.681	- 29.563	- 36.977	1.819
6000	10.146	83.851	- 29.545	- 37.099	1.779

Mer. 31, 1962; Dec. 31, 1965

IODINE MONOFLUORIDE (IF)

(IDEAL GAS)

MOL. WT. = 145.9028

Ground State Configuration $[1 \Sigma^+]$

$\Delta H_f^0 = -22.192 \pm 0.9$ kcal. mole⁻¹

$\Delta H_f^0 = -22.648 \pm 0.9$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

ϵ , cm.⁻¹

g

1

$\omega_e = 612$ cm.⁻¹

$r_e = 1.906$ Å

$\sigma = 1$

$\alpha_e = 0.00763$ cm.⁻¹

$\sigma = 1$

Heat of Formation.

R. A. Durie and A. G. Gaydon, J. Phys. Chem. **56**, 316 (1952), have obtained the dissociation limit (from the spectra) of IF as 23570 cm.⁻¹. The first excited states of F and I are 404 and 7598 cm.⁻¹ above the ground state respectively. There are two sets of dissociation products possible: $I(^2P_{1/2}) + F(^2P_{3/2})$ or $I(^2P_{3/2}) + F(^2P_{1/2})$. When corrected to the normal atoms, the observed limit gives $D_0(\text{IF}(g))$ 2.87 ± 0.04 e.v. or 66.18 ± 0.9 kcal. mole⁻¹ and 1.98 ± 0.04 e.v. or 45.66 ± 0.9 kcal. mole⁻¹ for dissociation energy respectively. Durie and Gaydon, loc. cit., favored the lower value. However L. Slutsky and S. H. Bauer, J. Am. Chem. Soc. **76**, 270 (1954) have pointed out a numerical error in their calculations, which removes the chief support for the lower value and presented additional evidence favoring the higher value. More weight was given to the higher value which gives ΔH_f^0 236.15 = -22.648 ± 0.9 kcal. mole⁻¹ for the reaction $1/2 I_2(g) + 1/2 F_2(g) = \text{IF}(g)$.

Heat Capacity and Entropy.

All molecular constants were obtained from W. H. Evans, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. Standards **55**, 147 (1955) except $r_e = 1.906$ Å was obtained from L. O. Cole and O. W. Elverum Jr., J. Chem. Phys. **20**, 1543 (1952) and ground state configuration was estimated by comparison with that for IFr and ICl from O. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

POTASSIUM FLUORIDE (KF)

GFW = 58.1004

(CRYSTAL)

Potassium Fluoride (KF)
(Crystal)

GFW = 58.1004

$$\Delta H_f^\circ = -135.5 \pm 0.1 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -135.9 \pm 0.1 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 6.50 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = 57.8 \text{ kcal/mol (to monomer)}$$

Heat of Formation

The heat of solution of KF(c) in water has been measured by several investigators. Their results have been converted to ΔH_{∞}° by Farker (5) and listed in the table below. Using $\Delta H_{\infty}^\circ = -4.24$, $\Delta H_{298}^\circ(K^+ \infty H_2O) = -60.32$ (6), and $\Delta H_{298}^\circ(F^- \infty H_2O) = -79.82$ kcal/mol (7), we obtain $\Delta H_{298}^\circ = -135.9 \pm 0.1$ kcal/mol which is adopted.

Investigator	Temperature, °K	Concentration, molality	No. of Determinations	ΔH_{∞}° , kcal/mol
1. Guntz (1884)	291	0.28	1	-3.95
2. Forrand (1911)	286	0.50	1	-4.54
3. Lange and Eichler (1927)	298	3.16 - 0.21	8	-4.24±0.4
4. Lange and Martin (1937)	298	0.31	1	-4.01

Heat Capacity and Entropy

The low temperature heat capacities, 16-323°K, were measured by Westrum and Pitzer (8). The high temperature enthalpies, 298-530°K and 291-1187°K, were determined by Westrum and Pitzer (8), and Lyashenko (9), respectively. However, the high temperature Cp values derived from both sets appear to be inconsistent with the low temperature Cp values. The heat capacities derived from the enthalpy data of Westrum and Pitzer are too high (3% at 530°K and less at lower temperatures) to be joined smoothly with their low temperature Cp's. The adopted enthalpy at 530°K is about 1.4% lower than the reported value. The heat capacity derived from the enthalpy data of Lyashenko is 2.5% lower than the adopted one at 900°K. The differences are smaller at lower temperatures. At 900°K, the adopted enthalpy is 1.3% higher than the reported value. The adopted heat capacities in the temperature range, 323-2000°K, are estimated by graphical comparison with other alkali fluorides and chlorides, and joined smoothly with the low temperature data at 298°K.

S₂₉₈° is derived based on the adopted low temperature heat capacities.

Melting Data

See the KF(t) table.

Heat of Sublimation

The value of ΔH_{298}° is obtained as the difference between ΔH_{298}° for KF(c) and KF(g).

References

1. A. Guntz, Ann. Chim. et Phys. [6] 3, 5 (1884).
2. R. de Forrand, Compt. Rend. 152, 1073 (1911).
3. E. Lange and A. Eichler, Z. Physik. Chem. 129, 285 (1927).
4. E. Lange and W. Martin, Z. Physik. Chem. 160, 233 (1937).
5. V. B. Parker, U. S. Natl. Bur. Std. NBS-RS 2, 1965.
6. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
7. JANAF table for HF(g) 12-31-68.
8. E. F. Westrum, Jr. and K. S. Pitzer, J. Am. Chem. Soc. 71, 1040 (1949).
9. V. S. Lyashenko, Metallurg (USSR) 10, 85 (1935).

Potassium Fluoride (KF)
(Liquid)

GFW = 58.1004

POTASSIUM FLUORIDE (KF)

(LIQUID)

GFW = 58.1004

$$\Delta H_{298.15}^{\circ} = 16.167 \text{ gibbs/mol}$$

$$\Delta H_m^{\circ} = 6.50 \text{ kcal/mol}$$

$$\Delta H_v^{\circ}(\text{to mixture}) = 33.9 \text{ kcal/mol of liquid}$$

Heat of Formation

The $\Delta H_{298}^{\circ}(t)$ is obtained from $\Delta H_{298}^{\circ}(c)$ by adding ΔH_m° and the difference between H_{1131}° - H_{298}° for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those of the alkali fluorides and chlorides, and is assumed to be constant in the temperature range, 298-1000°K. The Cp value, 16 gibbs/mol, derived from the enthalpy data of Lyashenko (12) appears low and is not adopted.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

It has been reported as 1119 (1, 2), 1129 (3, 4), 1131 (5, 6), and 1153°K (7). The value 1131°K is adopted. Kelley (8) evaluated the following freezing-point data of binary systems: KF-AlF₃ (9), KF-K₂SO₄ (10), KF-KCl (11), KF-K₂CO₃ (13), and KF-K₂PO₄ (14), and derived the values of ΔH_m° (in kcal/mol) as 5.5, 5.55, 6.51, 7.1, and 7.1 respectively. The best value is recommended as 6.50 kcal/mol. Other reported ΔH_m° values are 6.70 (2) and 6.75 ± 0.1 kcal/mol (12). The value of heat of melting is tentatively adopted as 6.50 kcal/mol.

Vaporization Data

The boiling point (Tb) is calculated to be the temperature at which the partial pressures of KF(g) and K₂F₂(g) equal one atmosphere. The composition of the gaseous mixture in equilibrium with KF(l) at Tb is calculated as K₂F₂ 21.1% and KF 78.9%. The heat required to vaporize one mole of liquid at Tb is evaluated to be 33.9 kcal. The experimental values for the boiling point are 1778°K (1) and 1771°K (15).

References

1. H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921).
2. B. S. Zakharova, L. P. Reshetnikova, and A. V. Novoselova, Vestn. Mosk. Univ., Ser. II 22, 102 (1967).
3. O. Schmitz-Dumont and E. Schmitz, Z. Anorg. Chem. 252, 329 (1944).
4. E. P. Dergunov and A. G. Bergman, Zh. Fiz. Khim. 22, 625 (1948).
5. J. W. Johnson and M. A. Bradig, J. Phys. Chem. 62, 604 (1958).
6. B. Porter and E. A. Brown, J. Am. Ceram. Soc. 45, 49 (1962).
7. G. Petit and A. Crémieu, Compt. Rend. 243, 360 (1956).
8. K. K. Kelley, U. S. Bur. Mines Bull. 393, 1936.
9. N. A. Puchin and A. B. Baskov, J. Russ. Phys. Chem. Soc. 45, 82 (1913); Z. Anorg. Chem. 81, 347 (1913).
10. B. Karandesff, Zentr. Min. Geol. 728, 1909.
11. W. Plato, Z. Physik. Chem. 55, 721 (1906).
12. V. S. Lyashenko, Metallurg (USSR) 10, 85 (1935).
13. M. Amadori, Atti Accad. Lincei, Ser. 5, 22, 366 (1913).
14. M. Amadori, Atti Accad. Lincei, Ser. 5, 23, 688 (1912).
15. O. Ruff, G. Schmidt, and S. Hugdan, Z. Anorg. Allg. Chem. 123, 83 (1922).

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	log Kp
0							
100							
200							
298	17.200	16.167	16.167	.000	-132.519	-125.508	92.000
300	17.200	16.273	16.167	-.032	-132.507	-125.465	91.401
400	17.200	21.222	16.842	1.752	-132.486	-123.101	67.259
500	17.200	25.060	18.116	3.472	-131.913	-120.621	52.611
600	17.200	28.196	19.542	5.192	-131.335	-118.656	43.221
700	17.200	30.684	20.973	6.832	-130.766	-116.605	36.309
800	17.200	32.544	22.354	8.412	-129.996	-114.605	31.309
900	17.200	35.170	23.668	10.352	-129.611	-112.692	27.345
1000	17.200	36.982	24.910	12.072	-129.055	-110.843	24.225
1100	17.200	38.621	26.003	13.792	-127.414	-108.024	21.462
1200	17.200	40.168	27.153	15.512	-125.673	-104.996	18.479
1300	17.200	41.633	28.281	17.232	-123.843	-101.767	15.287
1400	17.200	42.769	29.232	18.952	-121.922	-97.570	11.921
1500	17.200	43.956	30.175	20.672	-119.910	-94.201	8.511
1600	17.200	45.066	31.071	22.392	-117.806	-90.684	5.036
1700	17.200	46.102	31.925	24.112	-115.606	-87.056	1.506
1800	17.200	47.076	32.741	25.832	-113.316	-83.269	-1.984
1900	17.200	48.002	33.521	27.552	-110.937	-79.369	-5.497
2000	17.200	48.904	34.268	29.272	-108.468	-75.365	-8.967
2100	17.200	49.743	34.985	30.992	-105.908	-71.261	-12.414
2200	17.200	50.538	35.677	32.712	-103.256	-67.056	-15.741
2300	17.200	51.298	36.343	34.432	-100.512	-62.752	-18.956
2400	17.200	52.040	36.977	36.152	-97.676	-58.348	-22.059
2500	17.200	52.742	37.593	37.872	-94.750	-53.844	-25.059
2600	17.200	53.417	38.199	39.592	-91.734	-49.240	-27.959
2700	17.200	54.066	38.795	41.312	-88.628	-44.536	-30.759
2800	17.200	54.691	39.381	43.032	-85.442	-39.732	-33.459
2900	17.200	55.295	39.956	44.752	-82.176	-34.828	-36.059
3000	17.200	55.878	40.527	46.472	-78.830	-29.824	-38.559

Potassium Fluoride (KF) (Ideal Gas)

Ground State Configuration $1s^2$

$$\Delta H_f^\circ = -77.6 \pm 0.5 \text{ kcal/mol}$$

$$S_{298,15}^\circ = 54.135 \pm 0.01 \text{ gibbs/mol}$$

$$\Delta H_f^{298} = -78.1 \pm 0.5 \text{ kcal/mol}$$

$$GFW = 58.1004$$

Electronic Levels and Quantum Weights

$$\frac{E_i, \text{ cm}^{-1}}{0} = \frac{g_i}{1}$$

$$\omega_e x_e = 2.43 \text{ cm}^{-1} \quad \sigma = 1$$

$$\omega_e = 426.04 \text{ cm}^{-1}$$

$$B_e = 0.27994 \text{ cm}^{-1}$$

$$a_e = 0.002335 \text{ cm}^{-1}$$

$$r_e = 2.17155 \text{ \AA}$$

Heat of Formation

The total vapor pressures of KF(g) and $K_2F_2(g)$ over KF(c, ℓ) have been determined by many investigators using the boiling point (1, 2, 5), Knudsen-effusion (3), transpiration (4), and torsion-effusion (5) methods. A method of trial and error is employed to select the appropriate values for $\Delta H_{298}^\circ(\text{KF}, c)$ and $\Delta H_{298}^\circ(\text{KF}, \ell)$ such that by use of these two values and $\Delta H_{298}^\circ = 50 \text{ kcal/mol}$ for the reaction $K_2F_2(g) = 2\text{KF}(g)$ and the Gibbs energy functions for KF(c), KF(ℓ), KF(g), and $K_2F_2(g)$, the calculated total pressures of KF(g) and $K_2F_2(g)$ are consistent with the measured ones. Adopting $\Delta H_{298}^\circ = 57.6$ and $\Delta H_{298}^\circ = 54.42 \text{ kcal/mol}$, we evaluate the partial pressures of KF(g) and $K_2F_2(g)$ from the reported total pressure measurements. Based on the derived partial pressures for KF(g), the enthalpy changes for the processes: A. KF(c) = KF(g), and B. KF(ℓ) = KF(g) are calculated by the second and third law methods. Using the third law $\Delta H_{298}^\circ = -135.90$ and $-132.519 \text{ kcal/mol}$ for KF(c) and KF(ℓ), respectively, we obtain the ΔH_{298}° for KF(g). The results are presented in the table below.

The dissociation energy (D_0) of KF(g) has been determined as $117 \pm 8 \text{ kcal/mol}$ by flame photometry by Page and Sugden (2), and Bulawicz, Phillips, and Sugden (5), yielding $\Delta H_{298}^\circ(\text{KF}, g) = -77.6 \pm 8 \text{ kcal/mol}$. Barrow and Caunt (3) measured the fluctuation bands in the ultraviolet absorption spectra of KF and reported the upper limit for the $D_0(\text{KF}, g)$ value to be 121.8 kcal/mol which leads to $\Delta H_{298}^\circ(\text{KF}, g) = -81.4 \text{ kcal/mol}$ as the lower limit. Gaydon (10) reported $D_0 = 116.9 \pm 4.6 \text{ kcal/mol}$ for KF(g). The corresponding value of ΔH_{298}° is calculated as $-77.5 \pm 4.6 \text{ kcal/mol}$.

The heat of formation for KF(g) at 298°K is adopted as $-78.1 \pm 0.5 \text{ kcal/mol}$.

Investigator	Method	Temperature, $^\circ\text{K}$	No. of Points	Process	ΔH° , kcal/mol	Drift	ΔH_{298}° , kcal/mol
1. Wartenberg (1921)	boiling point	1624-1776	5	B	54.4 ± 0.9	-0.1 ± 0.5	-78.36
2. Ruff (1922)	boiling point	1551-1773	6	B	68.1 ± 2.5	-2.4 ± 1.5	-78.38
3. Nix (1938)	Knudsen-effusion	913-973	2	A	55.2 ± 0.3	-0.6 ± 0.3	-80.23
4. Naryshkin (1939)	transpiration	1073-1108	2	A	—	—	-78.67
5. Cantor (1958)	boiling point	1188-1233	2**	B	—	—	-77.92
6. Pugh (1958)	torsion-effusion	1200-1500	7*	B	54.4	-0.02	-78.14
		910-1020	6*	A	57.7	0.47	-77.78

* Data points calculated from the given vapor pressure equation.

** Only the data point at 1233°K is adopted for evaluation.

Heat Capacity and Entropy

The rotational transition spectrum of KF(g) has been measured in the millimeter- and submillimeter-wave region with a high resolution molecular-beam absorption spectrometer by Veasey and Gordy (13). From the derived potential constants the vibrational constants were calculated. The reported values for ω_e , $\omega_e x_e$, B_e , a_e and r_e are adopted.

Other values of ω_e reported are (in cm^{-1}): 390 ± 39 (11), 408 ± 25 (12), 426 ± 4 (13). The value of $\omega_e x_e$ has been determined as 1.45 cm^{-1} by Barrow and Caunt (3), and 2.4 cm^{-1} by Ritchie and Lew (12) and Baikov and Vasilevskii (13). Using the molecular beam electric resonance method, Green and Lew (14) measured the rotational transitions between the $J = 0$ and $J = 1$ states of K_2F_2 and reported the following values: $B_e = 0.27994 \text{ cm}^{-1}$, $a_e = 0.002335 \text{ cm}^{-1}$, and $r_e = 2.17144 \pm 0.00005 \text{ \AA}$ which are in excellent agreement with the adopted values. By use of the same method, Grabner and Hughes (15) investigated the rotational Stark spectrum of K_2F_2 and reported the K-F bond distance for the zeroth vibrational state as $2.55 \pm 0.06 \text{ \AA}$.

References

1. H. von Wartenberg and H. Schulz, Z. Electrochem. **27**, 568 (1921).
2. O. Ruff, G. Schmidt, and S. Hugdan, Z. Anorg. Allg. Chem. **123**, 83 (1922).
3. R. F. Barrow and A. D. Phillips, J. Chem. Phys. **42**, 1023 (1965).
4. I. Naryshkin, Zh. Fiz. Khim. **59**, 192 (1985).
5. S. Cantor and F. Blankenship, paper presented at the annual meeting of the American Chemical Society, Chicago, Sept. 7-12, 1958.
6. A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. **54**, 671 (1958).
7. F. M. Page and T. H. Sugden, Nature **163**, 1672 (1959).
8. R. F. Barrow and A. D. Phillips, and T. H. Sugden, Trans. Faraday Soc. **57**, 921 (1961).
9. A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, Chapman and Hall Ltd., London, 1968.
10. L. K. Grabner and V. Hughes, Phys. Rev. **79**, 819 (1950).
11. R. K. Ritchie and H. Lew, Can. J. Phys. **42**, 43 (1964).
12. V. I. Baikov and K. P. Vasilevskii, Opt. Spektrosk. **22**, 138 (1967).
13. G. E. Green and H. Lew, Can. J. Phys. **38**, 482 (1960).
14. S. E. Veasey and W. Gordy, Phys. Rev. **138** A1303 (1965).

Dec. 31, 1961; Mar. 31, 1964; June 30, 1969

T, $^\circ\text{K}$	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH°	ΔG°	$\log K_p$
0	0.000	0.000	INFINITE	-2.561	77.611	77.611	INFINITE
100	7.131	45.662	61.273	1.259	79.355	79.355	17.310
200	7.949	50.862	54.892	0.806	77.890	80.951	16.459
298	8.620	54.135	54.135	0.000	76.100	82.409	16.408
300	8.626	54.187	54.135	0.016	76.104	82.436	16.405
400	8.662	54.487	54.483	0.011	76.994	85.732	16.780
500	8.794	56.595	55.106	1.745	79.221	84.697	17.108
600	8.877	60.206	55.825	2.628	79.479	86.007	17.324
700	8.936	64.579	56.552	3.519	79.730	87.075	17.466
800	9.079	62.715	57.256	4.415	80.029	88.109	17.530
900	9.104	61.166	57.916	5.316	80.259	89.109	17.564
1000	9.045	64.786	56.569	6.210	80.430	90.083	17.568
1100	9.072	65.650	59.174	7.124	80.667	90.005	17.682
1200	9.096	66.480	59.747	8.032	80.768	89.124	16.232
1300	9.119	67.189	60.200	8.943	80.779	88.154	15.335
1400	9.141	67.807	60.634	9.843	80.779	87.154	14.435
1500	9.161	68.377	61.296	10.771	80.817	86.145	12.598
1600	9.181	69.069	61.764	11.688	80.854	85.574	11.669
1700	9.200	69.626	62.210	12.607	80.892	84.671	10.687
1800	9.216	70.132	62.637	13.526	80.915	83.617	9.651
1900	9.230	70.595	63.045	14.445	80.930	82.546	8.564
2000	9.255	71.124	63.438	15.375	100.008	81.946	8.999
2100	9.273	71.578	63.815	16.302	100.049	81.095	8.439
2200	9.290	72.009	64.178	17.230	100.092	80.181	7.965
2300	9.306	72.423	64.527	18.160	100.137	79.212	7.533
2400	9.321	72.821	64.864	19.089	100.181	78.202	7.140
2500	9.342	73.200	65.190	20.025	100.236	77.156	6.771
2600	9.359	73.567	65.505	20.960	100.291	76.553	6.434
2700	9.377	73.920	65.811	21.897	100.350	75.630	6.122
2800	9.394	74.261	66.108	22.835	100.416	74.512	5.835
2900	9.410	74.592	66.396	23.772	100.486	73.313	5.569
3000	9.427	74.911	66.672	24.717	100.567	72.074	5.309
3100	9.444	75.220	66.943	25.661	100.654	71.948	5.072
3200	9.461	75.521	67.206	26.606	100.751	71.019	4.850
3300	9.476	75.813	67.463	27.551	100.850	70.087	4.642
3400	9.490	76.095	67.712	28.500	100.976	69.157	4.442
3500	9.511	76.371	67.956	29.452	101.108	68.216	4.260
3600	9.528	76.639	68.193	30.404	101.254	67.274	4.084
3700	9.544	76.900	68.425	31.357	101.416	66.330	3.918
3800	9.561	77.155	68.651	32.313	101.600	65.389	3.760
3900	9.576	77.404	68.876	33.270	101.796	64.452	3.607
4000	9.594	77.646	69.099	34.228	102.030	63.462	3.467
4100	9.611	77.883	69.301	35.186	102.264	62.495	3.331
4200	9.627	78.115	69.508	36.150	102.566	61.591	3.201
4300	9.644	78.342	69.710	37.114	102.879	60.659	3.077
4400	9.660	78.564	69.906	38.080	103.196	59.706	2.958
4500	9.677	78.781	70.104	39.046	103.615	58.753	2.844
4600	9.694	78.994	70.295	40.015	104.043	57.549	2.734
4700	9.710	79.202	70.482	40.995	104.516	56.533	2.629
4800	9.727	79.407	70.666	41.957	105.035	55.504	2.527
4900	9.743	79.606	70.846	42.900	105.607	54.459	2.429
5000	9.760	79.805	71.024	43.845	106.231	53.419	2.335
5100	9.776	79.998	71.198	44.802	106.911	52.354	2.248
5200	9.793	80.188	71.369	45.861	107.649	51.277	2.155
5300	9.809	80.375	71.537	46.941	108.447	50.166	2.069
5400	9.826	80.558	71.702	47.882	109.307	49.032	1.986
5500	9.842	80.739	71.865	48.806	110.229	47.895	1.906
5600	9.859	80.916	72.025	49.771	111.212	46.816	1.827
5700	9.875	81.091	72.183	50.773	112.257	45.657	1.751
5800	9.892	81.263	72.336	51.766	113.363	44.440	1.676
5900	9.908	81.432	72.486	52.752	114.527	43.202	1.603
6000	9.924	81.599	72.641	53.747	115.749	42.001	1.532

LITHIUM FLUORIDE (LiF)

(CRYSTAL)

GFW = 25.9374

Lithium Fluoride (LiF)

(Crystal)

GFW = 25.9374

T, °K	Cp	gibbs/mol	$-(G^{\circ}-H^{\circ}_{298})/T$	$H^{\circ}-H^{\circ}_{298}$	ΔH°	ΔG°	Log Kp
0	3.000	0.000	INFINITE	1.547	-146.837	-146.837	INFINITE
100	1.161	1.161	15.761	1.460	-147.217	-145.122	317.164
200	7.840	4.945	9.375	.886	-147.133	-145.247	103.113
298	9.994	8.523	8.523	.000	-147.050	-145.050	102.466
300	10.023	8.585	8.523	.019	-147.449	-140.654	75.616
400	11.124	11.641	8.932	1.084	-147.390	-136.396	59.461
500	11.780	14.197	9.737	2.230	-147.065	-130.060	48.696
600	12.330	16.395	10.627	3.437	-147.088	-123.689	40.999
800	13.320	20.080	12.576	6.003	-147.655	-113.116	35.232
900	13.750	21.677	13.500	7.359	-147.672	-106.641	30.753
1000	14.240	23.153	14.392	8.760	-147.445	-100.641	27.175
1100	14.700	24.532	15.252	10.208	-147.176	-95.372	24.254
1200	15.130	25.826	16.080	11.699	-146.863	-90.600	21.655
1300	15.539	27.054	16.877	13.230	-146.506	-86.330	19.775
1400	15.981	28.218	17.646	14.800	-146.114	-82.454	18.023
1500	16.230	29.325	18.388	16.406	-145.683	-78.975	16.509
1600	16.537	30.383	19.105	18.045	-145.216	-75.810	15.189
1700	16.844	31.398	19.798	19.716	-144.715	-72.930	13.958
1800	17.142	32.368	20.470	21.417	-144.187	-70.312	12.850
1900	17.405	33.302	21.121	23.144	-143.633	-67.937	11.842
2000	17.643	34.201	21.753	24.897	-143.050	-65.875	10.922
2100	17.859	35.067	22.366	26.672	-142.437	-64.010	10.084
2200	18.054	35.907	22.953	28.468	-141.793	-62.339	9.319
2300	18.224	36.709	23.523	30.282	-141.128	-60.853	8.617
2400	18.373	37.488	24.108	32.112	-140.443	-59.543	7.977
2500	18.500	38.240	24.658	33.956	-139.738	-58.376	7.426
					-139.015	-57.346	6.957

Heat of Formation

The heats of solution and reaction of LiF(c) in water and hydrochloric acid have been measured by many investigators. The reported ΔH_{soln} values are listed in the table below. Using $\Delta H^{\circ}_{298}(\text{Li}^{\circ}, \infty \text{H}_2\text{O}) = -66.56 \text{ kcal/mol (g)}$, and $\Delta H^{\circ}_{298}(\text{F}^{\circ}, \infty \text{H}_2\text{O}) = -79.82 \text{ kcal/mol (g)}$, we calculate the corresponding ΔH°_{298} values for LiF(c). Based on the heat of solution of LiOH(c) in excess HF solution measured by Sinko (7), the value, $\Delta H^{\circ}_{298}(\text{LiF}, \text{c}) = -146.65 \pm 0.5 \text{ kcal/mol}$ is derived. The value of ΔH°_{298} for LiF(c) is adopted as $-147.45 \pm 0.2 \text{ kcal/mol}$.

Investigator	Solvent	Temperature, °K	ΔH° , kcal/mol (LiF·nH ₂ O)	ΔH° , kcal/mol Concentration (LiF·nH ₂ O)	ΔH° , kcal/mol Concentration (LiF·nH ₂ O)
1. de Forcrand (1911)	H ₂ O	288.2	unavailable	1.04	1.13 ± 0.05
2. Kolesov-Skuratov (1961)	H ₂ O	294.7	3800 H ₂ O	unavailable	1.10 ± 0.10
3. Wulff (1962)	HCl	298.2	unavailable	unavailable	1.07 ± 0.05
4. Stephenson et al. (1964)	H ₂ O	298.2	2780-5560 H ₂ O	unavailable	1.014 ± 0.055
5. Cox and Harrop (1964)	H ₂ O	298.2	50000 H ₂ O	unavailable	1.059 ± 0.028

*The heat of dilution data of Parker (5) are used to convert ΔH° to ΔH°_{298} .

Heat Capacity and Entropy

Clusius, Goldman, and Perlick (10) measured the low temperature heat capacities in the temperature range 19 to 272°K and Clusius and Eichenauer (11) from 10 to 111°K. Below 20°K a number of investigators have reported values of θ_p and the average value of 729 ± 6 is used here. The high temperature enthalpies from 298°K to the melting point 1221.3°K were measured by Douglas and Dever (12), and Voskresenskaya et al. (13). All these data are taken and smoothed by computer up to 400°K. Above 400°K the C_p values are obtained graphically by drawing a smooth line through the data points.

S°_{298} is derived from the adopted low temperature heat capacities, based on $S^{\circ}_{298} = 0.064 \text{ eu}$.

Melting Data

See the LiF(4) table for details.

Heat of Sublimation

The difference between ΔH°_{298} for LiF(g) and LiF(c) is ΔH°_{298} .

References

1. R. de Forcrand, Compt. Rend. 152, 27 (1911).
2. V. P. Kolesov and S. M. Skuratov, Russ. J. Inorg. Chem. (English Transl.) 6, 889 (1961).
3. C. A. Wulff, Ph.D. Thesis, Massachusetts Institute of Technology, 1962.
4. C. C. Stephenson, H. P. Hopkins and C. A. Wulff, J. Phys. Chem. 68, 1427 (1964).
5. J. D. Cox and D. Harrop, Trans. Faraday Soc. 51, 1328 (1965).
6. V. B. Parker, U. S. Natl. Bur. Std. NBS-NBS 2, 1965.
7. G. C. Sinko, Thermal Research Laboratory, The Dow Chemical Company, Midland, Michigan, private communication, February 1959.
8. S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958).
9. Derived from JANAF value of $\Delta H^{\circ}_{298}(\text{HF}, \text{g})$, dated Dec. 31, 1968.
10. K. Clusius, J. Goldman, and A. Perlick, Z. Naturforsch. 49, 424 (1949).
11. K. Clusius and W. Eichenauer, Z. Naturforsch. 2a, 715 (1956).
12. T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76, 4826 (1954).
13. N. K. Voskresenskaya, V. A. Sokolov, E. I. Banashek, and N. E. Smid, Akad. Nauk SSSR, Izvest. Sect. Fiz. Khim. Anal. 27, 233 (1956).

(LIQUID)

LITHIUM FLUORIDE (LiF)

GFW = 25.9374

Lithium Fluoride (LiF)

GFW = 25.9374

 $S_{298.15}^{\circ} = 10.269$ gibbs/mol $\Delta H_f^{\circ} = -143.081$ kcal/mol $T_m = 1121.3 \pm 1.0^{\circ}\text{K}$ $\Delta H_m^{\circ} = 6.474 \pm 0.005$ kcal/mol $T_b = 1980^{\circ}\text{K}$ $\Delta H_v^{\circ}(\text{to mixture}) = 35.08$ kcal/mol

T, K	C_p°	$\frac{\text{gibbs/mol}}{S^{\circ}}$	$-(C_p^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	$\frac{\text{kcal/mol}}{\Delta H_f^{\circ}}$	ΔC_p°	Log Kp
0							
100							
200							
298	15.340	10.269	10.269	0.000	-143.081	-136.647	100.311
300	15.340	10.363	10.269	0.028	-143.071	-136.609	99.665
400	15.340	10.776	10.870	1.562	-142.543	-134.602	73.652
500	15.340	18.200	12.007	3.096	-142.830	-132.846	58.067
600	15.340	20.996	13.279	4.630	-142.825	-130.887	47.975
700	15.340	23.361	14.355	7.168	-142.067	-127.165	34.740
800	15.340	25.683	15.355	9.698	-141.203	-125.384	30.447
900	15.340	27.216	16.058	10.766	-140.801	-123.648	27.023
1000	15.340	28.832	16.066				
1100	15.340	30.284	19.112	12.300	-140.401	-121.932	24.230
1200	15.340	31.689	20.100	13.636	-139.008	-118.266	19.950
1300	15.340	33.054	21.021	15.002	-137.212	-117.070	18.275
1400	15.340	34.392	21.921	16.436	-135.816	-115.502	16.829
1500	15.340	35.032	22.761				
1600	15.340	36.042	23.561	19.970	-136.421	-113.960	15.566
1700	15.340	36.972	24.323	21.008	-135.025	-112.446	13.051
1800	15.340	37.848	25.057	22.072	-133.629	-107.847	11.981
1900	15.340	38.678	25.746	23.572	-131.922	-103.690	11.980
2000	15.340	39.465	26.412	26.108	-131.349	-100.325	10.963
2100	15.340	40.214	27.052	27.640	-130.779	-96.789	10.073
2200	15.340	40.927	27.666	29.174	-130.212	-93.278	9.252
2300	15.340	41.608	28.252	30.708	-129.646	-89.799	8.502
2400	15.340	42.262	28.828	32.242	-129.083	-86.335	7.662
2500	15.340	42.888	29.378	33.776	-128.524	-82.898	7.247
2600	15.340	43.490	29.909	35.310	-127.967	-79.485	6.681
2700	15.340	44.069	30.423	36.844	-127.415	-76.072	6.174
2800	15.340	44.627	30.922	38.378	-126.864	-72.674	5.728
2900	15.340	45.165	31.402	39.912	-126.322	-69.286	5.228
3000	15.340	45.685	31.870	41.446	-125.783	-65.933	4.810

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Dec. 31, 1968

Heat of Formation

The $\Delta H_f^{\circ}(\text{LiF})$ is obtained from $\Delta H_f^{\circ}(\text{LiF})$ by adding ΔH_m° and the difference between $H_{1121.3}^{\circ}$ and H_{298}° for crystal and liquid.

Heat Capacity and Entropy

T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. **76**, 4876 (1954), and N. K. Voskresenskaya, V. A. Sokolov, E. I. Banashek, and N. E. Shmidt, Akad. Nauk SSSR, Izvest. Sekt. Fiz. - Khim. Anal. **27**, 733 (1956), have measured the enthalpies of LiF liquid to 1200 and 1400°K, respectively. Using the reported enthalpy data, a constant heat capacity is derived for each set. The adopted C_p for LiF(l) is the mean of the two derived heat capacities, and is extended arbitrarily to the temperatures above T_b and below T_m . The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting point has been determined by many investigators. See the table below for details. The adopted value, 1121.3 ± 1.0°K, is that reported by Douglas and Dever, loc. cit. The heat of melting is the mean of the ΔH_m° values reported by Douglas and Dever, loc. cit., and Voskresenskaya et al., loc. cit.

T_m , °K	Source
1115	H. von Wartenberg and H. Schulz, Z. Elektrochem. 27 , 568 (1921).
1115	G. Petit and A. Cremlieu, Compt. Rend. 243 , 360 (1956).
1119	H. Flood, V. Pykas, and S. Urnes, Z. Elektrochem. 59 , 364 (1955).
1120	V. P. Goryachava, A. G. Bergman, and A. G. Kislova, Zh. Neorg. Khim. 4 , 2744 (1959).
1121	H. M. Haendler, P. S. Sennett, and C. M. Wheeler, J. Electrochem. Soc. 106 , 264 (1959).
1121.2	Z. A. Mateiko and G. A. Bukhalova, Zh. Neorg. Khim. 4 , 1649 (1959).
1121.3	T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76 , 4876 (1954).
1123	G. A. Bukhalova and D. V. Semontova, Russ. J. Inorg. Chem. (English Transl.) 10 , 1027 (1965).

Vaporization Data

T_b is the temperature at which the partial pressures of LiF(g), $\text{Li}_2\text{F}_2(\text{g})$, and $\text{Li}_3\text{F}_3(\text{g})$, in equilibrium with LiF(l), equal one atmosphere. The vapor composition at the boiling point is evaluated as LiF 69%, Li_2F_2 26.6%, and Li_3F_3 4.44%. The heat required to vaporize one mole of liquid to form 0.739 mole of vapor mixture of the above composition at T_b is calculated to be 35.08 kcal.

The value of T_b for LiF(l) has been reported to be 1943 and 1949°K by O. Ruff, G. Schmidt, and S. Muggan, Z. Anorg. Allgem. Chem. **223**, 83 (1922), and H. von Wartenberg and H. Schulz, loc. cit., respectively, which were obtained by extrapolation of their vapor pressure data, measured by the boiling point method.

GF_F = 25.9374

(Ideal Gas)

LITHIUM FLUORIDE (LiF)

Log Kp

GF_F = 25.9374

(Ideal Gas)

Lithium Fluoride (LiF)

GF_F = 25.9374

T, °K	C _p	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _F	ΔG _F	Log Kp
0	0.000	0.000	INFINITE	2.109	81.390	81.399	INFINITE
100	6.960	40.092	40.092	1.610	81.171	82.669	1.81.330
200	7.094	48.940	48.940	1.710	81.261	82.660	92.606
298	7.178	47.840	47.840	1.710	81.450	82.660	83.386
300	7.495	47.687	47.687	1.610	81.454	86.449	62.978
400	7.879	50.096	48.139	1.783	81.691	86.449	66.124
500	8.178	51.888	48.715	1.566	82.709	86.569	63.151
600	8.391	53.399	49.373	2.215	83.009	90.012	33.415
700	8.564	54.705	50.644	2.415	83.297	92.207	22.789
800	8.660	55.864	50.699	4.123	83.552	95.533	25.533
900	8.747	56.879	51.330	4.994	83.610	94.668	22.963
1000	8.816	57.604	51.932	5.872	83.664	95.881	20.955
1100	8.872	58.067	52.505	6.757	84.314	97.053	19.283
1200	8.916	58.421	53.057	7.640	84.514	97.327	17.283
1300	8.959	58.713	53.587	8.540	84.604	99.327	16.694
1400	8.994	60.802	54.061	9.438	85.045	100.434	15.679
1500	9.025	61.424	54.531	10.339	85.283	101.525	14.792
1600	9.052	62.007	54.980	11.243	85.517	102.600	14.015
1700	9.076	62.556	55.419	12.149	85.747	103.660	13.293
1800	9.102	63.076	55.821	13.054	86.004	104.745	12.623
1900	9.124	63.569	56.216	13.970	86.249	105.850	11.920
2000	9.145	64.037	56.594	14.883	86.481	106.961	11.265
2100	9.165	64.484	56.961	15.798	86.707	108.076	10.596
2200	9.183	64.911	57.319	16.713	86.927	109.197	9.910
2300	9.200	65.319	57.652	17.628	87.141	110.324	9.211
2400	9.216	65.711	57.980	18.556	87.349	111.456	8.501
2500	9.238	66.088	58.294	19.479	87.554	112.594	7.772
2600	9.255	66.451	58.603	20.404	87.754	113.734	7.044
2700	9.268	66.798	58.904	21.328	87.949	114.874	6.316
2800	9.278	67.138	59.194	22.254	88.139	116.014	5.588
2900	9.285	67.464	59.474	23.181	88.324	117.154	4.860
3000	9.320	67.780	59.740	24.108	88.501	118.294	4.132
3100	9.335	68.086	60.004	25.032	88.677	119.434	3.404
3200	9.351	68.382	60.262	25.956	88.849	120.574	2.676
3300	9.366	68.670	60.512	26.880	89.016	121.714	1.948
3400	9.380	68.950	60.756	27.804	89.179	122.854	1.220
3500	9.396	69.222	60.994	28.728	89.339	123.994	0.492
3600	9.411	69.487	61.226	29.652	89.494	125.134	-0.236
3700	9.426	69.745	61.454	30.576	89.644	126.274	-0.964
3800	9.441	69.997	61.675	31.500	89.789	127.414	-1.692
3900	9.455	70.242	61.891	32.424	89.929	128.554	-2.420
4000	9.470	70.482	62.103	33.348	90.064	129.694	-3.148
4100	9.484	70.716	62.310	34.272	90.194	130.834	-3.876
4200	9.499	70.944	62.513	35.196	90.319	131.974	-4.604
4300	9.513	71.168	62.712	36.120	90.439	133.114	-5.332
4400	9.527	71.387	62.906	37.044	90.554	134.254	-6.060
4500	9.542	71.601	63.097	37.968	90.664	135.394	-6.788
4600	9.556	71.811	63.284	38.892	90.769	136.534	-7.516
4700	9.570	72.017	63.468	39.816	90.869	137.674	-8.244
4800	9.584	72.216	63.648	40.740	90.964	138.814	-8.972
4900	9.598	72.416	63.825	41.664	91.054	139.954	-9.700
5000	9.612	72.610	63.999	42.588	91.144	141.094	-10.428
5100	9.626	72.801	64.170	43.512	91.234	142.234	-11.156
5200	9.640	72.988	64.337	44.436	91.319	143.374	-11.884
5300	9.654	73.172	64.502	45.360	91.404	144.514	-12.612
5400	9.668	73.352	64.665	46.284	91.484	145.654	-13.340
5500	9.682	73.530	64.824	47.208	91.564	146.794	-14.068
5600	9.696	73.704	64.981	48.132	91.644	147.934	-14.796
5700	9.710	73.876	65.136	49.056	91.719	149.074	-15.524
5800	9.724	74.045	65.288	50.000	91.794	150.214	-16.252
5900	9.738	74.211	65.436	50.924	91.869	151.354	-16.980
6000	9.752	74.375	65.585	51.848	91.944	152.494	-17.708

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Dec. 31, 1968

Heat of Formation

The molecular species produced on vaporization of lithium fluoride have been studied by many investigators during the last ten years. The occurrence of dimer and trimer molecules in addition to the monomer has been established by use of mass spectroscopic (Δ , Δ , Δ), torsion effusion (Δ , Δ), molecular beam (Δ , Δ), and transpiration (Δ) methods. To evaluate ΔH_F° (LiF, g), we have used a trial and error variation of ΔH_F° and ΔH_F° for the monomer, dimer and trimer in order to obtain reasonable agreement with the observed total pressures, 997-1939 K. (Δ , Δ , Δ , Δ). Using, as guidelines, these total pressures and the equilibrium data for dimer and trimer (see these tables), we adopt ΔH_{298}° = 66.0, 69.57 and 79.73 and ΔH_{298}° = 61.63, 60.83 and 66.62 kcal/mol for LiF, Li₂F₂ and Li₃F₃, respectively. The adopted value ΔH_{298}° = 63.1 kcal/mol is in agreement with the reported values: 64.8 $\pm$ 2 (2), 63.6 $\pm$ 1 (6) and 63.0 $\pm$ 1.5 kcal/mol (8) at 1000 K.

A second and third law analysis of the total pressure data is given below. Monomer pressures for this analysis are obtained by deducing dimer and trimer pressures calculated from JANAF free energy functions and the adopted values of ΔH_{298}° and ΔH_{298}° .

The vapor pressure data reported by Eisenstadt et al. (9, 10) are too low and so not consistent with the others and are not used for evaluation. The transpiration data of Sense and Stone (11) and Knudsen-effusion data of Evseev et al. (13) are not considered for analysis because of the complications involved in converting the reported apparent pressures to the real total pressures of the gaseous mixtures containing monomer, dimer and trimer.

Herzberg (12) and Gaydon (13) reported the dissociation energies (D_0) of LiF(g) to be $\leq$ 6.6 and 5.95 $\pm$ 0.3 eV, respectively. Using these D_0 values, we derive ΔH_{298}° (LiF, g) = -95.9 and -80.9 $\pm$ 6.9 kcal/mol. By use of flame-photometric method, Page and Sugden (16) and Bulevich et al. (17) gave D_0 = 141 and 136 $\pm$ 8 kcal/mol, yielding ΔH_{298}° (LiF, g) = -84.7 and -79.7 $\pm$ 8 kcal/mol.

Investigator	Temperature, °K	Method	Process	No. of Points	Second Law	Third Law	Drift
1. Wartenberg (1921)	1676-1920	boiling point	I	5	67.6 $\pm$ 2.4	61.4	-3.6 $\pm$ 1.4
2. Ruff (1922)	1671-1939	boiling point	I	14	65.8 $\pm$ 0.7	60.8	-2.7 $\pm$ 0.4
3. Pugh (1958)*	1070-1120	torsion-effusion	II	6	69.1	66.8	-2.2
4. Porter (1958)	1073	mass spectrometry	II	1	—	67.7	-79.75
5. Cantor (1958)*	1378-1575	boiling point	I	10	64.5	61.6	-2.0
6. Hildenbrand (1964)*	997-1119	torsion-effusion	II	24	69.9	66.8	-3.0
	1125-1159	torsion-effusion	I	19	67.1	62.3	-4.2

* Data points are calculated from the given vapor pressure equation.

† Process I: LiF(c) = LiF(g); II: LiF(c) = LiF(g); ΔH_{298}° (LiF, g) values are calculated based on the third law ΔH_{298}° .

Heat Capacity and Entropy

The infrared spectrum of LiF(g) and microwave spectrum of Li₂F₂ have been observed by Vidale (18), and Wharten and Klemperer (21), respectively. The reported vibrational and rotational constants for Li₂F₂(g) and Li₂F₂(g), are adopted and corrected to the average isotopic species. Veasey and Gordy (19) measured the rotational transitions of Li₂F with a high resolution molecular-beam absorption spectrometer. By use of the electric resonance method of molecular beam spectroscopy, Braunstein and Trischka (22) observed the transitions between $v = 0$ and $v = 1$ vibrational states. The infrared spectrum of LiF(g) have also been measured by Vasilievskii and Baikov (20).

References

1. H. von Wartenberg and H. Schulz, Z. Electrochem. 27, 568 (1921).
2. O. Ruff, G. Schmidt, and S. Mugdan, Z. Anorg. Allgem. Chem. 123, 83 (1922).
3. R. C. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 671 (1958).
4. R. C. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 671 (1958).
5. S. Cantor and F. Blankenship, presented at American Chemical Society meeting at Chicago, September 7-12, 1958.
6. D. L. Hildenbrand and W. F. Hall, F. J. and N. D. Potter, J. Chem. Phys. 40, 2882 (1964).
7. J. Berkowitz and W. A. Chupka, J. Chem. Phys. 29, 653 (1958).
8. P. A. Akishin, L. N. Gorokhov, and L. N. Sidorov, Russ. J. Phys. Chem. 23, 797 (1959).
9. Eisenstadt, G. H. Rothberg, and P. Kusch, J. Chem. Phys. 23, 797 (1959).
10. K. A. Sense and R. W. Stork, Phys. Chem. 63, 141 (1959).
11. A. Buehler and J. L. Stauffer, "Thermodynamics," Vol. 1, International Atomic Energy Agency, Vienna, 1966, p. 271.
12. A. M. Evseev, G. V. Pozharovskaya, A. N. Nemyanov, and V. I. Gerasimov, Russ. J. Inorg. Chem. (English Transl.) 4, 997 (1959).
13. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc. New York, 1950.
14. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1966.
15. P. W. Bulevich, L. F. Phillips, and T. W. Sogard, Trans. Faraday Soc. 57, 921 (1961).
16. E. M. Bulevich, L. F. Phillips, and T. W. Sogard, Trans. Faraday Soc. 57, 921 (1961).
17. S. E. Veasey and W. Gordy, Phys. Rev. 138, A1303 (1965).
18. G. L. Vidale, J. Phys. Chem. 64, 314 (1960).
19. K. P. Vasilievskii and V. I. Baikov, Opt. Spectry. (USSR) (English Transl.) 11, 21 (1961).
20. L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, J. Chem. Phys. 38, 1203 (1963).
21. R. Braunstein and J. W. Trischka, Phys. Rev. 28, 1092 (1955).

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	-2.588	-21.390	-21.390	INFINITE	
100	8.059	67.043	-1.792	-21.417	-22.043	48.173	
200	9.004	59.676	-1.463	-21.475	-22.043	48.173	
298	9.495	58.775	-1.400	-22.000	-22.023	16.802	
300	10.307	58.839	-1.019	-22.005	-22.929	16.703	
400	11.331	61.953	-1.104	-22.282	-23.104	12.672	
500	12.031	64.562	-1.013	-23.299	-23.315	10.191	
600	12.502	66.800	-0.942	-23.577	-23.291	8.483	
700	12.824	68.753	-0.939	-23.824	-23.225	7.251	
800	13.052	70.481	-0.900	-24.054	-23.124	6.317	
900	13.217	72.028	-0.830	-24.276	-22.994	5.563	
1000	13.339	73.427	-0.766	-24.494	-22.839	4.991	
1100	13.433	74.703	-0.705	-24.709	-22.664	4.503	
1200	13.505	75.875	-0.652	-24.922	-22.469	4.092	
1300	13.563	76.958	-0.615	-25.135	-22.255	3.741	
1400	13.609	77.965	-0.581	-25.346	-22.026	3.438	
1500	13.646	78.905	-0.554	-25.558	-21.781	3.173	
1600	13.678	79.787	-0.527	-25.768	-21.522	2.940	
1700	13.704	80.617	-0.500	-25.974	-21.252	2.725	
1800	13.725	81.401	-0.473	-26.176	-20.973	2.521	
1900	13.744	82.144	-0.446	-26.374	-20.682	2.325	
2000	13.760	82.849	-0.419	-26.568	-20.382	2.135	
2100	13.774	83.521	-0.392	-26.759	-20.077	1.955	
2200	13.786	84.162	-0.365	-26.946	-19.762	1.776	
2300	13.796	84.775	-0.338	-27.130	-19.438	1.600	
2400	13.805	85.362	-0.311	-27.310	-19.106	1.428	
2500	13.811	85.926	-0.284	-27.486	-18.768	1.260	
2600	13.821	86.468	-0.257	-27.659	-18.425	1.096	
2700	13.827	86.990	-0.230	-27.829	-18.078	0.936	
2800	13.833	87.493	-0.203	-27.996	-17.727	0.780	
2900	13.838	87.978	-0.176	-28.160	-17.372	0.628	
3000	13.843	88.447	-0.149	-28.321	-17.013	0.480	
3100	13.847	88.901	-0.122	-28.479	-16.650	0.336	
3200	13.851	89.341	-0.095	-28.634	-16.283	0.196	
3300	13.855	89.767	-0.068	-28.786	-15.913	0.060	
3400	13.858	90.181	-0.041	-28.936	-15.540	-0.080	
3500	13.861	90.583	-0.014	-29.083	-15.164	-0.220	
3600	13.864	90.973	0.013	-29.227	-14.785	-0.360	
3700	13.866	91.353	0.040	-29.368	-14.402	-0.500	
3800	13.868	91.723	0.067	-29.506	-14.016	-0.640	
3900	13.871	92.083	0.094	-29.641	-13.627	-0.780	
4000	13.873	92.434	0.121	-29.773	-13.235	-0.920	
4100	13.874	92.777	0.148	-29.903	-12.840	-1.060	
4200	13.876	93.111	0.175	-30.030	-12.442	-1.200	
4300	13.878	93.438	0.202	-30.155	-12.041	-1.340	
4400	13.879	93.757	0.229	-30.278	-11.638	-1.480	
4500	13.881	94.069	0.256	-30.399	-11.232	-1.620	
4600	13.882	94.374	0.283	-30.517	-10.823	-1.760	
4700	13.883	94.673	0.310	-30.633	-10.411	-1.900	
4800	13.884	94.965	0.337	-30.747	-10.000	-2.040	
4900	13.885	95.251	0.364	-30.859	-9.588	-2.180	
5000	13.886	95.532	0.391	-30.969	-9.175	-2.320	
5100	13.887	95.807	0.418	-31.077	-8.761	-2.460	
5200	13.888	96.076	0.445	-31.183	-8.346	-2.600	
5300	13.889	96.341	0.472	-31.287	-7.930	-2.740	
5400	13.890	96.600	0.499	-31.389	-7.513	-2.880	
5500	13.891	96.855	0.526	-31.489	-7.095	-3.020	
5600	13.891	97.106	0.553	-31.587	-6.676	-3.160	
5700	13.892	97.352	0.580	-31.683	-6.255	-3.300	
5800	13.893	97.593	0.607	-31.777	-5.833	-3.440	
5900	13.893	97.831	0.634	-31.869	-5.410	-3.580	
6000	13.894	98.064	0.661	-31.959	-4.985	-3.720	

Dec. 31, 1960; Sept. 30, 1965

Point Group C_s

S_{298.15} = [58.775] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

ΔH_f⁰ = [-21 ± 10] kcal. mole⁻¹

ΔF_f⁰ 298.15 = [-22 ± 10] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

(Wavenumbers)

[800] (1)

[500] (1)

[950] (1)

Bond Distances: Li-O = [1.59] Å

Bond Angle: P-O-Li = [104]°

Product of the Moments of Inertia: I_AI_BI_C = [4.21684 X 10⁻¹¹⁶] g.³ cm.⁶

σ = 1

Heat of Formation

The heat of formation (ΔH_f⁰ 298.15) for LiFO(g) was calculated from ΔH_f⁰ 298.15 = 139 kcal. mole⁻¹ for the reaction LiFO(g) = Li(g) + F(g) + O(g) where the value of ΔH_f⁰ 298.15 was estimated to be the sum of the P-O and Li-O bond energies. The values of the P-O and Li-O bond energies were obtained from those in P₂O(g) and Li₂O(g) molecules, respectively.

Heat Capacity and Entropy

The P-O and Li-O bond distances were assumed to be the same as those in P₂O(g) and Li₂O(g) molecules, respectively. The P-O-Li bond angle and vibrational frequencies were estimated by comparison with the corresponding values for the same oxide molecules. The three principal moments of inertia are: I_A = 5.1543 X 10⁻³⁵, I_B = 1.2729 X 10⁻³⁵ and I_C = 6.4272 X 10⁻³⁵ g. cm.²

Magnesium Monofluoride (MgF)

(Ideal Gas) GFW = 43.3104

T, K	C _p ^o	S ^o	-(G ^o -H ^o) _{298.15} /T	H ^o -H ^o _{298.15}	ΔH ^o	ΔG ^o	Log K _p
0	6.200	-0.00	INF	1.143	-52.922	-52.922	INF
100	6.925	44.892	59.371	1.484	-52.795	-55.795	120.258
200	7.280	49.759	53.497	1.740	-51.002	-57.299	43.459
288	7.782	52.771	52.771	1.009	-53.100	-59.294	43.459
300	7.700	52.830	52.731	0.118	-53.104	-59.294	43.459
400	7.168	52.136	52.132	0.118	-53.104	-59.294	43.459
500	6.413	56.987	53.700	1.448	-51.519	-61.163	27.696
600	5.574	58.536	54.380	2.491	-53.754	-65.311	23.789
700	4.584	59.866	55.071	3.357	-54.009	-67.216	20.996
800	3.462	61.031	55.735	4.062	-54.293	-69.384	18.973
900	2.252	62.059	56.206	4.591	-54.591	-71.525	15.650
1000	1.000	62.959	56.596	5.000	-54.900	-73.625	11.242
1100	0.205	63.846	57.000	5.350	-55.220	-75.680	10.430
1200	0.000	64.622	57.414	5.650	-55.540	-77.690	9.714
1300	0.000	65.398	57.830	5.900	-55.860	-79.660	9.077
1400	0.000	66.174	58.246	6.110	-56.180	-81.590	8.512
1500	0.000	66.950	58.662	6.280	-56.500	-83.480	8.012
1600	0.000	67.726	59.080	6.410	-56.820	-85.330	7.575
1700	0.000	68.502	59.500	6.500	-57.140	-87.140	7.199
1800	0.000	69.278	59.914	6.550	-57.460	-88.910	6.875
1900	0.000	70.054	60.330	6.570	-57.780	-90.640	6.592
2000	0.000	70.830	60.746	6.560	-58.100	-92.330	6.350
2100	0.000	71.606	61.162	6.520	-58.420	-93.980	6.148
2200	0.000	72.382	61.578	6.450	-58.740	-95.590	5.975
2300	0.000	73.158	61.994	6.350	-59.060	-97.160	5.825
2400	0.000	73.934	62.410	6.220	-59.380	-98.690	5.690
2500	0.000	74.710	62.826	6.060	-59.700	-100.180	5.565
2600	0.000	75.486	63.242	5.870	-60.020	-101.630	5.450
2700	0.000	76.262	63.658	5.650	-60.340	-103.040	5.345
2800	0.000	77.038	64.074	5.400	-60.660	-104.410	5.250
2900	0.000	77.814	64.490	5.120	-60.980	-105.740	5.165
3000	0.000	78.590	64.906	4.810	-61.300	-107.030	5.090
3100	0.000	79.366	65.322	4.470	-61.620	-108.280	5.025
3200	0.000	80.142	65.738	4.100	-61.940	-109.490	4.970
3300	0.000	80.918	66.154	3.710	-62.260	-110.660	4.925
3400	0.000	81.694	66.570	3.300	-62.580	-111.790	4.890
3500	0.000	82.470	66.986	2.870	-62.900	-112.880	4.865
3600	0.000	83.246	67.402	2.420	-63.220	-113.930	4.840
3700	0.000	84.022	67.818	1.950	-63.540	-114.940	4.815
3800	0.000	84.798	68.234	1.460	-63.860	-115.910	4.790
3900	0.000	85.574	68.650	0.950	-64.180	-116.840	4.765
4000	0.000	86.350	69.066	0.420	-64.500	-117.730	4.740
4100	0.000	87.126	69.482	-0.110	-64.820	-118.580	4.715
4200	0.000	87.902	69.898	-0.620	-65.140	-119.390	4.690
4300	0.000	88.678	70.314	-1.110	-65.460	-120.160	4.665
4400	0.000	89.454	70.730	-1.580	-65.780	-120.890	4.640
4500	0.000	90.230	71.146	-2.030	-66.100	-121.580	4.615
4600	0.000	91.006	71.562	-2.460	-66.420	-122.230	4.590
4700	0.000	91.782	71.978	-2.870	-66.740	-122.840	4.565
4800	0.000	92.558	72.394	-3.260	-67.060	-123.410	4.540
4900	0.000	93.334	72.810	-3.630	-67.380	-123.940	4.515
5000	0.000	94.110	73.226	-3.980	-67.700	-124.430	4.490
5100	0.000	94.886	73.642	-4.310	-68.020	-124.880	4.465
5200	0.000	95.662	74.058	-4.620	-68.340	-125.290	4.440
5300	0.000	96.438	74.474	-4.910	-68.660	-125.660	4.415
5400	0.000	97.214	74.890	-5.180	-68.980	-126.000	4.390
5500	0.000	97.990	75.306	-5.430	-69.300	-126.310	4.365
5600	0.000	98.766	75.722	-5.660	-69.620	-126.580	4.340
5700	0.000	99.542	76.138	-5.870	-69.940	-126.810	4.315
5800	0.000	100.318	76.554	-6.060	-70.260	-127.000	4.290
5900	0.000	101.094	76.970	-6.230	-70.580	-127.160	4.265
6000	0.000	101.870	77.386	-6.380	-70.900	-127.290	4.240

Dec. 31, 1960; June 30, 1964; Mar. 31, 1967

MAGNESIUM MONOFLUORIDE (MgF) (IDEAL GAS) GFW = 43.3104 FMG

Ground State Configuration 2Σ $\Delta H_f^o = -53.0 \pm 1.3$ kcal/mol

$S_{298.15}^o = 52.791$ gibbs/mol $\Delta H_f^{298.15} = -53.1 \pm 1.3$ kcal/mol

Electronic Levels and Quantum Weights

$$\frac{E_i}{\text{cm}^{-1}} = \frac{E_1}{2}$$

$$w_e = 717.6 \text{ cm}^{-1}$$

$$B_e = 0.5199 \text{ cm}^{-1}$$

$$\alpha_e = [0.00386] \text{ cm}^{-1}$$

Heat of Formation.

The equilibrium constants for the decomposition of MgF(g) into Mg(g), MgF₂(c) and MgF₂(g) were determined by T. C. Ehlert, Ph.D. Thesis, University of Wisconsin, 1963. Using this data, the heats of decomposition are evaluated by both the third and second law methods. The results are presented in the table below. The equilibrium constants for the reaction $\text{AlF}_3(\text{g}) + 2\text{Mg}(\text{g}) \rightarrow \text{AlF}(\text{g}) + 2\text{MgF}(\text{g})$ were also reported by T. C. Ehlert, loc. cit. The heat of reaction is calculated by the third and second law methods, respectively. The dissociation energy (D_0^o) of MgF(g) was reported to be 3.2 ± 0.7 and 4.2 eu by A. O. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953, and G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., 1950, respectively. The corresponding values of $\Delta H_f^{298.15}$ for MgF(g) are derived. The results are also listed in the table. The value of $\Delta H_f^{298.15}$ for MgF(g) adopted is the average of the first two $\Delta H_f^{298.15}$ values.

Investigator	Chemical Reaction	Third Law Value	Second Law Value	$\Delta H_f^{298.15}$ kcal/mol
T. C. Ehlert	$2\text{MgF}(\text{g}) = \text{Mg}(\text{g}) + \text{MgF}_2(\text{g})$	-34.76 $\pm$ 0.74	-70 $\pm$ 19	-52.8 $\pm$ 1.3*
	$2\text{MgF}(\text{g}) = \text{Mg}(\text{g}) + \text{MgF}_2(\text{c})$	-126.66 $\pm$ 0.80	-92 $\pm$ 21	-53.4 $\pm$ 1.2*
G. Herzberg	$\text{AlF}_3(\text{g}) + 2\text{Mg}(\text{g}) = \text{AlF}(\text{g}) + 2\text{MgF}(\text{g})$	18.66 $\pm$ 0.40	2.7 $\pm$ 3.2	-67.7 $\pm$ 1.0*
A. O. Gaydon	$\text{MgF}(\text{g}) \rightarrow \text{Mg}(\text{g}) + \text{F}(\text{g})$	$D_0^o = 4.2$ eV		-42.6 $\pm$ 16.1
	$\text{MgF}(\text{g}) \rightarrow \text{Mg}(\text{g}) + \text{F}(\text{g})$	$D_0^o = 3.2 \pm 0.7$ eV		-19.6 $\pm$ 16.1

*Based on $\Delta H_f^{298.15}$ value by the third law method.

Heat Capacity and Entropy.

All the molecular constants are taken from G. Herzberg, loc. cit., except α_e which is estimated.

T, °K.	C_p	S°	$-(H^\circ - H^\circ_{298})/T$	ΔH°_f	ΔF°_f	$\log K_p$
0	0.000	0.000	INFINITE	59.501	59.501	INFINITE
100	6.997	43.760	77.713	59.506	59.501	129.091
200	7.007	48.590	52.081	59.501	59.501	64.072
298	7.253	51.427	51.427	59.500	59.500	42.669
400	7.250	51.427	51.427	59.500	59.500	42.669
500	7.250	51.427	51.427	59.500	59.500	42.669
600	7.253	51.427	51.427	59.500	59.500	42.669
700	7.253	51.427	51.427	59.500	59.500	42.669
800	7.253	51.427	51.427	59.500	59.500	42.669
900	7.253	51.427	51.427	59.500	59.500	42.669
1000	7.253	51.427	51.427	59.500	59.500	42.669
1100	7.253	51.427	51.427	59.500	59.500	42.669
1200	7.253	51.427	51.427	59.500	59.500	42.669
1300	7.253	51.427	51.427	59.500	59.500	42.669
1400	7.253	51.427	51.427	59.500	59.500	42.669
1500	7.253	51.427	51.427	59.500	59.500	42.669
1600	7.253	51.427	51.427	59.500	59.500	42.669
1700	7.253	51.427	51.427	59.500	59.500	42.669
1800	7.253	51.427	51.427	59.500	59.500	42.669
1900	7.253	51.427	51.427	59.500	59.500	42.669
2000	7.253	51.427	51.427	59.500	59.500	42.669
2100	7.253	51.427	51.427	59.500	59.500	42.669
2200	7.253	51.427	51.427	59.500	59.500	42.669
2300	7.253	51.427	51.427	59.500	59.500	42.669
2400	7.253	51.427	51.427	59.500	59.500	42.669
2500	7.253	51.427	51.427	59.500	59.500	42.669
2600	7.253	51.427	51.427	59.500	59.500	42.669
2700	7.253	51.427	51.427	59.500	59.500	42.669
2800	7.253	51.427	51.427	59.500	59.500	42.669
2900	7.253	51.427	51.427	59.500	59.500	42.669
3000	7.253	51.427	51.427	59.500	59.500	42.669
3100	7.253	51.427	51.427	59.500	59.500	42.669
3200	7.253	51.427	51.427	59.500	59.500	42.669
3300	7.253	51.427	51.427	59.500	59.500	42.669
3400	7.253	51.427	51.427	59.500	59.500	42.669
3500	7.253	51.427	51.427	59.500	59.500	42.669
3600	7.253	51.427	51.427	59.500	59.500	42.669
3700	7.253	51.427	51.427	59.500	59.500	42.669
3800	7.253	51.427	51.427	59.500	59.500	42.669
3900	7.253	51.427	51.427	59.500	59.500	42.669
4000	7.253	51.427	51.427	59.500	59.500	42.669
4100	7.253	51.427	51.427	59.500	59.500	42.669
4200	7.253	51.427	51.427	59.500	59.500	42.669
4300	7.253	51.427	51.427	59.500	59.500	42.669
4400	7.253	51.427	51.427	59.500	59.500	42.669
4500	7.253	51.427	51.427	59.500	59.500	42.669
4600	7.253	51.427	51.427	59.500	59.500	42.669
4700	7.253	51.427	51.427	59.500	59.500	42.669
4800	7.253	51.427	51.427	59.500	59.500	42.669
4900	7.253	51.427	51.427	59.500	59.500	42.669
5000	7.253	51.427	51.427	59.500	59.500	42.669
5100	7.253	51.427	51.427	59.500	59.500	42.669
5200	7.253	51.427	51.427	59.500	59.500	42.669
5300	7.253	51.427	51.427	59.500	59.500	42.669
5400	7.253	51.427	51.427	59.500	59.500	42.669
5500	7.253	51.427	51.427	59.500	59.500	42.669
5600	7.253	51.427	51.427	59.500	59.500	42.669
5700	7.253	51.427	51.427	59.500	59.500	42.669
5800	7.253	51.427	51.427	59.500	59.500	42.669
5900	7.253	51.427	51.427	59.500	59.500	42.669
6000	7.253	51.427	51.427	59.500	59.500	42.669

Dec. 31, 1960; June 30, 1965

NITROGEN MONOFLUORIDE (NF)

(IDEAL GAS)

MOL. WT. = 33.0051

Ground State Configuration ($\frac{1}{2}$)

$S^\circ_{298.15} = 51.427$ cal. deg.⁻¹ mole⁻¹

$\Delta H^\circ_f = 59.5 \pm 8$ kcal. mole

$\Delta H^\circ_f = 59.5 \pm 8$ kcal. mole

Electronic Levels and Quantum Weight

$\frac{E_1, \text{ cm.}^{-1}}{0} = \frac{g_1}{5}$

$\nu_0 = 1115$ cm.⁻¹

$\nu_0 \nu_e = [12.175]$

$\nu_e = [1.51 \text{ \AA}]$

$\sigma = 1$

$r_e = [1.51 \text{ \AA}]$

Heat of Formation.

The heat of formation was obtained by taking an average of two estimates of the dissociation energy of NF.

The first estimate of 5.15 e.v. (72.4 kcal./mole) was obtained from V. C. Price, T. R. Pasmore and D. M. Rossner Discussion Faraday Soc. 55, 201 - 11 (1963). The second estimate of 70.4 kcal./mole was obtained by taking one-half the dissociation energy of NF₂ (g) calculated from JANAF values. The ΔH°_f 298.15 for NF (g) was then calculated with auxiliary JANAF data from a dissociation energy of 71.4 kcal./mole.

Heat Capacity and Entropy.

The ΔH°_f value was obtained from infrared studies of D. E. Milligan and M. E. Jacox, J. Chem. Phys. 40, 2461 (1964). The r_e value was estimated from Duggeheimer's relation for single bonded molecules. [K. M. Duggeheimer, Proc. Phys. Soc. (London), 59, 456 (1946)] The enthalpicity constant x_0 was estimated by assuming the separation of the vibrational levels to be a linear function of the vibrational quantum number. The ν_e value was then calculated using the Morse potential function; B_0 was determined from the bond length. The ground state configuration was assumed to be the same as that in NFR. The principal moment of inertia is 3.05247×10^{-39} g. cm.²

Nitrosyl Fluoride (ONF)

(Ideal Gas) Mol. Wt. = 49.01

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
100	8.000	INF	2.558	15.129	15.129	INF
200	8.632	52.523	1.923	15.383	13.213	14.616
298	9.083	52.523	1.923	15.383	13.213	14.616
300	9.089	52.523	1.923	15.383	13.213	14.616
400	9.409	52.523	1.923	15.383	13.213	14.616
500	9.629	52.523	1.923	15.383	13.213	14.616
600	9.769	52.523	1.923	15.383	13.213	14.616
700	9.849	52.523	1.923	15.383	13.213	14.616
800	9.899	52.523	1.923	15.383	13.213	14.616
900	9.929	52.523	1.923	15.383	13.213	14.616
1000	9.949	52.523	1.923	15.383	13.213	14.616
1100	9.969	52.523	1.923	15.383	13.213	14.616
1200	9.979	52.523	1.923	15.383	13.213	14.616
1300	9.989	52.523	1.923	15.383	13.213	14.616
1400	9.999	52.523	1.923	15.383	13.213	14.616
1500	10.000	52.523	1.923	15.383	13.213	14.616
1600	10.000	52.523	1.923	15.383	13.213	14.616
1700	10.000	52.523	1.923	15.383	13.213	14.616
1800	10.000	52.523	1.923	15.383	13.213	14.616
1900	10.000	52.523	1.923	15.383	13.213	14.616
2000	10.000	52.523	1.923	15.383	13.213	14.616
2100	10.000	52.523	1.923	15.383	13.213	14.616
2200	10.000	52.523	1.923	15.383	13.213	14.616
2300	10.000	52.523	1.923	15.383	13.213	14.616
2400	10.000	52.523	1.923	15.383	13.213	14.616
2500	10.000	52.523	1.923	15.383	13.213	14.616
2600	10.000	52.523	1.923	15.383	13.213	14.616
2700	10.000	52.523	1.923	15.383	13.213	14.616
2800	10.000	52.523	1.923	15.383	13.213	14.616
2900	10.000	52.523	1.923	15.383	13.213	14.616
3000	10.000	52.523	1.923	15.383	13.213	14.616
3100	10.000	52.523	1.923	15.383	13.213	14.616
3200	10.000	52.523	1.923	15.383	13.213	14.616
3300	10.000	52.523	1.923	15.383	13.213	14.616
3400	10.000	52.523	1.923	15.383	13.213	14.616
3500	10.000	52.523	1.923	15.383	13.213	14.616
3600	10.000	52.523	1.923	15.383	13.213	14.616
3700	10.000	52.523	1.923	15.383	13.213	14.616
3800	10.000	52.523	1.923	15.383	13.213	14.616
3900	10.000	52.523	1.923	15.383	13.213	14.616
4000	10.000	52.523	1.923	15.383	13.213	14.616
4100	10.000	52.523	1.923	15.383	13.213	14.616
4200	10.000	52.523	1.923	15.383	13.213	14.616
4300	10.000	52.523	1.923	15.383	13.213	14.616
4400	10.000	52.523	1.923	15.383	13.213	14.616
4500	10.000	52.523	1.923	15.383	13.213	14.616
4600	10.000	52.523	1.923	15.383	13.213	14.616
4700	10.000	52.523	1.923	15.383	13.213	14.616
4800	10.000	52.523	1.923	15.383	13.213	14.616
4900	10.000	52.523	1.923	15.383	13.213	14.616
5000	10.000	52.523	1.923	15.383	13.213	14.616
5100	10.000	52.523	1.923	15.383	13.213	14.616
5200	10.000	52.523	1.923	15.383	13.213	14.616
5300	10.000	52.523	1.923	15.383	13.213	14.616
5400	10.000	52.523	1.923	15.383	13.213	14.616
5500	10.000	52.523	1.923	15.383	13.213	14.616
5600	10.000	52.523	1.923	15.383	13.213	14.616
5700	10.000	52.523	1.923	15.383	13.213	14.616
5800	10.000	52.523	1.923	15.383	13.213	14.616
5900	10.000	52.523	1.923	15.383	13.213	14.616
6000	10.000	52.523	1.923	15.383	13.213	14.616

June 30, 1961

FNO

MOL. WT. = 49.01

(IDEAL GAS)

NITROSYL FLUORIDE (ONF)

$\Delta H_f^o = -15.1 \pm 0.4 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o = -15.7 \pm 0.4 \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = 59.273 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Point group C_{2v}

Vibrational Levels and Multiplicities

ω , cm.⁻¹
 1844.03 (1)
 521 (1)
 765.85 (1)

Bond lengths and angles: N-O distance = 1.13 Å N-F distance = 1.52 Å O-N-F angle = 110.2°
 Moments of inertia: I_A = 8.8135 X 10⁻⁴⁰ g. cm.² I_B = 70.8354 X 10⁻⁴⁰ g. cm.² I_C = 79.8375 X 10⁻⁴⁰ g. cm.²
 $\sigma = 1$

Heat of Formation

For the reaction 2NO(g) + F₂(g) → 2ONF(g), H. S. Johnston and H. J. Bertin, J. Am. Chem. Soc. 81, 5402 (1959), report ΔH_f^o 298.15 = -74.8 ± 0.8 kcal., determined calorimetrically. This yields -15.7 ± 0.4 kcal. mole⁻¹ for ΔH_f^o 298.15.

Heat Capacity and Entropy

C. V. Stephenson and E. A. Jones, J. Chem. Phys. 20, 135 (1952), report the frequencies, obtained from the infrared spectrum, and moments of inertia, obtained from the microwave spectrum.

FNO

NITRYL FLUORIDE (NO₂F)

(IDEAL GAS)

MOL. WT. = 65.0039

Point Group C_{2v} $\Delta H_f^\circ 0 = -24.8 \pm 5 \text{ kcal. mole}^{-1}$ $\Delta H_f^\circ 298.15 = -26.0 \pm 5 \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = 82.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega_e, \text{cm.}^{-1}$	$\omega_e, \text{cm.}^{-1}$
1312 (1)	1793 (1)
822 (1)	570 (1)
460 (1)	742 (1)

Bond Distances: N-F = 1.40 Å

Bond Angle: O-N-O = 129.5°

Product of the Moments of Inertia: $I_A I_B I_C = 6.401698 \times 10^{-115} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of reaction at 25°C for direct synthesis of nitryl fluoride from nitrogen dioxide with fluorine ($\text{NO}_2(\text{g}) + 1/2 \text{F}_2(\text{g}) = \text{NO}_2\text{F}(\text{g})$) has been measured calorimetrically as $-33.9 \text{ kcal. mole}^{-1}$ by J. D. Breszale and R. O. MacLaren, "Thermochemistry of Oxygen-Fluorine Bonding" (Final Tech. Summary Report, Contract No. Nonr 3433(00), ARPA Order No. 184-62) United Technology Corporation, Sunnyvale, Calif., Mar. 1963. The heat of formation, $\Delta H_f^\circ 298 = -26.0 \text{ kcal. mole}^{-1}$, for $\text{NO}_2\text{F}(\text{g})$ was then derived. The values of $\Delta H_f^\circ 298 = -20 \pm 5$ and $-19 \pm 2 \text{ kcal. mole}^{-1}$ were issued in their second and third quarterly tech. reports, and have been quoted in the literature by E. Tschukow-Roux, J. Phys. Chem. 66, 1636 (1962).

G. Hetherington and P. L. Robinson, Special Publication No. 10, The Chem. Soc., London, 1957 quoted $\Delta H_f^\circ = 26 \text{ kcal. mole}^{-1}$ (presumably it has a minus sign) for $\text{NO}_2\text{F}(\text{g})$ which was derived from the heat of solution measured by Nichols and Robinson, a private communication to Hetherington and Robinson.

Heat Capacity and Entropy.

D. F. Smith and D. W. Magnuson, Phys. Rev. 87, 226 (1952), have measured the moments of inertia from microwave spectrum of $\text{NO}_2\text{F}(\text{g})$. In order to calculate the bond distances, given as N-F = 1.35 Å and N-O = 1.23 Å, the bond angle O-N-O was assumed to be 125°. The selected bond distances and angle were obtained from L. Clayton, Q. Williams and T. Weatherly, J. Chem. Phys. 30, 1328 (1959). Clayton et al. assumed the bond angle O-N-O in $\text{NO}_2\text{F}(\text{g})$ should be the same as that in $\text{NO}_2\text{Cl}(\text{g})$, and then calculated the bond distances N-F and N-O from Smith and Magnuson's data of the moments of inertia.

The selected vibrational frequencies were obtained from the infrared and Raman spectra measurements by R. Dodd, J. Rolfe and L. Woodward, Trans. Faraday Soc. 52, 145 (1956).

The three principal moments of inertia are $I_A = 6.3659 \times 10^{-39}$, $I_B = 7.3383 \times 10^{-39}$ and $I_C = 13.7041 \times 10^{-39} \text{ g. cm.}^2$

Mar. 31, 1962; Dec. 31, 1965

Fluorine Nitrate (FNO₃)
(Ideal Gas) Mol. Wt. = 81.008

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	9.000	INFINITE	-	3.390	4.313	INFINITE	4.313	INFINITE	INFINITE
100	9.245	56.55	1.126	3.390	4.313	17.822	4.313	17.822	17.822
200	12.747	66.95	71.92	3.390	4.313	2.828	4.313	2.828	2.828
298	15.589	69.988	69.988	3.390	4.313	2.500	4.313	2.500	12.896
300	15.638	70.085	69.989	3.390	4.313	2.466	4.313	2.466	12.885
400	17.951	74.915	70.612	3.390	4.313	2.381	4.313	2.381	12.443
500	19.687	79.117	75.118	3.390	4.313	2.415	4.313	2.415	12.182
600	20.975	82.826	73.433	3.390	4.313	2.447	4.313	2.447	12.002
700	21.933	86.135	75.015	3.390	4.313	2.738	4.313	2.738	11.665
800	22.654	89.113	76.505	3.390	4.313	2.968	4.313	2.968	11.753
900	23.203	91.814	78.138	3.390	4.313	3.253	4.313	3.253	11.660
1000	23.629	94.282	79.531	3.390	4.313	3.496	4.313	3.496	11.579
1100	23.963	96.550	81.067	3.390	4.313	3.778	4.313	3.778	11.506
1200	24.229	98.647	82.446	3.390	4.313	4.067	4.313	4.067	11.442
1300	24.444	100.595	83.768	3.390	4.313	4.358	4.313	4.358	11.383
1400	24.620	102.414	85.036	3.390	4.313	4.652	4.313	4.652	11.328
1500	24.765	104.117	86.252	3.390	4.313	4.945	4.313	4.945	11.279
1600	24.886	105.720	87.419	3.390	4.313	5.236	4.313	5.236	11.232
1700	24.988	107.231	88.540	3.390	4.313	5.527	4.313	5.527	11.189
1800	25.075	108.662	89.619	3.390	4.313	5.811	4.313	5.811	11.149
1900	25.149	110.020	90.657	3.390	4.313	6.091	4.313	6.091	11.111
2000	25.213	111.312	91.658	3.390	4.313	6.367	4.313	6.367	11.075
2100	25.268	112.543	92.623	3.390	4.313	6.638	4.313	6.638	11.041
2200	25.317	113.720	93.556	3.390	4.313	6.899	4.313	6.899	11.009
2300	25.359	114.846	94.457	3.390	4.313	7.157	4.313	7.157	10.978
2400	25.396	115.926	95.329	3.390	4.313	7.408	4.313	7.408	10.950
2500	25.430	116.964	96.174	3.390	4.313	7.649	4.313	7.649	10.922
2600	25.460	117.962	96.993	3.390	4.313	7.885	4.313	7.885	10.896
2700	25.487	118.923	97.787	3.390	4.313	8.114	4.313	8.114	10.871
2800	25.510	119.850	98.554	3.390	4.313	8.335	4.313	8.335	10.848
2900	25.529	120.746	99.298	3.390	4.313	8.549	4.313	8.549	10.825
3000	25.551	121.612	100.008	3.390	4.313	8.755	4.313	8.755	10.803
3100	25.569	122.450	100.747	3.390	4.313	8.956	4.313	8.956	10.782
3200	25.585	123.262	101.438	3.390	4.313	9.148	4.313	9.148	10.762
3300	25.600	124.049	102.111	3.390	4.313	9.334	4.313	9.334	10.743
3400	25.613	124.814	102.768	3.390	4.313	9.512	4.313	9.512	10.725
3500	25.625	125.557	103.409	3.390	4.313	9.685	4.313	9.685	10.707
3600	25.637	126.279	104.034	3.390	4.313	9.852	4.313	9.852	10.690
3700	25.647	126.981	104.645	3.390	4.313	10.012	4.313	10.012	10.674
3800	25.657	127.665	105.241	3.390	4.313	10.167	4.313	10.167	10.659
3900	25.666	128.332	105.825	3.390	4.313	10.316	4.313	10.316	10.643
4000	25.674	128.982	106.396	3.390	4.313	10.459	4.313	10.459	10.629
4100	25.681	129.616	106.954	3.390	4.313	10.596	4.313	10.596	10.615
4200	25.689	130.235	107.501	3.390	4.313	10.730	4.313	10.730	10.601
4300	25.695	130.839	108.037	3.390	4.313	10.859	4.313	10.859	10.588
4400	25.700	131.430	108.562	3.390	4.313	10.982	4.313	10.982	10.575
4500	25.707	132.008	109.077	3.390	4.313	11.101	4.313	11.101	10.563
4600	25.713	132.573	109.581	3.390	4.313	11.216	4.313	11.216	10.552
4700	25.718	133.126	110.076	3.390	4.313	11.325	4.313	11.325	10.540
4800	25.723	133.667	110.562	3.390	4.313	11.432	4.313	11.432	10.529
4900	25.727	134.198	111.039	3.390	4.313	11.535	4.313	11.535	10.518
5000	25.731	134.718	111.508	3.390	4.313	11.634	4.313	11.634	10.508
5100	25.735	135.227	111.968	3.390	4.313	11.729	4.313	11.729	10.498
5200	25.739	135.727	112.420	3.390	4.313	11.822	4.313	11.822	10.488
5300	25.742	136.217	112.864	3.390	4.313	11.911	4.313	11.911	10.479
5400	25.745	136.696	113.296	3.390	4.313	12.000	4.313	12.000	10.470
5500	25.749	137.171	113.731	3.390	4.313	12.081	4.313	12.081	10.461
5600	25.752	137.635	114.154	3.390	4.313	12.160	4.313	12.160	10.452
5700	25.755	138.091	114.570	3.390	4.313	12.237	4.313	12.237	10.444
5800	25.758	138.538	114.979	3.390	4.313	12.312	4.313	12.312	10.436
5900	25.761	138.978	115.382	3.390	4.313	12.384	4.313	12.384	10.428
6000	25.763	139.412	115.776	3.390	4.313	12.453	4.313	12.453	10.420

March 31, 1963

FNO₃

MOL. WT. = 81.008

(IDEAL GAS)

FLUORINE NITRATE (FNO₃)

ΔH_f^o = [4.3 ± 0.5] kcal. mole⁻¹

ΔH_f^o 298.15 = 2.5 ± 0.5 kcal. mole⁻¹

Point Group C_{3v}

S_{298.15}^o = [70] cal. deg.⁻¹ mole⁻¹

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[1300] (1)	[760] (1)
[800] (1)	[980] (1)
[680] (1)	[370] (1)
[1700] (1)	[130] (1)
[450] (1)	

Bond Distance: O-N = 1.29 ± 0.05 Å N-O' = 1.39 ± 0.05 Å O'-F = 1.42 ± 0.05 Å

Bond Angle: O-N-O = 125° ± 5° F-O'-N = 105° ± 5°

Angle between NO₂F plane and O₂NO' plane = 90°.

Product of the Moments of Inertia: I_AI_BI_C = 3.88637 X 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation.

The value, 2.5 ± 0.5 kcal. mole⁻¹, for the heat of formation of FNO₃(g) was obtained from R. Anderson, et al., "Thermochemistry of Oxygen-Fluorine Bonding," UTC 2002-Q74, United Technology Corporation, Sunnyvale, California, March 1, 1961, through February 28, 1962. The value of ΔH_f^o reported by O. G. Telakin, et al., Russ. J. Phys. Chem., 36, 561 (1962) was -4.2 ± 0.9 kcal. mole⁻¹ at 294°K.

Heat Capacity and Entropy.

Vibrational frequencies were estimated by comparison with those of HNO₃(g) reported by A. Palm and M. Kilpatrick, J. Chem. Phys. 23, 1562 (1955). Bond distances and angles were taken from L. Pauling and L. O. Brockway, J. Am. Chem. Soc. 59, 13 (1937). The three principal moments of inertia are: 8.8598 X 10⁻³⁸, 1.8572 X 10⁻³⁸, and 2.3618 X 10⁻³⁸ g. cm.². The possible existence of restricted internal rotation in the molecule was not considered. Thus the values of C_p and S^o calculated may be low.

FNO₃

Sodium Fluoride (NaF)

(Crystal) GFw = 41.9882

$$\Delta H_f^\circ = -135.95 \pm 0.2 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -137.52 \pm 0.2 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 7.97 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = 88.1 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 12.24 \pm 0.02 \text{ gibbs/mol}$$

$$T_m = 1269 \pm 2^\circ\text{K}$$

Heat of Formation

The heats of solution and reaction of NaF(c) have been determined by many investigators. Incorporating their reported data with auxiliary ΔH_{298}° values (1, 2), we calculate the corresponding values of ΔH_{298}° (NaF, c). The results are presented in the table below. The adopted ΔH_{298}° (NaF, c) is $-137.52 \pm 0.2 \text{ kcal/mol}$.

Investigator	Reaction*	Temperature, °K	Concentration NaF/H ₂ O	No. of determinations	ΔH_{298}° kcal/mol	ΔH_{298}° kcal/mol
1. Guntz (1884)	A	285	400	1	0.13	-137.42
2. Latimer - Jolly (1953)	A	298	1850	2	0.23 ± 0.01	-137.52
3. Hepler et al. (1953)	A	298	1540	1	0.22 ± 0.01	-137.51
4. Davies - Benson (1985)	A	298	222	1	0.24 ± 0.01	-137.53
5. Thomson (1882)	B	291	—	2	18.24 ± 0.15	-137.36
6. Wartenberg - Fitzner (1928)	C	293	—	1	-39.3 ± 0.1	-137.62
7. Schmitz - Schumaker (1947)	C	291	—	1	-39.5	-137.82
8. Coughlin (1958)	D	298	—	6	-1.40 ± 0.06	-137.56
9. Vorob'yev - Skuratov (1960)	E	298	—	5	-325.5 ± 2.2	-137.13

*A represents NaF(c) = NaF(in H₂O) and $\Delta H_{298}^\circ = \Delta H_{298}^\circ$; B, NaOH(200 H₂O) + HF(200 H₂O) = NaF(401 H₂O) + H₂O(lat+mol H₂O); C, NaCl(c) + 1/2 F₂(g) = NaF(c) + 1/2 Cl₂(g); D, NaCl(c) + HF(5.716 H₂O) = NaF(c) + HCl(12.731 H₂O); E, 4Na(c) + CF₄(g) = 4NaF(c) + C (graphite).

Heat Capacity and Entropy

The low temperature heat capacities, 0.05 - 15°K and 54.01 - 295.86°K, were measured by Harrison et al. (10) and King (11), respectively. These two sets of data are joined smoothly with the high temperature heat capacities at 298°K which were derived from the enthalpy measurements, 406.1 - 1282.2°K, determined by O'Brien and Kelley (12). The Cp values above 1282.2°K are obtained by linear extrapolation. S₂₉₈ is calculated using the adopted low temperature heat capacities and S₂₉₈ = 0.555 eu.

Frank (13) commented that the temperature measurements of O'Brien and Kelley (12) seemed to be about 20°K high at 1000°K with a smaller error at lower temperatures. A correction for the assumed error in the temperature measurement was used in the previous JANAF table. However, Douglas and Dittmars (14) have questioned this correction, since new enthalpy data for AlF₃ yielded Cp values in better agreement with the original Cp values of O'Brien and Kelley than with the corrected values of Frank. The α + β transition of AlF₃(c) was found in the range 723 - 8°K, while O'Brien and Kelley selected 727°K based on a point at 728.1°K in the β region and a point at 724.9°K in the pretransition region. Frank's correction yields an error of 8° at 727°K, yet the true error appears to be negligible (<2°) for AlF₃(c). Based on the above reasoning and the comparison of the Cp curve of NaF(c) with those of NaCl(c), LiCl(c), and LiF(c) in the temperature range 300 - 1300°K, we adopt the high temperature enthalpy data of O'Brien and Kelley without any correction.

The low temperature heat capacities in the temperature ranges 81 - 190 and 198 - 273°K were also measured by Koref (15); and high temperature enthalpies at temperatures 268 - 1071 and 290 - 1287°K were reported by Krestovnikov and Karetnikov (16), and Lyashenko (17), respectively. They are not used for evaluation.

Melting Data

See the NaF(l) table for details.

Heat of Sublimation

ΔH_{298}° is the difference between ΔH_{298}° for NaF(g) and NaF(c).

References

1. A. Guntz, Ann. Chim. Phys. [6] **3**, 5 (1884).
2. W. H. Latimer and W. L. Jolly, J. Am. Chem. Soc. **75**, 1948 (1953).
3. D. H. Hepler, W. L. Jolly, and G. C. Bond, J. Am. Chem. Soc. **75**, 2809 (1953).
4. D. H. Hepler and G. C. Bond, J. Am. Chem. Soc. **75**, 2810 (1953).
5. J. Thomson, Thermochemische Untersuchungen, Vol. I, J. Barth Verlag, Leipzig, 1882, p. 157.
6. H. Wartenberg and O. Fitzner, Z. Anorg. Allgem. Chem. **151**, 313 (1928).
7. H. Schmitz and H. J. Schumacher, Z. Naturforsch. **2A**, 352 (1947).
8. J. P. Coughlin, J. Am. Chem. Soc. **80**, 1807 (1958).
9. V. P. Vorob'yev and S. H. Skuratov, Russ. J. Inorg. Chem. (English Transl.), **5**, 679 (1960).
10. J. P. Coughlin, J. Am. Chem. Soc. **79**, 2056 (1957).
11. E. G. King, J. Am. Chem. Soc. **79**, 2056 (1957).
12. C. J. O'Brien and K. K. Kelley, J. Am. Chem. Soc. **79**, 5616 (1957).
13. W. B. Frank, J. Phys. Chem. **65**, 2081 (1961).
14. T. B. Douglas and D. A. Dittmars, Natl. Bur. Std. Rept. **9389**, 1966.
15. A. Koref, Ann. Physik (4) **35**, 49 (1911).
16. A. Krestovnikov and E. A. Karetnikov, Dokl. Akad. Nauk SSSR, **13**, 103 (1959).
17. V. S. Lyashenko, Metallurg (USSR) **10**, 85 (1915).

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1958

Sodium Fluoride (NaF)

(Liquid)

GFW = 41.9882

SODIUM FLUORIDE (NaF)

(LIQUID)

GFW = 41.9882

$$S_{298.15}^{\circ} = 17.559 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = -130.545 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 7.97 \text{ kcal/mol}$$

$$\Delta H_m^{\circ}(\text{to mixture}) = 42.1 \text{ kcal/mol of NaF(l)}$$

$$T_m = 1269 \pm 2^{\circ}\text{K}$$

$$T_b = 2060^{\circ}\text{K}$$

Heat of Formation

$\Delta H_{298}^{\circ}(\text{l})$ is obtained from $\Delta H_{298}^{\circ}(\text{c})$ by adding ΔH_m° and the difference between H_{1269}° and H_{298}° for crystal and liquid.

Heat Capacity and Entropy

The heat capacities of NaF(l) are derived from the enthalpy data, 1267.6 - 1746.5°K, determined by O'Brien and Kelley (1). A glass transition temperature is assumed at 900°K, i.e. the heat capacities below 900°K are taken from those for NaF(c). The Cp values above 1746.5°K are obtained by extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

The value of T_m has been reported as (°K): 1313 (2), 1285 (3), 1270 (3, 4, 5), 1269 (6), 1268 (7, 8, 9), 1267 (10, 11, 12), 1265 (13), 1263 (14), and 1253 (15). We select $T_m = 1269^{\circ}\text{K}$. The value 1285°K reported by O'Brien and Kelley seems unreasonably high and is not adopted. The cause of this discrepancy is still unresolved (17). The heat of melting is calculated as the difference between the adopted enthalpies for NaF(c) and NaF(l) at 1269°K. Kelley (18) derived ΔH_m° to be 5.87 - 8.43 kcal/mol, based on 13 sets of molten salts equilibrium data involving NaF. The value $\Delta H_m^{\circ} = 8.03$ kcal/mol reported by O'Brien and Kelley is not used.

Vaporization Data

T_b is the temperature at which the partial pressures of NaF(g) and $\text{Na}_2\text{F}_2(\text{g})$ in equilibrium with NaF(l) equal one atmosphere. The vapor composition at T_b is evaluated as NaF 84.81 and Na_2F_2 15.19. The heat required to vaporize one mole of liquid to form 0.868 mole of vapor mixture of the above composition at T_b is calculated to be 47.1 kcal/mol. Ruff et al. (16) measured the vapor pressure of NaF(l) in the temperature range of 1899 - 1974°K and reported $T_b = 1978^{\circ}\text{K}$.

References

1. C. J. O'Brien and K. K. Kelley, *J. Am. Chem. Soc.* **79**, 5616 (1957).
2. N. Puschin and A. Baskow, *Z. Anorg. Chem.* **81**, 347 (1913).
3. N. S. Kurnakow and S. F. Zemczuznyj, *Z. Anorg. Chem.* **52**, 186 (1907).
4. G. J. Landon and A. R. Ubbelohde, *Proc. Roy. Soc. (London)* **240A**, 160 (1957).
5. M. Rolin, *Bull. Soc. Chim. France*, **1960**, 671 (1960).
6. K. A. Sasse, C. A. Alexander, R. E. Bowman, R. W. Stone, R. B. Filbert, Jr., *J. Phys. Chem.* **61**, 384 (1957).
7. H. S. Booth and B. A. Starrs, *J. Phys. Chem.* **35**, 3553 (1931).
8. M. A. Bredig, J. M. Johnson, and W. T. Smith, Jr., *J. Am. Chem. Soc.* **77**, 307 (1955).
9. S. Cantor, *J. Phys. Chem.* **65**, 2208 (1961).
10. B. Porter and E. A. Brown, *J. Am. Ceram. Soc.* **45**, 49 (1962).
11. N. W. F. Phillips, R. H. Singleton, and E. A. Hollingshead, *J. Electrochem. Soc.* **102**, 690 (1955).
12. J. Brynestad, K. Griethelm, and S. Urnes, *Metallurgia Ital.* **52**, NO.8, 495 (1960).
13. W. Plato, *Z. Physik. Chem.* **58**, 350 (1907).
14. A. G. Bergman and E. P. Dergunov, *Compt. Rend. Acad. Sci. U.R.S.S.* **31**, 753 (1941).
15. O. Ruff and W. Plato, *Ber.* **36**, 2363 (1903).
16. O. Ruff, G. Schmidt and S. Hugdan, *Z. Anorg. Allgem. Chem.* **123**, 83 (1922).
17. K. K. Kelley, private communication, May 31, 1963, U. S. Bureau of Mines, Berkeley, California.
18. K. K. Kelley, *U. S. Bur. Mines Bull.* **393**, 1936.

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^{\circ}}$	$-(G^{\circ}-H_{298}^{\circ})/T$	$H^{\circ}-H_{298}^{\circ}$	$\frac{\text{kcal/mol}}{\Delta H^{\circ}}$	ΔG°	Log Kp
0							
100							
200	11.106	17.559	17.559	.000	-130.545	-124.891	91.548
268							
300	11.215	17.659	17.560	.021	-130.543	-124.856	90.937
400	12.422	18.083	18.008	1.178	-131.115	-122.921	87.161
500	12.422	23.682	18.635	2.384	-131.054	-120.078	82.636
600	12.590	25.906	19.863	3.626	-130.948	-118.852	83.292
700	12.936	27.873	20.870	4.902	-130.804	-116.848	86.481
800	13.315	29.664	21.856	6.214	-130.620	-114.866	91.380
900	13.770	31.271	22.807	7.585	-130.395	-112.909	97.418
1000	14.716	33.112	23.747	9.385	-129.729	-111.003	24.260
1100	17.280	34.779	24.676	11.114	-129.122	-109.162	21.688
1200	19.960	36.269	25.581	12.826	-128.579	-107.314	19.472
1300	16.700	37.616	26.456	14.508	-128.085	-105.465	17.350
1400	16.500	38.856	27.297	16.168	-127.640	-103.703	15.250
1500	16.340	39.976	28.105	17.809	-127.349	-102.044	13.174
1600	16.210	41.029	28.881	19.437	-127.107	-100.484	12.619
1700	16.100	42.008	29.624	21.052	-126.934	-98.965	11.424
1800	16.010	42.926	30.338	22.658	-126.826	-97.487	10.387
1900	15.930	43.789	31.024	24.254	-126.780	-96.050	9.486
2000	15.860	44.604	31.682	25.844	-126.791	-94.652	8.721
2100	15.800	45.377	32.316	27.427	-126.860	-93.295	8.081
2200	15.750	46.111	32.927	29.004	-126.987	-91.980	7.533
2300	15.710	46.810	33.515	30.577	-127.170	-90.703	7.077
2400	15.680	47.477	34.086	32.146	-127.410	-89.463	6.707
2500	15.660	48.117	34.632	33.712	-127.700	-88.256	6.413
2600	15.610	48.729	35.162	35.274	-128.042	-87.080	6.184
2700	15.580	49.316	35.676	36.834	-128.437	-85.943	6.014
2800	15.560	49.884	36.173	38.391	-128.886	-84.843	5.896
2900	15.550	50.430	36.656	39.946	-129.390	-83.776	5.821
3000	15.520	50.956	37.123	41.499	-129.950	-82.741	5.786
3100	15.500	51.465	37.578	43.049	-130.570	-81.736	5.761
3200	15.480	51.957	38.020	44.599	-131.250	-80.761	5.746
3300	15.470	52.433	38.449	46.147	-131.980	-79.816	5.741
3400	15.460	52.896	38.867	47.694	-132.760	-78.891	5.746
3500	15.450	53.343	39.275	49.239	-133.590	-77.986	5.751

Ground State Configuration 1₂

$$\Delta H_F^\circ = -69.03 \pm 0.5 \text{ kcal/mol}$$

$$\Delta H_F^\circ = -69.42 \pm 0.5 \text{ kcal/mol}$$

Electronic Levels and Quantum Weights

$$\frac{g_i}{\sum_i g_i} = \frac{1}{2}$$

$$\omega_e = 536.10 \pm 0.35 \text{ cm}^{-1}$$

$$\rho_e = 0.4369 \text{ cm}^{-1}$$

$$\sigma_e = 0.00456 \text{ cm}^{-1}$$

$$\sigma = 1$$

$$\rho_e = 1.9260 \text{ \AA}$$

Heat of Formation

The total pressures of NaF(g) and Na₂F₂(g), in equilibrium with NaF(c, *l*) at temperatures 1020 - 1974°K, have been determined by many investigators, using manometric (1, 2, 5), torsion-effusion (6, 8), Knudsen-effusion (3, 7), transpiration (9), and molecular-beam velocity-selector (9, 10) methods. In order to evaluate ΔH_F° (NaF, g) we have used a trial and error variation of ΔH_F° and ΔH_F° for the monomer and dimer such that the ΔH_F° values derived by the second and third law methods are in reasonable agreement.

Incorporating ΔH_F° = 68.12 and ΔH_F° = 61.12 and 58.75 kcal/mol for NaF and Na₂F₂, respectively, with JANAF functions for NaF(c), NaF(l), NaF(g) and Na₂F₂(g), we derive the partial pressures of NaF monomer from the reported total pressures. Based on the calculated partial pressures of NaF(g), the corresponding heats of vaporization are evaluated by the second and third law methods. Using the third law ΔH_F° and ΔH_F° = -137.52 and -130.545 kcal/mol for NaF(c) and NaF(l), we obtain values of ΔH_F° for NaF(g). The results are presented in the table below. The ΔH_F° (NaF, g) value adopted is -69.42 kcal/mol.

The vapor pressure data reported by Miller and Kusch (3) and Eisenstadt et al. (10) are not consistent with the other sets and are not used for evaluation.

Gaydon (11) and Herzberg (12) reported D_0° = 114.2 ± 6.9 (4.95 ± 0.3 eV) and 122.2 kcal/mol (5.3 eV), respectively. Using JANAF ΔH_F° values for Na(g) and F(g), we obtain ΔH_F° (NaF, g) = -70.5 ± 5.8 and -78.5 kcal/mol. Employing flame-photometric method, Bulewicz et al. (13) and Page and Sugden (14) derived D_0° = 121 ± 7 and 119 ± 120 kcal/mol for NaF(g), which lead to ΔH_F° (NaF, g) = -77.3 ± 7 and -75 to -76 kcal/mol.

Investigator	Temperature °K	Process	No. of Points	Second Law	Third Law	Drift
1. Wartenberg - Schulz (1921)	1669 - 1830	B	5	67.76 ± 0.11	59.90	-4.5 ± 0.1
2. Ruff et al. (1922)	1699 - 1974	B	14	64.07 ± 0.58	59.54	-2.4 ± 0.3
3. Niwa (1938)	1053 - 1112	A	5	63.18 ± 1.04	66.68	3.2 ± 1.0
4. Sense et al. (1957)	1208 - 1265	A	7	71.26 ± 0.63	68.25	-2.4 ± 0.5
5. Cantor - Blankenship (1958)	1274 - 1348	B	9	65.88 ± 0.76	61.14	-3.6 ± 0.6
6. Pugh - Barrow (1958)	1023 - 1166	A	7*	66.13	60.84	-3.6
7. Porter - Schoonmaker (1958)	1121	A	1	68.13	68.14	0.0
8. Entner - Neckel (1967)	1016 - 1236	A	6*	68.54 ± 0.10	67.74	-0.7 ± 0.1
* Data points calculated from a given total pressure equation.						
** Process A: NaF(c) = NaF(g); B: NaF(l) = NaF(g).						

Heat Capacity and Entropy

Veazey and Gordy (15) have measured the rotational transitions of NaF in the millimeter- and sub-millimeter-wave region with a high-resolution molecular-beam absorption spectrometer. The derived values of ω_e , $\omega_e x_e$, B_e , $B_e x_e$ and r_e are adopted here.

Using the molecular beam electric resonance method, Bauer and Lew (16) measured the transition between the $J = 0$ and $J = 1$ rotational levels of Na₂F₂ in the three lowest vibrational states. Radio-frequency transitions for Na₂F₂ have been observed by Hollowell et al. (19). Infrared spectra of NaF have been analyzed by Sneison and Pitzer (17), Ritchie and Lew (18), and Baikov and Vasilevskii (20). The molecular constants derived by the above authors are similar to the values adopted, except the value $\omega_e = 550 \text{ cm}^{-1}$ (17) which is different from the value 536.1 cm⁻¹ reported by Veazey and Gordy (15).

References

- H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921).
- O. Ruff, G. Schmidt, and S. Mugdan, Z. Anorg. Allgem. Chem. 123, 83 (1922).
- K. Aiba, J. Fac. Sci. Hokkaido Imp. Univ. Ser. III, 2, 201 (1938).
- S. Cantor and F. Blankenship, R. E. Boman, R. W. Stone, and R. B. Filbert, Jr., J. Phys. Chem. 61, 384 (1957).
- A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 577 (1958).
- R. F. Porter and R. C. Schoonmaker, J. Chem. Phys. 28, 1070 (1958).
- P. Entner and A. Neckel, Monatsh. Chem. 98, 1083 (1967).
- K. E. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956).
- A. G. Gaydon, "Infrared Spectra of Diatomic Molecules," Chapman and Hall Ltd., London, 1968.
- G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand Reinhold Co., New York, 1950.
- F. M. Page and T. M. Sugden, Nature 183, 1672 (1959).
- F. M. Page and W. Gordy, Phys. Rev. 138, A 1303 (1965).
- S. K. Veazey and H. Gordy, J. Phys. Chem. 67, 1461 (1963).
- A. Sneison and K. S. Pitzer, J. Phys. Chem. 62, 882 (1958).
- R. K. Ritchie and H. Lew, Can. J. Phys. 41, 1921 (1963).
- C. D. Hollowell, A. J. Hebert, and K. Street, Jr., J. Chem. Phys. 41, 3540 (1964).
- V. I. Baikov and K. P. Vasilevskii, Opt. Spectry, 22 198 (1967).

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1968

Sodium Fluoride (NaF)

(Ideal Gas) GF_N = 41.9882

T, °K	C _p	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _F	Log K _p
100	7.016	43.787	56.875	-2.205	-69.029	INFINITE
200	7.643	48.823	52.716	-1.509	-70.775	15.4679
298	8.178	51.993	51.093	-0.779	-72.472	79.1264
300	8.185	52.034	51.063	-0.815	-72.472	79.1264
400	8.494	54.435	52.308	-0.511	-70.317	53.951
500	8.674	56.351	52.932	-1.710	-70.403	33.5561
600	8.789	57.993	53.638	2.593	-70.866	26.409
700	8.866	59.383	54.352	3.466	-71.115	20.912
800	8.912	60.567	55.076	4.340	-71.215	16.741
900	8.972	61.587	55.712	5.251	-71.586	14.397
1000	9.010	62.484	56.344	6.150	-71.819	11.8025
1100	9.043	63.354	56.943	7.053	-72.059	10.596
1200	9.071	64.182	57.518	7.959	-72.318	9.5316
1300	9.095	64.975	58.060	8.776	-72.591	8.6059
1400	9.121	65.735	58.580	9.521	-72.831	7.8123
1500	9.144	66.475	59.047	10.691	-73.040	7.1435
1600	9.166	67.196	59.511	11.607	-73.218	6.5821
1700	9.186	67.892	59.955	12.524	-73.373	6.1205
1800	9.204	68.566	60.386	13.344	-73.512	5.7485
1900	9.224	69.224	60.795	14.164	-73.635	5.4485
2000	9.244	69.868	61.175	15.289	-73.745	5.2085
2100	9.263	70.501	61.550	16.215	-73.847	5.0285
2200	9.281	71.124	61.911	17.142	-73.944	4.8985
2300	9.297	71.738	62.266	18.068	-74.036	4.8085
2400	9.317	72.341	62.611	19.002	-74.124	4.7485
2500	9.335	72.934	62.948	19.934	-74.208	4.7085
2600	9.352	73.519	63.278	20.869	-74.288	4.6885
2700	9.370	74.094	63.603	21.805	-74.364	4.6785
2800	9.387	74.661	63.924	22.741	-74.436	4.6745
2900	9.404	75.221	64.241	23.676	-74.504	4.6745
3000	9.421	75.776	64.554	24.612	-74.568	4.6745
3100	9.438	76.327	64.864	25.546	-74.629	4.6745
3200	9.455	76.874	65.171	26.481	-74.686	4.6745
3300	9.472	77.417	65.476	27.415	-74.740	4.6745
3400	9.489	77.956	65.778	28.349	-74.791	4.6745
3500	9.506	78.491	66.077	29.283	-74.839	4.6745
3600	9.523	79.019	66.373	30.217	-74.884	4.6745
3700	9.539	79.542	66.667	31.151	-74.926	4.6745
3800	9.555	80.061	66.958	32.085	-74.965	4.6745
3900	9.572	80.576	67.246	33.019	-75.001	4.6745
4000	9.589	81.087	67.533	33.953	-75.034	4.6745
4100	9.606	81.594	67.818	34.887	-75.064	4.6745
4200	9.623	82.097	68.101	35.821	-75.091	4.6745
4300	9.639	82.596	68.382	36.755	-75.116	4.6745
4400	9.656	83.091	68.661	37.689	-75.139	4.6745
4500	9.672	83.582	68.938	38.623	-75.159	4.6745
4600	9.689	84.069	69.213	39.557	-75.176	4.6745
4700	9.705	84.552	69.486	40.491	-75.191	4.6745
4800	9.721	85.031	69.757	41.425	-75.204	4.6745
4900	9.736	85.506	70.026	42.359	-75.215	4.6745
5000	9.752	85.977	70.294	43.293	-75.224	4.6745
5100	9.771	86.444	70.561	44.227	-75.231	4.6745
5200	9.788	86.907	70.826	45.161	-75.236	4.6745
5300	9.804	87.366	71.091	46.095	-75.239	4.6745
5400	9.821	87.821	71.356	47.029	-75.240	4.6745
5500	9.837	88.272	71.621	47.963	-75.239	4.6745
5600	9.854	88.720	71.886	48.897	-75.236	4.6745
5700	9.870	89.165	72.151	49.831	-75.231	4.6745
5800	9.887	89.607	72.416	50.765	-75.224	4.6745
5900	9.903	89.956	72.681	51.699	-75.215	4.6745
6000	9.919	90.299	72.946	52.633	-75.204	4.6745

Fluorine Monoxide (F0)
(Ideal Gas)

GF_W = 34.998

T, °K	C _p ^o	S ^o gibbs/mol	-(G ^o -H ^o)/T kcal/mol	H ^o -H ^o 300 ΔH ^o	Log K _p
0	6.900	INFINITE	-	2.895	INFINITE
100	6.926	84.076	56.040	25.998	25.998
200	7.029	84.910	52.423	25.997	25.997
298	7.319	85.765	51.765	26.000	26.000
300	7.326	85.810	51.765	26.000	26.000
400	7.694	85.756	52.037	26.011	26.011
500	8.007	85.720	52.619	26.027	26.027
600	8.266	85.702	53.263	26.047	26.047
700	8.426	85.688	53.919	26.067	26.067
800	8.562	85.682	54.583	26.084	26.084
900	8.687	85.687	55.192	26.101	26.101
1000	8.790	85.704	55.774	26.116	26.116
1100	8.874	85.732	56.336	26.129	26.129
1200	8.945	85.761	56.875	26.141	26.141
1300	9.003	85.794	57.397	26.151	26.151
1400	9.055	85.837	57.894	26.160	26.160
1500	9.102	85.881	58.339	26.168	26.168
1600	9.135	85.928	58.783	26.173	26.173
1700	9.166	85.977	59.209	26.179	26.179
1800	9.193	86.026	59.617	26.181	26.181
1900	9.219	86.075	60.008	26.182	26.182
2000	9.244	86.124	60.384	26.182	26.182
2100	9.267	86.173	60.747	26.180	26.180
2200	9.289	86.222	61.096	26.175	26.175
2300	9.309	86.271	61.433	26.170	26.170
2400	9.328	86.320	61.756	26.162	26.162
2500	9.345	86.369	62.073	26.151	26.151
2600	9.360	86.418	62.378	26.139	26.139
2700	9.374	86.467	62.674	26.126	26.126
2800	9.386	86.516	62.961	26.110	26.110
2900	9.397	86.565	63.239	26.093	26.093
3000	9.408	86.614	63.510	26.073	26.073
3100	9.419	86.663	63.773	26.053	26.053
3200	9.429	86.712	64.029	26.030	26.030
3300	9.439	86.761	64.278	26.006	26.006
3400	9.449	86.810	64.522	25.980	25.980
3500	9.457	86.859	64.756	25.953	25.953
3600	9.464	86.908	64.990	25.925	25.925
3700	9.471	86.957	65.216	25.895	25.895
3800	9.478	87.006	65.437	25.865	25.865
3900	9.485	87.055	65.653	25.833	25.833
4000	9.512	87.104	65.865	25.800	25.800
4100	9.529	87.153	66.071	25.766	25.766
4200	9.547	87.202	66.274	25.732	25.732
4300	9.564	87.251	66.472	25.698	25.698
4400	9.581	87.300	66.667	25.664	25.664
4500	9.600	87.349	66.857	25.628	25.628
4600	9.618	87.398	67.044	25.589	25.589
4700	9.637	87.447	67.227	25.552	25.552
4800	9.656	87.496	67.406	25.516	25.516
4900	9.675	87.545	67.581	25.481	25.481
5000	9.694	87.594	67.758	25.442	25.442
5100	9.714	87.643	67.929	25.405	25.405
5200	9.733	87.692	68.096	25.368	25.368
5300	9.753	87.741	68.259	25.332	25.332
5400	9.773	87.790	68.418	25.298	25.298
5500	9.795	87.839	68.583	25.260	25.260
5600	9.816	87.888	68.741	25.224	25.224
5700	9.838	87.937	68.895	25.190	25.190
5800	9.860	87.986	69.046	25.157	25.157
5900	9.882	88.035	69.198	25.125	25.125
6000	9.905	88.084	69.349	25.090	25.090

Dec. 31, 1960; June 30, 1965; Dec. 31, 1966

FLUORINE MONOXIDE (F0)

(IDEAL GAS)

GF_W = 34.998

Ground State Configuration [2Π]
S_{298.15} = 51.77 ± 0.3 gibbs/mol
ΔH_F^o = [26 ± 10] kcal/mol
ΔH_F^o_{298.15} = [26 ± 10] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[4]
[29000]	[4]
$w_e x_e = [15]$ cm ⁻¹	$\sigma = 1$
$\alpha_e = [0.020]$ cm ⁻¹	$r_e = [1.30]$ Å
$w_e = 1056$ cm ⁻¹	
$B_e = [1.148]$ cm ⁻¹	

Heat of Formation

Several values have been proposed for the heat of formation of F0(g). V. H. Dibeler, R. M. Reese and J. L. Franklin, J. Chem. Phys. 27, 1296 (1957), obtained D₀(F0,g) = 24 kcal from electron impact studies. However, theoretical estimates give D₀ values in the range 45 - 56 kcal. W. C. Price, T. R. Pasmore and D. M. Roessler, Discussions Faraday Soc. 35, 207 (1963), estimated 52 kcal for D₀(F0,g).

From a consideration of the central bond energies in FNP and HNH with that in HOOH, using all JANAP values of 101, 109 and 50 kcal, we predict the bond dissociation energy in F0-OF to be 46 ± 4 kcal, which yields D₀(F0,g) = 51 ± 2 kcal. The average F-O bond dissociation energy in F₂O(g) is 49.8 ± 0.5 kcal. Also, since there is one less antibonding electron in F0 than in F₂, we should expect the F-O bond to be greater than that in F₂(38 kcal). Thus a median value of D₀(F0,g) = 51.4 ± 10 kcal is adopted here which leads to ΔH_F^o(F0) = 26 kcal/mol.

Heat Capacity and Entropy

The fundamental frequency is obtained by adding 2w_ex_e to the value reported by A. Arkell, R. R. Reinhard and L. P. Larson, J. Am. Chem. Soc. 87, 1016 (1965), from matrix isolation studies. The bond length was taken equal to that in the isoelectronic molecule O₂(g). The value of w_ex_e was obtained from the Morse potential function and the assumed dissociation energy. The rotational constant α_e was also estimated from the above parameters and the Morse potential curve. The 2Π ground state is that predicted by molecular orbital theory and the first excited state would also be 2Π. By analogy with the isoelectronic O₂⁻(g) states, the first excited level was estimated at 29000 cm⁻¹.

T, °K.	C _p	S° -(F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	7.000	INFINITE	INFINITE	2.468	-102.906	-102.906	INFINITE
100	7.009	49.337	64.127	1.080	-103.116	-103.116	256.717
200	10.109	55.558	69.887	1.069	-103.332	-104.275	113.491
298	11.585	59.887	74.902	1.069	-103.550	-104.682	76.730
300	11.608	59.958	74.987	1.071	-103.563	-104.689	76.733
400	12.618	63.447	80.356	1.236	-103.689	-105.049	57.393
500	13.267	66.337	81.271	2.553	-103.811	-105.374	46.057
600	13.690	68.796	82.326	3.492	-103.927	-105.672	38.400
700	13.975	70.811	83.466	4.674	-104.036	-105.946	32.490
800	14.173	72.809	84.646	6.074	-104.136	-106.207	28.017
900	14.315	74.487	85.488	8.009	-104.231	-106.452	25.852
1000	14.420	76.001	86.465	10.436	-104.317	-106.696	23.317
1100	14.500	77.279	87.395	10.492	-104.463	-106.910	21.240
1200	14.562	78.811	88.123	13.496	-104.589	-107.165	19.405
1300	14.611	80.126	88.926	15.357	-104.710	-107.248	16.741
1400	14.652	81.407	89.601	16.824	-104.824	-107.314	15.635
1500	14.688	82.834	91.222	18.294	-104.932	-107.364	14.665
1600	14.708	84.226	92.766	19.264	-105.036	-107.409	13.802
1700	14.730	85.591	94.261	21.260	-105.163	-107.422	13.052
1800	14.749	86.951	95.716	22.715	-105.287	-107.425	12.356
1900	14.766	88.348	97.433	24.715	-105.408	-107.425	11.727
2000	14.778	89.444	98.750	26.192	-105.521	-107.425	11.147
2100	14.789	90.567	100.464	28.671	-105.659	-107.413	10.618
2200	14.799	91.716	102.166	28.311	-105.787	-107.407	10.151
2300	14.808	92.214	103.765	28.311	-105.907	-107.407	9.660
2400	14.816	92.816	105.268	30.117	-106.016	-107.407	9.280
2500	14.823	93.444	106.812	31.594	-106.168	-107.407	8.901
2600	14.829	94.031	107.309	33.076	-106.293	-105.896	8.522
2700	14.834	94.571	107.757	34.076	-106.368	-105.852	8.147
2800	14.839	95.070	108.398	34.984	-106.444	-105.852	7.766
2900	14.844	95.531	108.710	35.527	-106.568	-105.852	7.386
3000	14.848	96.153	109.150	36.012	-106.688	-105.852	7.016
3100	14.851	96.651	109.577	40.497	-106.727	-104.427	7.302
3200	14.854	97.051	110.000	40.497	-106.727	-104.427	7.302
3300	14.857	97.570	110.398	41.668	-106.778	-103.779	6.819
3400	14.860	98.031	110.792	44.984	-106.815	-103.444	6.649
3500	14.863	98.444	111.175	46.440	-106.831	-103.098	6.437
3600	14.865	98.853	111.550	47.926	-106.889	-101.299	6.169
3700	14.867	99.267	111.927	50.000	-106.920	-101.299	5.771
3800	14.869	99.667	112.300	52.387	-107.062	-101.928	5.120
3900	14.871	99.853	112.620	52.387	-107.062	-101.928	4.882
4000	14.872	100.429	113.061	51.484	-107.418	-88.255	4.482
4100	14.874	100.797	113.294	55.301	-107.700	-88.970	4.529
4200	14.875	101.155	113.620	56.848	-107.716	-81.678	4.250
4300	14.877	101.516	113.946	57.848	-107.716	-78.063	3.798
4400	14.878	101.877	114.271	58.426	-107.716	-74.746	3.484
4500	14.879	102.151	114.597	61.312	-107.716	-71.740	3.484
4600	14.880	102.426	114.922	62.400	-107.716	-68.408	3.250
4700	14.881	102.701	115.247	64.258	-107.716	-63.069	3.026
4800	14.882	103.026	115.572	67.264	-107.716	-58.162	2.707
4900	14.883	103.351	115.897	68.752	-107.716	-53.691	2.603
5000	14.884	103.676	116.222	68.752	-107.716	-50.962	2.464
5100	14.885	103.944	116.547	70.261	-107.716	-48.167	2.232
5200	14.885	104.212	116.872	73.268	-107.716	-43.751	2.007
5300	14.886	104.480	117.200	74.787	-107.716	-40.163	1.782
5400	14.887	104.895	117.600	74.787	-107.716	-41.613	1.576
5500	14.887	105.168	117.914	76.195	-107.716	-37.991	1.510
5600	14.888	105.444	118.239	76.195	-107.716	-34.567	1.300
5700	14.889	105.720	118.564	77.684	-107.716	-31.567	1.104
5800	14.889	106.000	118.889	80.632	-107.716	-28.567	0.914
5900	14.890	106.276	119.214	82.151	-107.716	-26.227	0.736
6000	14.890	106.551	119.539	83.660	-107.716	-24.227	0.586

Sept. 30, 1963

FOTI

MOL. WT. = 82.9

(IDEAL GAS)

TITANIUM OXIDE FLUORIDE (TiOF)

 $\Delta H_f^\circ = -103.0$ kcal. mole⁻¹ $\Delta H_f^\circ = -103.5$ kcal. mole⁻¹Point Group [C_{2v}]S°_{298.15} = [89.837] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

 ω_e , cm.⁻¹

[800] (1)

[300] (2)

[740] (1)

Bond Distances: Ti-O = [1.62] Å Ti-F = [1.74] Å

Bond Angle: O-Ti-F = [180°]

σ = 1

Rotational Constant: B₀ = [0.1705] cm.⁻¹

Heat of Formation

ΔH_f° 0 was estimated as -103 kcal. mole⁻¹ by J. S. Oordon, AstroSystems, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. ΔH_f° 298.15 was then calculated.

Heat Capacity and Entropy

Molecular constants were estimated by J. S. Oordon, loc. cit. Principal moment was 16.419 X 10⁻³⁹ g. cm.²

Monofluorine Dioxide (F₀₂)
(Ideal Gas) GFW = 50.9972

T, °K	C _p ^a	S ^b	-(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	ΔH _f ^c	Log K _p
0	∞	∞	∞	∞	∞	∞
100	13.242	51.736	70.617	2.888	3.442	INFINITE
200	9.611	57.864	62.864	1.888	4.201	9.181
298	10.611	61.903	61.903	0.906	5.272	5.761
300	10.626	61.968	61.903	0.920	6.376	4.674
400	11.319	65.125	62.329	1.119	3.003	6.397
500	11.843	67.710	63.154	2.278	3.027	4.660
600	12.247	69.807	64.101	3.483	3.062	3.785
700	12.550	71.512	66.021	4.703	3.083	3.563
800	12.800	73.051	67.882	5.923	3.103	3.371
900	12.986	74.451	69.694	7.143	3.117	3.186
1000	13.132	75.747	71.459	8.363	3.121	3.108
1100	13.248	76.955	73.185	9.583	3.245	3.044
1200	13.340	78.082	74.872	10.798	3.286	2.990
1300	13.416	79.132	76.521	12.000	3.308	2.944
1400	13.478	80.108	78.132	13.192	3.335	2.904
1500	13.529	81.012	79.697	14.375	3.359	2.869
1600	13.572	81.846	81.223	15.551	3.380	2.839
1700	13.608	82.608	82.713	16.726	3.400	2.812
1800	13.639	83.300	84.169	17.892	3.419	2.786
1900	13.665	83.925	85.596	19.049	3.437	2.765
2000	13.688	84.494	86.997	20.198	3.453	2.745
2100	13.708	85.006	88.368	21.339	3.468	2.728
2200	13.725	85.464	89.709	22.472	3.482	2.711
2300	13.740	85.870	91.021	23.600	3.495	2.694
2400	13.754	86.235	92.305	24.722	3.507	2.677
2500	13.766	86.561	93.564	25.839	3.518	2.660
2600	13.776	86.846	94.798	26.951	3.528	2.643
2700	13.784	87.091	96.008	28.058	3.537	2.626
2800	13.790	87.298	97.194	29.160	3.545	2.610
2900	13.802	87.466	98.356	30.258	3.552	2.593
3000	13.809	87.601	99.494	31.352	3.558	2.577
3100	13.815	87.716	100.608	32.442	3.563	2.561
3200	13.821	87.812	101.698	33.528	3.567	2.545
3300	13.826	87.890	102.764	34.610	3.570	2.529
3400	13.831	87.951	103.808	35.688	3.573	2.513
3500	13.835	88.000	104.831	36.762	3.575	2.497
3600	13.839	88.036	105.835	37.832	3.577	2.481
3700	13.843	88.061	106.819	38.898	3.578	2.465
3800	13.846	88.078	107.784	39.960	3.579	2.449
3900	13.849	88.086	108.730	40.998	3.580	2.433
4000	13.853	88.086	109.657	42.022	3.581	2.417
4100	13.856	88.078	110.567	43.042	3.582	2.401
4200	13.858	88.061	111.460	44.049	3.583	2.385
4300	13.860	88.036	112.337	45.043	3.584	2.369
4400	13.863	88.000	113.198	46.024	3.585	2.353
4500	13.865	87.955	114.044	47.000	3.586	2.337
4600	13.867	87.902	114.875	47.962	3.587	2.321
4700	13.868	87.841	115.692	48.919	3.588	2.305
4800	13.870	87.772	116.495	49.872	3.589	2.289
4900	13.872	87.700	117.284	50.821	3.590	2.273
5000	13.873	87.625	118.059	51.756	3.591	2.257
5100	13.875	87.548	118.821	52.677	3.592	2.241
5200	13.876	87.468	119.570	53.584	3.593	2.225
5300	13.877	87.384	120.305	54.478	3.594	2.209
5400	13.878	87.297	121.027	55.359	3.595	2.193
5500	13.880	87.207	121.737	56.227	3.596	2.177
5600	13.881	87.114	122.434	57.082	3.597	2.161
5700	13.882	87.018	123.118	57.925	3.598	2.145
5800	13.883	86.920	123.789	58.756	3.599	2.129
5900	13.884	86.819	124.447	59.575	3.600	2.113
6000	13.884	86.716	125.092	60.382	3.601	2.097

Sept. 30, 1966

F₀₂

MONOFLUORINE DIOXIDE (F₀₂) (IDEAL GAS) OPW = 50.9972

Point Group C_{2v}
S_{298.15} = 61.9 gibbs/mol
Ground State Quantum Weight = 2

ΔH_f⁰ = 3.4 ± 5 kcal/mol
ΔH_f^{298.15} = 3.0 ± 5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	
1495.0 (1)	
584.5 (1)	
376.0 (1)	

Bond Distance: O-O = 1.22 Å O-P = 1.58 Å

Bond Angle: O-O-P = 109.5°

Product of the Moments of Inertia: I_AI_BI_C = 7.7504 x 10⁻¹¹⁶ g³cm⁶

G° = 1

Heat of Formation.

The heat of formation for F₂O₂(g) is unavailable in the literature. Based on a kinetic study of the thermal decomposition of F₂O₂(g) reported by R. J. Schumacher and P. Priach, Z. physik. Chem. **B24**, 332 (1934), the enthalpy change for the reaction F₂O₂(g) = F(g) + O₂(g) was estimated to be +17.3 kcal/mol by J. B. Levy and B. K. Kaaley, J. Phys. Chem. **69**, 408 (1965), assuming that the activation energy for the reverse reaction is negligible. From this data the value of ΔH_f^{298.15}(F₂O₂, g) was calculated as +3.2 kcal/mol, using ΔH_f^{298.15} = +4.73 kcal/mol for F₂O₂(g) determined calorimetrically by A. D. Kirshenbaum, A. V. Grosse and J. G. Aston, J. Am. Chem. Soc. **81**, 6398 (1959).

Based on the assumption that the enthalpy change for the reaction F₂O₂(g) = F(g) + O₂(g) is 16.5 kcal/mol, which is half of the enthalpy change for the reaction F₂O₂(g) = 2F(g) + O₂(g), the heat of formation (ΔH_f^{298.15}) for F₂O₂(g) was derived as +2.4 kcal/mol.

The value of ΔH_f^{298.15}(F₂O₂, g) adopted is 3 ± 5 kcal/mol.

Heat Capacity and Entropy.

The vibrational frequencies for F₂O₂(g) were assumed to be the same as those obtained from matrix isolation by P. N. Noble and G. C. Pimentel, J. Chem. Phys. **44**, 3641 (1966). These authors have observed two more frequencies for isotopically substituted F₂O₂ and combined them with those observed by R. D. Spratley, J. J. Turner and G. C. Pimentel, J. Chem. Phys. **44**, 2063 (1966), and performed a normal coordinate analysis. The results confirm the fact that the bond distances and angles in F₂O₂ are essentially the same as those reported for F₂O₂(g) by R. H. Jackson, J. Chem. Soc., 4585 (1962). The same molecular structure for F₂O₂ was also deduced from electron spin resonance and electron paramagnetic resonance data reported by R. W. Fassenden and R. H. Schuler, J. Chem. Phys. **44**, 434 (1966) and P. H. Kasal and A. D. Kirshenbaum, J. Am. Chem. Soc. **87**, 3069 (1965), respectively. Hence this molecular structure was adopted. Two vibrational frequencies, ν₁ and ν₃, for F₂O₂ molecule were also observed by A. Arkell, J. Am. Chem. Soc. **87**, 4057 (1965).

The three principal moments of inertia are: I_A = 1.1103 x 10⁻³⁹, I_B = 7.8182 x 10⁻³⁹ and I_C = 8.9285 x 10⁻³⁹ g cm².

F₀₂

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 49.975

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0	0.000	0.000	INFINITE	-2.117	-14.200	-14.200	-14.200	INFINITE
100	6.959	45.962	60.183	-1.422	-13.944	-10.356	-35.743	35.743
200	7.135	50.519	54.421	-0.770	-13.910	-18.795	-40.538	40.538
298	7.257	53.744	53.744	0.000	-14.000	-21.117	-45.322	45.322
300	7.266	53.791	53.744	0.014	-14.002	-21.221	-45.459	45.459
400	7.956	56.023	54.046	0.791	-14.143	-23.606	-48.897	48.897
500	8.277	57.831	54.628	1.601	-14.307	-25.955	-51.344	51.344
600	8.430	59.350	55.201	2.435	-14.490	-28.248	-53.896	53.896
700	8.566	60.660	55.697	3.286	-14.698	-30.568	-56.537	56.537
800	8.664	61.811	56.027	4.147	-14.933	-32.810	-59.250	59.250
900	8.737	62.836	57.261	5.017	-15.197	-34.984	-62.037	62.037
1000	8.794	63.760	57.865	5.894	-15.494	-37.000	-64.896	64.896
1100	8.849	64.600	58.440	6.776	-15.827	-38.938	-67.824	67.824
1200	8.876	65.371	58.986	7.662	-16.190	-40.802	-70.824	70.824
1300	8.907	66.082	59.505	8.551	-16.582	-42.692	-73.896	73.896
1400	8.933	66.743	59.999	9.443	-17.003	-44.608	-77.037	77.037
1500	8.956	67.361	60.469	10.337	-17.454	-46.550	-80.248	80.248
1600	8.976	67.930	60.918	11.234	-17.936	-48.518	-83.530	83.530
1700	8.994	68.484	61.347	12.132	-18.449	-50.512	-86.884	86.884
1800	9.011	69.008	61.758	13.033	-18.994	-52.532	-90.312	90.312
1900	9.026	69.486	62.152	13.935	-19.572	-54.576	-93.812	93.812
2000	9.041	69.949	62.530	14.838	-20.184	-56.654	-97.384	97.384
2100	9.054	70.391	62.894	15.743	-20.830	-58.766	-101.024	101.024
2200	9.067	70.811	63.244	16.650	-21.512	-60.912	-104.732	104.732
2300	9.079	71.216	63.583	17.569	-22.230	-63.092	-108.508	108.508
2400	9.091	71.602	63.909	18.495	-22.984	-65.306	-112.352	112.352
2500	9.102	71.974	64.224	19.434	-23.774	-67.554	-116.264	116.264
2600	9.113	72.331	64.529	20.385	-24.600	-69.836	-120.244	120.244
2700	9.123	72.677	64.824	21.347	-25.462	-72.152	-124.292	124.292
2800	9.133	73.007	65.111	22.310	-26.360	-74.500	-128.408	128.408
2900	9.143	73.328	65.389	23.274	-27.294	-76.880	-132.592	132.592
3000	9.153	73.638	65.658	24.238	-28.264	-79.292	-136.844	136.844
3100	9.163	73.936	65.921	25.203	-29.270	-81.732	-141.164	141.164
3200	9.172	74.220	66.179	26.168	-30.312	-84.200	-145.552	145.552
3300	9.181	74.511	66.424	27.134	-31.390	-86.696	-150.008	150.008
3400	9.191	74.786	66.666	28.100	-32.504	-89.220	-154.532	154.532
3500	9.200	75.052	66.902	29.067	-33.654	-91.772	-159.124	159.124
3600	9.209	75.312	67.132	30.034	-34.840	-94.352	-163.784	163.784
3700	9.218	75.566	67.356	31.000	-36.062	-96.964	-168.512	168.512
3800	9.227	75.810	67.576	31.966	-37.320	-99.600	-173.308	173.308
3900	9.235	76.050	67.790	32.932	-38.614	-102.260	-178.172	178.172
4000	9.244	76.284	67.999	33.898	-39.944	-105.348	-183.104	183.104
4100	9.253	76.512	68.204	34.862	-41.310	-108.464	-188.112	188.112
4200	9.261	76.733	68.404	35.826	-42.712	-111.608	-193.188	193.188
4300	9.270	76.953	68.601	36.790	-44.154	-114.880	-198.332	198.332
4400	9.278	77.166	68.793	37.754	-45.626	-118.180	-203.544	203.544
4500	9.287	77.375	68.981	38.718	-47.138	-121.508	-208.824	208.824
4600	9.295	77.579	69.166	39.682	-48.690	-124.864	-214.172	214.172
4700	9.303	77.777	69.346	40.646	-50.282	-128.248	-219.588	219.588
4800	9.312	77.975	69.525	41.610	-51.914	-131.660	-225.072	225.072
4900	9.320	78.167	69.699	42.574	-53.586	-135.100	-230.624	230.624
5000	9.329	78.356	69.871	43.538	-55.298	-138.572	-236.248	236.248
5100	9.337	78.540	70.039	44.502	-57.050	-142.076	-241.944	241.944
5200	9.345	78.720	70.202	45.466	-58.842	-145.612	-247.712	247.712
5300	9.353	78.896	70.360	46.430	-60.674	-149.180	-253.552	253.552
5400	9.362	79.075	70.526	47.394	-62.546	-152.780	-259.464	259.464
5500	9.370	79.247	70.683	48.358	-64.458	-156.408	-265.448	265.448
5600	9.378	79.415	70.838	49.322	-66.410	-160.064	-271.496	271.496
5700	9.386	79.588	70.988	50.286	-68.402	-163.748	-277.608	277.608
5800	9.394	79.745	71.139	51.250	-70.434	-167.460	-283.784	283.784
5900	9.403	79.905	71.286	52.214	-72.506	-171.200	-289.924	289.924
6000	9.411	80.064	71.431	53.178	-74.618	-174.968	-296.136	296.136

Dec. 31, 1960; Sept. 30, 1962

Phosphorus Monofluoride (PF) (Ideal Gas)

Mol. Wt. = 49.975

 $\Delta H_f^\circ 298.15 = -14 \pm 3 \text{ kcal. mole}^{-1}$ $S^\circ 298.15 = 53.7 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ Ground State Configuration $\sum$

Electronic Level and Multiplicity

$$\frac{\epsilon, \text{ cm.}^{-1}}{\epsilon_1}$$

$$\frac{0}{3}$$

 $\omega_e = 846.75 \text{ cm.}^{-1}$ $\omega_e x_e = 4.499 \text{ cm.}^{-1}$ $B_e = 0.5665 \text{ cm.}^{-1}$ $d_e = 0.00456 \text{ cm.}^{-1}$ $r_e = 1.590 \text{ \AA}$ $\sigma = 1$

Heat of Formation. $\Delta H_f^\circ 298.15$ was derived from a D_0° calculated with spectroscopic constants reported by A. E. Douglas and M. Prackowiak, Can. J. Phys. 40, 832 (1962). The D_0° value was calculated using the dissociation and spectroscopic relations given by O. Herzberg in "Spectra of Diatomic Molecules", D. van Nostrand Co., N. Y., 2nd Ed. (1950) pages 93 and 100. If the PF molecule dissociates to the ground state atoms, $P(^3S_{3/2}) + F(^2P_{3/2})$, the corresponding $\Delta H_f^\circ 298.15$ is $-15 \pm 3 \text{ kcal. mole}^{-1}$. If the dissociation is to the phosphorus ground state and the excited fluorine state, $P(^4S_{3/2}) + F(^2P_{1/2})$, the corresponding $\Delta H_f^\circ 298.15$ is $-14 \pm 3 \text{ kcal. mole}^{-1}$. The dissociation to an excited $F(^2P_{1/2})$ atom was assumed to obtain the selected $\Delta H_f^\circ 298.15 = -14 \pm 3 \text{ kcal. mole}^{-1}$.

The heat of formation was estimated to be $-17 \text{ kcal. mole}^{-1}$ by J. S. Gordon, "Thermodynamic Data for Combustion Products", January, 1960, Thiokol Chemical Corp. This estimate when changed from white(α) to red(V) phosphorus reference state ($-13 \text{ kcal. mole}^{-1}$) agrees within uncertainty limits with the derived $\Delta H_f^\circ 298.15$ values.

Heat Capacity and Entropy. The molecular constants were reported by Douglas and Prackowiak (loc. cit.). They photographed and analyzed the electronic spectra of PF in the emission spectrum of a discharge through a mixture of PF_3 and He.

Phosphorus Sulfide Fluoride (PSF)
(Ideal Gas) Mol. Wt. = 82.041 INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH°	ΔF°	Log K _p
0	8.155	56.356	7.702	-	35.564	-	35.564	1.671
100	8.165	56.356	7.702	-	35.564	-	35.564	1.671
200	8.171	56.356	7.702	-	35.564	-	35.564	1.671
250	8.171	56.356	7.702	-	35.564	-	35.564	1.671
300	8.171	56.356	7.702	-	35.564	-	35.564	1.671
350	8.171	56.356	7.702	-	35.564	-	35.564	1.671
400	8.171	56.356	7.702	-	35.564	-	35.564	1.671
450	8.171	56.356	7.702	-	35.564	-	35.564	1.671
500	8.171	56.356	7.702	-	35.564	-	35.564	1.671
550	8.171	56.356	7.702	-	35.564	-	35.564	1.671
600	8.171	56.356	7.702	-	35.564	-	35.564	1.671
650	8.171	56.356	7.702	-	35.564	-	35.564	1.671
700	8.171	56.356	7.702	-	35.564	-	35.564	1.671
750	8.171	56.356	7.702	-	35.564	-	35.564	1.671
800	8.171	56.356	7.702	-	35.564	-	35.564	1.671
850	8.171	56.356	7.702	-	35.564	-	35.564	1.671
900	8.171	56.356	7.702	-	35.564	-	35.564	1.671
950	8.171	56.356	7.702	-	35.564	-	35.564	1.671
1000	8.171	56.356	7.702	-	35.564	-	35.564	1.671
1100	8.171	56.356	7.702	-	35.564	-	35.564	1.671
1200	8.171	56.356	7.702	-	35.564	-	35.564	1.671
1300	8.171	56.356	7.702	-	35.564	-	35.564	1.671
1400	8.171	56.356	7.702	-	35.564	-	35.564	1.671
1500	8.171	56.356	7.702	-	35.564	-	35.564	1.671
1600	8.171	56.356	7.702	-	35.564	-	35.564	1.671
1700	8.171	56.356	7.702	-	35.564	-	35.564	1.671
1800	8.171	56.356	7.702	-	35.564	-	35.564	1.671
1900	8.171	56.356	7.702	-	35.564	-	35.564	1.671
2000	8.171	56.356	7.702	-	35.564	-	35.564	1.671
2100	8.171	56.356	7.702	-	35.564	-	35.564	1.671
2200	8.171	56.356	7.702	-	35.564	-	35.564	1.671
2300	8.171	56.356	7.702	-	35.564	-	35.564	1.671
2400	8.171	56.356	7.702	-	35.564	-	35.564	1.671
2500	8.171	56.356	7.702	-	35.564	-	35.564	1.671
2600	8.171	56.356	7.702	-	35.564	-	35.564	1.671
2700	8.171	56.356	7.702	-	35.564	-	35.564	1.671
2800	8.171	56.356	7.702	-	35.564	-	35.564	1.671
2900	8.171	56.356	7.702	-	35.564	-	35.564	1.671
3000	8.171	56.356	7.702	-	35.564	-	35.564	1.671
3100	8.171	56.356	7.702	-	35.564	-	35.564	1.671
3200	8.171	56.356	7.702	-	35.564	-	35.564	1.671
3300	8.171	56.356	7.702	-	35.564	-	35.564	1.671
3400	8.171	56.356	7.702	-	35.564	-	35.564	1.671
3500	8.171	56.356	7.702	-	35.564	-	35.564	1.671
3600	8.171	56.356	7.702	-	35.564	-	35.564	1.671
3700	8.171	56.356	7.702	-	35.564	-	35.564	1.671
3800	8.171	56.356	7.702	-	35.564	-	35.564	1.671
3900	8.171	56.356	7.702	-	35.564	-	35.564	1.671
4000	8.171	56.356	7.702	-	35.564	-	35.564	1.671
4100	8.171	56.356	7.702	-	35.564	-	35.564	1.671
4200	8.171	56.356	7.702	-	35.564	-	35.564	1.671
4300	8.171	56.356	7.702	-	35.564	-	35.564	1.671
4400	8.171	56.356	7.702	-	35.564	-	35.564	1.671
4500	8.171	56.356	7.702	-	35.564	-	35.564	1.671
4600	8.171	56.356	7.702	-	35.564	-	35.564	1.671
4700	8.171	56.356	7.702	-	35.564	-	35.564	1.671
4800	8.171	56.356	7.702	-	35.564	-	35.564	1.671
4900	8.171	56.356	7.702	-	35.564	-	35.564	1.671
5000	8.171	56.356	7.702	-	35.564	-	35.564	1.671
5100	8.171	56.356	7.702	-	35.564	-	35.564	1.671
5200	8.171	56.356	7.702	-	35.564	-	35.564	1.671
5300	8.171	56.356	7.702	-	35.564	-	35.564	1.671
5400	8.171	56.356	7.702	-	35.564	-	35.564	1.671
5500	8.171	56.356	7.702	-	35.564	-	35.564	1.671
5600	8.171	56.356	7.702	-	35.564	-	35.564	1.671
5700	8.171	56.356	7.702	-	35.564	-	35.564	1.671
5800	8.171	56.356	7.702	-	35.564	-	35.564	1.671
5900	8.171	56.356	7.702	-	35.564	-	35.564	1.671
6000	8.171	56.356	7.702	-	35.564	-	35.564	1.671

Dec. 31, 1960; Sept. 30, 1962

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.00	INFINITE	-2.215	8.516	-	-	INFINITE
100	7.033	51.377	65.466	-1.619	8.590	-10.813	-10.813	14.149
200	7.403	56.444	60.768	-1.184	8.809	-12.949	-12.949	10.950
298	8.224	59.627	59.627	-0.000	9.000	-14.939	-14.939	10.909
300	8.231	59.678	59.677	+0.015	9.004	-14.976	-14.976	10.909
400	8.259	59.954	59.954	+0.584	9.202	-16.936	-16.936	9.253
500	8.280	60.008	60.008	+1.715	9.416	-18.847	-18.847	8.236
600	8.281	65.601	61.287	+4.588	9.650	-20.710	-20.710	7.543
700	8.849	66.960	62.003	+3.470	11.064	-22.343	-22.343	6.975
800	9.899	68.145	62.698	+4.357	11.331	-23.936	-23.936	6.539
900	10.833	69.135	63.363	+5.249	11.591	-25.488	-25.488	6.191
1000	9.903	70.138	63.994	+6.144	11.844	-27.008	-27.008	5.907
1100	9.997	70.994	64.592	7.043	12.091	-28.535	-28.535	5.669
1200	9.024	71.778	65.159	7.944	12.329	-30.018	-30.018	5.467
1300	9.052	72.502	65.696	8.847	12.563	-31.482	-31.482	5.292
1400	9.081	73.174	66.206	9.754	12.795	-32.930	-32.930	5.140
1500	9.113	73.801	66.692	10.664	13.025	-34.358	-34.358	5.006
1600	9.149	74.391	67.155	11.577	13.256	-35.774	-35.774	4.886
1700	9.188	74.946	67.597	12.494	13.487	-37.173	-37.173	4.779
1800	9.230	75.473	68.020	13.415	13.721	-38.562	-38.562	4.682
1900	9.274	75.974	68.426	14.340	13.956	-39.936	-39.936	4.593
2000	9.323	76.450	68.815	15.270	14.193	-41.296	-41.296	4.512
2100	9.373	76.906	69.190	16.204	14.431	-42.643	-42.643	4.437
2200	9.424	77.343	69.550	17.144	14.670	-43.978	-43.978	4.367
2300	9.477	77.763	69.898	18.089	14.911	-45.303	-45.303	4.300
2400	9.532	78.168	70.236	19.040	15.154	-46.618	-46.618	4.234
2500	9.582	78.558	70.560	19.995	15.399	-47.923	-47.923	4.168
3000	9.635	78.935	70.875	20.956	15.646	-49.218	-49.218	4.103
3100	9.686	79.299	71.183	21.922	15.894	-50.503	-50.503	4.037
3200	9.737	79.652	71.476	22.893	16.143	-51.778	-51.778	3.971
3300	9.789	79.995	71.764	23.866	16.393	-53.043	-53.043	3.905
3400	9.833	80.327	72.044	24.850	16.644	-54.298	-54.298	3.839
3500	9.878	80.651	72.316	25.836	16.896	-55.543	-55.543	3.773
3600	9.921	80.965	72.582	26.826	17.149	-56.778	-56.778	3.707
3700	9.962	81.271	72.840	27.820	17.403	-58.003	-58.003	3.641
3800	10.001	81.569	73.093	28.818	17.658	-59.218	-59.218	3.575
3900	10.038	81.859	73.339	29.820	17.914	-60.423	-60.423	3.509
4000	10.072	82.142	73.580	30.826	18.171	-61.618	-61.618	3.443
4100	10.103	82.419	73.815	31.834	18.429	-62.803	-62.803	3.377
4200	10.134	82.689	74.045	32.846	18.687	-63.978	-63.978	3.311
4300	10.163	82.952	74.270	33.861	18.946	-65.143	-65.143	3.245
4400	10.189	83.210	74.490	34.879	19.205	-66.298	-66.298	3.179
4500	10.213	83.462	74.706	35.899	19.465	-67.443	-67.443	3.113
4600	10.235	83.708	74.917	36.921	19.725	-68.578	-68.578	3.047
4700	10.256	83.949	75.125	37.946	19.986	-69.703	-69.703	2.981
4800	10.275	84.185	75.328	38.972	20.247	-70.818	-70.818	2.915
4900	10.292	84.416	75.527	40.001	20.509	-71.923	-71.923	2.849
5000	10.308	84.643	75.723	41.031	20.771	-73.018	-73.018	2.783
5100	10.323	84.865	75.915	42.062	21.034	-74.103	-74.103	2.717
5200	10.337	85.092	76.104	43.095	21.297	-75.178	-75.178	2.651
5300	10.349	85.295	76.289	44.130	21.561	-76.243	-76.243	2.585
5400	10.360	85.505	76.472	45.165	21.825	-77.298	-77.298	2.519
5500	10.370	85.710	76.651	46.202	22.090	-78.343	-78.343	2.453
5600	10.379	85.911	76.827	47.239	22.355	-79.378	-79.378	2.387
5700	10.388	86.109	77.000	48.278	22.620	-80.403	-80.403	2.321
5800	10.396	86.303	77.171	49.317	22.885	-81.418	-81.418	2.255
5900	10.403	86.494	77.338	50.357	23.150	-82.423	-82.423	2.189
6000	10.409	86.682	77.504	51.397	23.415	-83.418	-83.418	2.123
6100	10.415	86.866	77.666	52.438	23.680	-84.403	-84.403	2.057
6200	10.420	87.047	77.826	53.480	23.945	-85.378	-85.378	1.991
6300	10.425	87.225	77.984	54.522	24.210	-86.343	-86.343	1.925
6400	10.429	87.401	78.140	55.565	24.475	-87.298	-87.298	1.859

June 30, 1962

Lead Monofluoride (PbF) (Ideal Gas)

Mol. Wt. = 226.21

 ΔH_f^0 298.15 = -9.0 ± 8.2 kcal. mole⁻¹ $S_{298.15}^0$ = 59.627 cal. deg.⁻¹ mole⁻¹Ground State Configuration $^2\Pi$

Electronic Levels and Multiplicities

ϵ , cm. ⁻¹	E_1
0	2
8266	2

 $\omega_e = 507.2$ cm.⁻¹ $\omega_e x_e = 2.30$ cm.⁻¹ $B_e = [0.2397]$ cm.⁻¹ $\alpha_e = [0.0017]$ cm.⁻¹ $\sigma = 1$

Heat of Formation. ΔH_f^0 298.15 was calculated from the dissociation energy of PbF(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ϵ , ω_e , and $\omega_e x_e$ were given by G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950. B_e and α_e were estimated by J. S. Gordon, Astrosystems, Inc., private communication, May, 1962.

T, °K	Cp	gibbs/mol S°	(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	6.000	INFINITE	INFINITE	2.208	16.001	16.001	INFINITE
100	7.602	56.692	56.692	0.16	16.002	16.002	22.950
200	7.602	56.692	56.692	0.00	16.000	16.000	17.223
298	8.466	56.692	56.692	0.16	16.002	23.543	17.151
300	8.461	56.744	56.692	0.00	16.123	26.034	15.256
400	9.156	57.279	57.033	1.890	16.231	26.394	12.459
500	9.636	61.377	57.678	1.840	16.231	30.950	11.273
600	9.942	63.163	58.464	2.820	16.333	33.377	10.421
700	10.128	64.711	59.248	3.624	16.440	35.769	9.777
800	10.236	66.071	60.018	4.843	16.564	38.163	9.272
900	10.298	67.281	60.759	5.870	16.711	40.350	8.864
1000	10.334	68.386	61.466	6.702	16.866	42.917	8.527
1100	10.357	69.354	62.139	7.436	17.086	45.218	8.235
1200	10.373	70.256	62.779	8.073	18.250	47.460	7.979
1300	10.387	71.087	63.386	10.011	18.378	49.693	7.757
1400	10.401	71.857	63.964	11.050	18.521	51.913	7.564
1500	10.417	72.575	64.514	12.091	18.680	54.122	7.393
1600	10.433	73.248	65.039	13.134	18.858	56.508	7.104
1700	10.450	73.881	65.541	14.178	19.056	60.681	6.850
1800	10.469	74.479	66.021	15.224	19.276	62.662	6.607
1900	10.487	75.045	66.481	16.271	19.518	64.599	6.400
2000	10.506	75.584	66.923	17.321	24.229	67.400	6.221
2100	10.525	76.097	67.348	18.373	24.493	69.834	5.863
2200	10.543	76.587	67.757	19.426	24.756	71.924	5.803
2300	10.561	77.056	68.151	20.481	25.018	73.928	5.746
2400	10.577	77.506	68.531	21.538	25.280	75.856	5.692
2500	10.593	77.938	68.899	22.597	25.542	77.696	5.640
2600	10.607	78.354	69.255	23.657	25.804	79.457	5.593
2700	10.620	78.754	69.599	24.718	26.065	81.346	5.546
2800	10.633	79.141	69.933	25.781	26.326	83.157	5.498
2900	10.644	79.514	70.257	26.844	26.587	84.963	5.451
3000	10.654	79.875	70.572	27.909	26.849	86.770	5.404
3100	10.662	80.224	70.877	28.975	27.110	88.584	5.357
3200	10.670	80.563	71.175	30.042	27.372	90.404	5.310
3300	10.677	80.891	71.464	31.109	27.634	92.239	5.263
3400	10.683	81.210	71.746	32.177	27.896	94.081	5.216
3500	10.689	81.520	72.021	33.246	28.160	95.935	5.169
3600	10.694	81.821	72.289	34.315	130.049	97.804	5.122
3700	10.698	82.114	72.551	35.385	130.285	99.684	5.075
3800	10.701	82.400	72.806	36.455	130.535	101.574	5.028
3900	10.705	82.678	73.056	37.525	130.800	103.474	4.981
4000	10.707	82.949	73.300	38.595	131.077	105.384	4.934
4100	10.710	83.213	73.538	39.666	131.369	107.304	4.887
4200	10.712	83.471	73.772	40.737	131.673	109.234	4.840
4300	10.714	83.723	74.000	41.809	131.990	111.174	4.793
4400	10.717	83.970	74.224	42.880	132.319	113.124	4.746
4500	10.718	84.211	74.443	43.952	132.660	115.084	4.699
4600	10.720	84.446	74.658	45.024	133.011	117.044	4.652
4700	10.722	84.677	74.869	46.096	133.374	119.004	4.605
4800	10.724	84.902	75.076	47.168	133.748	120.964	4.558
4900	10.726	85.124	75.278	48.241	134.131	122.924	4.511
5000	10.729	85.340	75.476	49.314	134.523	124.884	4.464
5100	10.731	85.553	75.673	50.387	134.924	126.844	4.417
5200	10.733	85.761	75.865	51.460	135.334	128.804	4.370
5300	10.736	85.966	76.054	52.533	135.752	130.764	4.323
5400	10.739	86.166	76.239	53.607	136.177	132.724	4.276
5500	10.742	86.363	76.421	54.681	136.606	134.684	4.229
5600	10.745	86.557	76.601	55.756	137.047	136.644	4.182
5700	10.748	86.747	76.777	56.830	137.491	138.604	4.135
5800	10.752	86.934	76.951	57.905	137.941	140.564	4.088
5900	10.756	87.118	77.121	58.981	138.396	142.524	4.041
6000	10.760	87.299	77.289	60.056	138.856	144.484	3.994

June 30, 1961; June 30, 1964; Sept. 30, 1964; Dec. 31, 1967

TITANIUM MONOFLUORIDE (TiF)

(IDEAL GAS)

GFW = 66.8984

Ground State Configuration (° 2)

 $S^{\circ}_{298.15} = 56.7 \pm 2.0$ gibbs/mol $\Delta H^{\circ}_0 = [-16 \pm 10]$ kcal/mol $\Delta H^{\circ}_{298.15} = [-16 \pm 10]$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	[4]	[6000]	[4]
[1000]	[4]	[8000]	[4]
[2000]	[4]	[10000]	[4]
[4000]	[4]		

 $\omega_e X_e = [590]$ cm⁻¹ $\omega_e = [6.6]$ cm⁻¹ $\alpha_e = [0.328]$ cm⁻¹ $\sigma = 1$ $r_e = [1.95]$ Å

Heat of Formation

The heat of formation, ΔH°_{298} , of TiF(g) is calculated from the dissociation energy, D°_0 . The dissociation energy is estimated as 148 ± 6 kcal/mol using the corresponding quantity for TiF₂(g) and the relation $D(\text{HF})/D(\text{HF}_2) = 0.46 \pm 0.02$ which Zmbov and Margrave (1) found held for other mono- and di-fluorides.

Heat Capacity and Entropy

The vibrational frequency, ω_e , and anharmonic vibrational term, $\omega_e X_e$, are estimated from those of the alkali and mercury monohalides. The interatomic distance, r_e , is estimated from those of TiCl(g), TiF₂(g) and TiF₃(g). B_e is calculated from r_e . The ground state term and electronic levels are estimated from the ground state multiplet of Ti (2).

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).
2. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Tungsten Monofluoride (WF)
(Ideal Gas) GFW = 202.8484

T, °K	C _p ^o	S ^o - (C _p ^o - H ^o)/T	H ^o - H ^o ₂₉₈	Kcal/mol ΔH ^o	Log K _p
0	0.000	INFINITE	- 2.140	92.404	INFINITE
100	6.463	52.019	66.466	92.558	- 195.946
200	7.555	58.510	77.557	92.695	- 194.505
298	7.755	59.903	81.503	92.798	- 194.366
300	7.764	59.951	81.548	92.806	- 194.366
400	8.140	62.240	88.141	92.819	- 194.354
500	8.386	64.085	91.638	92.826	- 194.354
600	8.547	65.429	94.497	92.826	- 194.354
700	8.659	66.956	96.776	92.826	- 194.354
800	8.743	68.118	98.421	92.826	- 194.354
900	8.811	69.151	99.491	92.826	- 194.354
1000	8.872	70.083	100.000	92.826	- 194.354
1100	8.930	70.931	100.897	92.826	- 194.354
1200	8.985	71.711	101.241	92.826	- 194.354
1300	9.040	72.432	101.966	92.826	- 194.354
1400	9.094	73.104	102.677	92.826	- 194.354
1500	9.146	73.733	103.284	92.826	- 194.354
1600	9.197	74.325	103.800	92.826	- 194.354
1700	9.247	74.884	104.233	92.826	- 194.354
1800	9.295	75.414	104.585	92.826	- 194.354
1900	9.342	75.918	104.853	92.826	- 194.354
2000	9.389	76.398	105.119	92.826	- 194.354
2100	9.436	76.857	105.380	92.826	- 194.354
2200	9.483	77.298	105.637	92.826	- 194.354
2300	9.531	77.720	105.891	92.826	- 194.354
2400	9.578	78.127	106.142	92.826	- 194.354
2500	9.625	78.519	106.390	92.826	- 194.354
2600	9.672	78.898	106.637	92.826	- 194.354
2700	9.719	79.265	106.881	92.826	- 194.354
2800	9.766	79.620	107.122	92.826	- 194.354
2900	9.812	79.965	107.361	92.826	- 194.354
3000	9.859	80.301	107.600	92.826	- 194.354
3100	9.906	80.628	107.838	92.826	- 194.354
3200	9.953	80.947	108.075	92.826	- 194.354
3300	10.000	81.259	108.311	92.826	- 194.354
3400	10.046	81.563	108.546	92.826	- 194.354
3500	10.093	81.861	108.780	92.826	- 194.354
3600	10.140	82.153	109.013	92.826	- 194.354
3700	10.187	82.439	109.245	92.826	- 194.354
3800	10.234	82.720	109.476	92.826	- 194.354
3900	10.281	83.000	109.706	92.826	- 194.354
4000	10.328	83.276	109.935	92.826	- 194.354
4100	10.375	83.553	110.164	92.826	- 194.354
4200	10.422	83.831	110.392	92.826	- 194.354
4300	10.469	84.108	110.620	92.826	- 194.354
4400	10.516	84.385	110.848	92.826	- 194.354
4500	10.563	84.661	111.075	92.826	- 194.354
4600	10.610	84.938	111.302	92.826	- 194.354
4700	10.657	85.215	111.529	92.826	- 194.354
4800	10.704	85.492	111.756	92.826	- 194.354
4900	10.751	85.769	111.983	92.826	- 194.354
5000	10.798	86.046	112.210	92.826	- 194.354
5100	10.845	86.323	112.437	92.826	- 194.354
5200	10.892	86.600	112.664	92.826	- 194.354
5300	10.939	86.877	112.891	92.826	- 194.354
5400	10.986	87.154	113.118	92.826	- 194.354
5500	11.033	87.431	113.345	92.826	- 194.354
5600	11.080	87.708	113.572	92.826	- 194.354
5700	11.127	87.985	113.799	92.826	- 194.354
5800	11.174	88.262	114.026	92.826	- 194.354
5900	11.221	88.539	114.253	92.826	- 194.354
6000	11.268	88.816	114.480	92.826	- 194.354

Sept. 30, 1962; Mar. 31, 1967

TUNGSTEN MONOFLUORIDE (WF) (IDEAL GAS) OFW = 202.8484

Ground State Configuration [2Δ]
S_{298.15} = [59.9] gibbs/mol
ΔH_{f^o} = [92.4 ± 15] kcal/mol
ΔH_{f^o} = [92.3 ± 15] kcal/mol

Electronic Levels and Quantum Weights

ε ₁ cm ⁻¹	g ₁	ε ₂ cm ⁻¹	g ₂
0	[4]	0	[4]
[5000]	[2]	[15000]	[20]

W_eX_e = [2.9] cm⁻¹ σ = 1
B_e = [0.2923] cm⁻¹ r_e = [1.83] Å

Heat of Formation

The heat of formation, ΔH_{f^o}(WF₂g) = 92.3 kcal/mol, is calculated from the bond dissociation energy D₂₉₈^o(WF) = 130 ± 15 kcal/mol. This value of D₂₉₈^o is estimated to be slightly higher than the average bond dissociation energy of WF₂(g) by analogy with the WCl₂ system.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in WF₆(g). This distance is then used with Ouggenheimer's relation to calculate the fundamental vibrational frequency, ν_e (K. M. Ouggenheimer, Proc. Phys. Soc. 58, 456 (1946)). The anharmonicity correction x_e is estimated roughly by assuming x_e = ω_e/4(D₀ + 0.5 ω_e) = 0.0042. The rotational constant B_e is calculated from the estimated bond distance. The value of σ_e is calculated from the Morse potential function. The moment of inertia is 9.575 x 10⁻³⁹ g cm².

The ground state configuration, low lying electronic levels and their quantum weights are estimated based on the tentative molecular orbital diagram for TaO given by N. Weitzner, Jr., and D. McLeod, Jr., J. Chem. Phys. 42, 882 (1965). Using this scheme, we obtain the ground state configuration as n²d⁴, which yields a ³Δ ground state. The first excited state is assumed to have n²d⁴ which yields a ³Δ state. Higher levels are considered to be formed by transition to n² antibonding orbitals, and by analogy with TaO these are assumed to lie in the 15000 cm⁻¹ region. The degeneracy of these levels is estimated roughly from the large number of possible configurations.

Zirconium Monofluoride (ZrF)

(Ideal Gas) GF_W = 110.2184

T, °K	C _p ^a	S ^b -(C _p ^a - T ³)/T	ΔH ^c -H ^o -H ^o ₂₉₈	ΔG ^c	Log K _p
0	0.000	197.141E	2.171	20.005	197.141E
100	6.979	50.198	17.491	17.491	17.491
200	7.442	55.168	19.941	14.894	16.227
298	7.949	58.941	19.600	12.439	9.116
300	7.998	59.277	19.797	12.393	9.078
400	8.364	60.742	19.648	12.343	9.048
500	8.611	62.596	19.401	12.306	9.026
600	8.809	64.114	19.180	12.276	8.999
700	8.993	65.485	18.930	12.250	8.968
800	9.176	66.698	18.681	12.224	8.934
900	9.355	67.769	18.453	12.198	8.899
1000	9.528	68.784	18.240	12.171	8.864
1100	9.691	69.750	18.046	12.144	8.829
1200	9.842	70.672	17.869	12.117	8.794
1300	9.979	71.553	17.707	12.090	8.759
1400	10.102	72.398	17.557	12.063	8.724
1500	10.212	73.208	17.422	12.036	8.689
1600	10.309	73.982	17.297	12.009	8.654
1700	10.393	74.724	17.180	11.982	8.619
1800	10.467	75.432	17.072	11.955	8.584
1900	10.531	76.104	16.972	11.928	8.549
2000	10.587	76.753	16.878	11.901	8.514
2100	10.635	77.379	16.790	11.874	8.479
2200	10.675	77.977	16.707	11.847	8.444
2300	10.713	78.549	16.629	11.820	8.409
2400	10.748	79.097	16.555	11.793	8.374
2500	10.779	79.624	16.485	11.766	8.339
2600	10.807	80.132	16.418	11.739	8.304
2700	10.831	80.621	16.354	11.712	8.269
2800	10.851	81.091	16.292	11.685	8.234
2900	10.868	81.542	16.232	11.658	8.199
3000	10.882	81.977	16.174	11.631	8.164
3100	10.897	82.397	16.119	11.604	8.129
3200	10.914	82.802	16.067	11.577	8.094
3300	10.930	83.193	16.017	11.550	8.059
3400	10.946	83.570	15.969	11.523	8.024
3500	10.962	83.935	15.924	11.496	7.989
3600	10.978	84.288	15.880	11.469	7.954
3700	10.994	84.630	15.837	11.442	7.919
3800	11.010	84.961	15.795	11.415	7.884
3900	11.027	85.280	15.754	11.388	7.849
4000	11.043	85.588	15.714	11.361	7.814
4100	11.060	85.885	15.674	11.334	7.779
4200	11.077	86.172	15.635	11.307	7.744
4300	11.095	86.448	15.596	11.280	7.709
4400	11.112	86.714	15.558	11.253	7.674
4500	11.129	86.970	15.521	11.226	7.639
4600	11.149	87.217	15.484	11.199	7.604
4700	11.167	87.455	15.448	11.172	7.569
4800	11.186	87.684	15.412	11.145	7.534
4900	11.205	87.904	15.377	11.118	7.499
5000	11.224	88.115	15.342	11.091	7.464
5100	11.243	88.318	15.307	11.064	7.429
5200	11.263	88.513	15.272	11.037	7.394
5300	11.283	88.700	15.237	11.010	7.359
5400	11.302	88.879	15.202	10.983	7.324
5500	11.322	89.050	15.167	10.956	7.289
5600	11.342	89.213	15.132	10.929	7.254
5700	11.362	89.369	15.097	10.902	7.219
5800	11.383	89.517	15.062	10.875	7.184
5900	11.403	89.658	15.027	10.848	7.149
6000	11.423	89.793	15.000	10.821	7.114

June 30, 1961; Sept. 30, 1964; June 30, 1969

Ground State Configuration [4f₇]S_{298.15} = [58 ± 2] gibbs/molΔH₀^o = [20.0 ± 5] kcal/molΔH_{298.15}^o = [19.8 ± 5] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	[4]	(18000)	[4]
[3000]	[4]	[24000]	[4]
[6000]	[4]	[30000]	[4]
[12000]	[4]		

 $\omega_e X_e = [4.0] \text{ cm}^{-1}$ $\sigma = 1$ $\omega_e = [628.0] \text{ cm}^{-1}$ $r_e = [1.90] \text{ \AA}$ $B_e = [0.29699] \text{ cm}^{-1}$

Heat of Formation

Based on [D(ZrF)/D(ZrF₂)] = 0.46, as indicated by recent work on the fluorides of Groups II and IV elements (1, 2, 3, 4, 5), and D₀(ZrF₂) = 318.1 kcal/mol, the D₀(ZrF) is calculated as 146.3 kcal/mol. Using ΔH₀^o(Zr, g) = 147.99, ΔH₀^o(F, g) = 18.36, and D₀(ZrF₂, g) = 146.3 kcal/mol, we derive ΔH₀^o(ZrF, g) = 20.0 or ΔH₀^o(ZrF, g) = 19.8 ± 5 kcal/mol which is adopted. The ΔH₂₉₈^o for ZrF(g) was evaluated as approximately 16 ± 5 kcal/mol by Murad and Hildenbrand (8), employing different D(ZrF₂) value. Their value is in agreement with the adopted one, within the assigned uncertainty.

Heat Capacity and Entropy

The ground state configuration is taken from the ground state multiplet of Zr⁴⁺ (g). The electronic levels are estimated as three times higher than those of TiF(g) and the quantum weights are assumed to be the same. ω_e is taken to be approximately the same as the Zr-F stretching frequency ν_1 for ZrF₄(g). B_e is calculated from the formula $B_e = (2.798076 \times 10^{-39})/I_e$ where $I_e = \mu r_e^2$, μ = reduced mass of ZrF(g), $r_e = 1.90 \text{ \AA}$ which is estimated from those of ZrF₄, CF₄, ClF and other related gaseous molecules. a_e is derived from B_e , ω_e , and $\omega_e X_e$ (estimated), according to the method suggested by Herzberg (2). The moment of inertia is $9.473 \times 10^{-39} \text{ c cm}^2$.

References

1. G. D. Blue, J. W. Green, R. G. Bautista, and J. L. Margrave, J. Phys. Chem. **67**, 877 (1963).
2. H. L. Hildenbrand and E. Murad, J. Chem. Phys. **44**, 1524 (1966).
3. G. D. Blue, J. W. Green, T. C. Ehler, and J. L. Margrave, Nature **113**, 804 (1963).
4. T. C. Ehler and J. L. Margrave, J. Chem. Phys. **41**, 1066 (1964).
5. R. A. Kent, T. C. Ehler, and J. L. Margrave, J. Am. Chem. Soc. **86**, 5080 (1964).
6. C. E. Moore, "Atomic Energy Levels," Vol. II, Natl. Bur. Std. Circ. 467, 1952.
7. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
8. E. Murad and D. L. Hildenbrand, J. Chem. Phys. **45**, 4751 (1966).

Fluorine, Diatomic (F₂)
(Reference State - Ideal Gas)

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF°	Log K _p
200	5.495	48.447	0.00	0.00	0.00	0.00
250	5.495	48.447	0.00	0.00	0.00	0.00
300	5.495	48.447	0.00	0.00	0.00	0.00
350	5.495	48.447	0.00	0.00	0.00	0.00
400	5.495	48.447	0.00	0.00	0.00	0.00
450	5.495	48.447	0.00	0.00	0.00	0.00
500	5.495	48.447	0.00	0.00	0.00	0.00
550	5.495	48.447	0.00	0.00	0.00	0.00
600	5.495	48.447	0.00	0.00	0.00	0.00
650	5.495	48.447	0.00	0.00	0.00	0.00
700	5.495	48.447	0.00	0.00	0.00	0.00
750	5.495	48.447	0.00	0.00	0.00	0.00
800	5.495	48.447	0.00	0.00	0.00	0.00
850	5.495	48.447	0.00	0.00	0.00	0.00
900	5.495	48.447	0.00	0.00	0.00	0.00
950	5.495	48.447	0.00	0.00	0.00	0.00
1000	5.495	48.447	0.00	0.00	0.00	0.00
1100	5.495	48.447	0.00	0.00	0.00	0.00
1200	5.495	48.447	0.00	0.00	0.00	0.00
1300	5.495	48.447	0.00	0.00	0.00	0.00
1400	5.495	48.447	0.00	0.00	0.00	0.00
1500	5.495	48.447	0.00	0.00	0.00	0.00
1600	5.495	48.447	0.00	0.00	0.00	0.00
1700	5.495	48.447	0.00	0.00	0.00	0.00
1800	5.495	48.447	0.00	0.00	0.00	0.00
1900	5.495	48.447	0.00	0.00	0.00	0.00
2000	5.495	48.447	0.00	0.00	0.00	0.00
2100	5.495	48.447	0.00	0.00	0.00	0.00
2200	5.495	48.447	0.00	0.00	0.00	0.00
2300	5.495	48.447	0.00	0.00	0.00	0.00
2400	5.495	48.447	0.00	0.00	0.00	0.00
2500	5.495	48.447	0.00	0.00	0.00	0.00
2600	5.495	48.447	0.00	0.00	0.00	0.00
2700	5.495	48.447	0.00	0.00	0.00	0.00
2800	5.495	48.447	0.00	0.00	0.00	0.00
2900	5.495	48.447	0.00	0.00	0.00	0.00
3000	5.495	48.447	0.00	0.00	0.00	0.00
3100	5.495	48.447	0.00	0.00	0.00	0.00
3200	5.495	48.447	0.00	0.00	0.00	0.00
3300	5.495	48.447	0.00	0.00	0.00	0.00
3400	5.495	48.447	0.00	0.00	0.00	0.00
3500	5.495	48.447	0.00	0.00	0.00	0.00
3600	5.495	48.447	0.00	0.00	0.00	0.00
3700	5.495	48.447	0.00	0.00	0.00	0.00
3800	5.495	48.447	0.00	0.00	0.00	0.00
3900	5.495	48.447	0.00	0.00	0.00	0.00
4000	5.495	48.447	0.00	0.00	0.00	0.00
4100	5.495	48.447	0.00	0.00	0.00	0.00
4200	5.495	48.447	0.00	0.00	0.00	0.00
4300	5.495	48.447	0.00	0.00	0.00	0.00
4400	5.495	48.447	0.00	0.00	0.00	0.00
4500	5.495	48.447	0.00	0.00	0.00	0.00
4600	5.495	48.447	0.00	0.00	0.00	0.00
4700	5.495	48.447	0.00	0.00	0.00	0.00
4800	5.495	48.447	0.00	0.00	0.00	0.00
4900	5.495	48.447	0.00	0.00	0.00	0.00
5000	5.495	48.447	0.00	0.00	0.00	0.00
5100	5.495	48.447	0.00	0.00	0.00	0.00
5200	5.495	48.447	0.00	0.00	0.00	0.00
5300	5.495	48.447	0.00	0.00	0.00	0.00
5400	5.495	48.447	0.00	0.00	0.00	0.00
5500	5.495	48.447	0.00	0.00	0.00	0.00
5600	5.495	48.447	0.00	0.00	0.00	0.00
5700	5.495	48.447	0.00	0.00	0.00	0.00
5800	5.495	48.447	0.00	0.00	0.00	0.00
5900	5.495	48.447	0.00	0.00	0.00	0.00
6000	5.495	48.447	0.00	0.00	0.00	0.00

December 31, 1960.

Fluorine, Diatomic (F₂) (Reference State - Ideal Gas)

Mol. Wt. = 38.00
ΔH°_f 298.15 = 0 kcal. mole⁻¹
S° 298.15 = 48.45 cal. deg.⁻¹ mole⁻¹
Ground State Configuration 1Σ
ω_e = 823.1 cm.⁻¹ ω_ex_e = 15.01 cm.⁻¹
B_e = 0.6585 cm.⁻¹ α_e = 0.022 cm.⁻¹
D_e = 5.346 X 10⁻⁶ cm.⁻¹ r_e = 1.409 Å
σ = 2

Heat Capacities and Entropies. Molecular and spectroscopic constants calculated from Raman measurements of D. Andrychuk, Can. J. Phys. 29, 151 (1951), and the dissociation energy listed by J. O. Stamper and R. P. Barrow, Trans. Faraday Soc. 54, 1592 (1958).

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
	cal. mole ⁻¹ deg. ⁻¹			kcal. mole ⁻¹			
0	0.000	0.000	INFINITE	- 3.049	- 168.564	- 168.564	INFINITE
100	7.994	7.374	33.204	- 2.583	- 168.896	- 165.417	361.502
200	13.530	14.824	22.204	- 1.476	- 168.911	- 161.417	110.184
298	16.280	20.790	20.790	0.000	- 168.700	- 158.507	115.421
300	16.300	20.891	20.790	0.030	- 168.695	- 158.444	115.421
400	17.200	25.708	21.441	1.707	- 168.414	- 155.069	84.722
500	17.900	29.624	22.698	3.463	- 168.140	- 151.765	66.333
600	18.440	32.938	24.135	5.281	- 167.884	- 148.515	54.094
700	18.850	35.812	25.603	7.146	- 167.659	- 145.305	45.364
800	19.180	38.351	27.041	9.048	- 167.491	- 142.125	38.825
900	19.440	40.626	28.426	10.980	- 167.411	- 138.959	33.742
1000	19.650	42.684	29.751	12.934	- 167.499	- 135.796	29.077
1100	19.769	44.562	31.013	14.904	- 167.796	- 132.607	26.345
1200	19.880	46.287	32.215	16.887	- 167.873	- 129.410	23.568
1300	19.955	47.881	33.359	18.879	- 167.607	- 126.214	21.218
1400	20.020	49.363	34.450	20.877	- 167.355	- 123.040	19.207
1500	20.072	50.746	35.491	22.882	- 167.114	- 119.883	17.466
1600	20.120	52.041	36.485	24.892	- 166.888	- 116.743	15.946
1700	20.164	53.264	37.437	26.906	- 166.667	- 113.609	14.605
1800	20.200	54.418	38.348	28.924	- 166.862	- 110.475	13.413
1900	20.229	55.510	39.223	30.946	- 170.441	- 107.158	12.325
2000	20.250	56.549	40.064	32.970	- 170.400	- 103.830	11.345

MOL. WT. = 93.8438

(CRYSTAL)

IRON DIFLUORIDE (FeF₂)

$\Delta H_f^0 = -168.6 \pm 10$ kcal. mole⁻¹
 ΔH_f^0 298.15 = -168.7 ± 10 kcal. mole⁻¹
 $\Delta H_m^0 = [12.4]$ kcal. mole⁻¹
 ΔH_g^0 298.15 = 75.6 ± 2.0 kcal. mole⁻¹

$S_{298.15}^0 = 20.79 \pm 0.04$ cal. deg.⁻¹ mole⁻¹
 $T_m = [1373]^\circ K.$

Heat of Formation.

The equilibrium pressures for the reaction $FeF_2(c) + H_2(g) = Fe(c) + 2HF(g)$ have been measured by K. Jelinek and A. Rudat, Z. anorg. allgem. Chem. 175, 281 (1928) at 775, 875 and 975°K. The enthalpy change (ΔH_f^0 298.15) of the reaction was evaluated by the second and third law methods to be 27.19 and 39.08 kcal. mole⁻¹, respectively. Based on the third law value of ΔH_f^0 298.15, the ΔH_f^0 298.15 (FeF₂, c) was calculated to be -168.7 ± 10 kcal. mole⁻¹. The drift in the third law values of ΔH_f^0 298.15 was evaluated to be 13.3 ± 1.8 e.u.

Heat Capacity and Entropy.

T_m was estimated as 1100°C based on the data reported by W. Biltz and E. Rehlf, Z. anorg. allgem. Chem. 165, 363 (1927). The value of ΔH_f^0 was calculated using $\Delta S_m^0 = 9$ e.u. which was assumed to be the same as the corresponding value for MgF₂(c). The value of ΔH_f^0 298.15 was obtained from E. Catalano and J. M. Stout, loc. cit., in which a sharp maximum C_p of 17.8 cal. deg.⁻¹ mole⁻¹ at 78.35°K. was reported. The $S_{298.15}^0$ value was based on $S_{15}^0 = 0.039$ e.u.

Melting Data.

T_m was estimated as 1100°C based on the data reported by W. Biltz and E. Rehlf, Z. anorg. allgem. Chem. 165, 363 (1927). The value of ΔH_f^0 was calculated using $\Delta S_m^0 = 9$ e.u. which was assumed to be the same as the corresponding value for MgF₂(c).

Heat of Sublimation.

The value of ΔH_g^0 298.15 was obtained from J. L. Margrave, "Research in Fluorine Chemistry", Progress Report No. 7, 1 January to 31 March 1965, William Marsh Rice University, Houston, Texas. See FeF₂(g) table for details.

Iron Difluoride (FeF₂)

(Liquid)

Mol. wt. = 93.8438

F₂Fe

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _f
0							
100							
200							
298	23.400	21.951	21.951	0.000	-161.229	-151.383	110.961
300	23.500	22.096	21.951	0.043	-161.211	-151.322	110.232
400	23.500	28.857	22.873	2.393	-160.257	-148.171	80.953
500	23.500	34.101	24.614	4.743	-159.389	-145.233	63.487
600	23.500	38.385	26.563	7.093	-158.601	-142.500	51.903
700	23.500	42.008	28.517	9.443	-157.891	-140.874	43.669
800	23.500	45.146	30.404	11.793	-157.275	-139.345	37.519
900	23.500	47.914	32.199	14.443	-156.777	-137.884	32.753
1000	23.500	50.340	33.896	16.493	-156.469	-136.472	28.950
1100	23.500	52.630	35.499	18.843	-156.386	-135.071	25.842
1200	23.500	54.674	37.013	21.193	-156.096	-133.696	23.256
1300	23.500	56.555	38.445	23.543	-155.472	-132.354	21.073
1400	23.500	58.297	39.801	25.893	-154.868	-131.061	19.210
1500	23.500	59.918	41.089	28.243	-154.282	-129.809	17.601
1600	23.500	61.435	42.314	30.593	-153.716	-128.597	16.199
1700	23.500	62.859	43.481	32.943	-153.459	-127.412	14.965
1800	23.500	64.203	44.595	35.293	-153.022	-126.248	13.871
1900	23.500	65.473	45.661	37.643	-152.473	-125.191	12.873
2000	23.500	66.679	46.682	39.993	-151.906	-124.246	11.975
2100	23.500	67.825	47.662	42.343	-151.566	-123.288	11.165
2200	23.500	68.918	48.603	44.693	-151.193	-122.467	10.430
2300	23.500	69.963	49.509	47.043	-150.846	-121.725	9.761
2400	23.500	70.963	50.393	49.393	-150.506	-121.067	9.148
2500	23.500	71.923	51.225	51.743	-150.173	-120.467	8.586
2600	23.500	72.844	52.039	54.093	-149.846	-119.900	8.068
2700	23.500	73.731	52.826	56.443	-149.525	-119.371	7.590
2800	23.500	74.586	53.588	58.793	-149.210	-118.871	7.147
2900	23.500	75.410	54.326	61.143	-148.902	-118.395	6.734
3000	23.500	76.207	55.043	63.493	-148.601	-117.943	6.351

IRON DIFLUORIDE (FeF₂)

(LIQUID)

MOL. WT. = 93.8438

F₂FeS°_{298.15} = [21.951] cal. deg.⁻¹ mole⁻¹ΔH_f^o_{298.15} = [-161.229] kcal. mole⁻¹T_m = [1373]°K.ΔH_m^o = [12.4] kcal. mole⁻¹T_b = [2110]°K.ΔH_v^o = [53.64] kcal. mole⁻¹

Heat of Formation.

The value of ΔH_f^o_{298.15} (FeF₂, l) was obtained from ΔH_f^o_{298.15} (FeF₂, c) by adding ΔH_m^o and the difference between H_m^o - H_l^o_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity for FeF₂(l) was estimated by comparison with those for FeCl₂(c), MgCl₂(c), MgF₂(c), CaCl₂(c) and CaF₂(c). The C_p(FeF₂, l) value was assumed to be constant in the temperature range, 298.15 - 3000°K. The entropy (S°_{298.15}) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See the FeF₂(c) table for details.

Vaporization Data.

T_b is calculated as the temperature at which the free energy change of the reaction FeF₂(l) = FeF₂(g) approaches zero. The difference between ΔH_f^o for FeF₂(l) and FeF₂(g) at T_b is ΔH_v^o.

F₂Fe

Point Group [D_{∞h}]
S_{298.15}° = [63.4] cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ = -92.9 ± 3.4 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -93.1 ± 3.4 kcal. mole⁻¹

Electronic Levels and Quantum Weights

ε ₁ , cm. ⁻¹	g ₁
0	[5]
[1000]	[10]
[4000]	[5]
[6000]	[5]

Vibrational Frequencies and Degeneracies

ω _j , cm. ⁻¹
[550] (1)
[190] (2)
[714] (1)

Bond Distances Fe-F = [1.8] Å
Bond Angle: F-Fe-F = [180]°
Rotational Constant: B₀ = 0.13692 cm.⁻¹

σ = 2

Heat of Formation.

The rate of sublimation of FeF₂(c) was measured between 965 and 1149°K. by the Knudsen technique employing the high temperature magnetic mass spectrometer by John L. Margrave, "Research in Fluorine Chemistry", Progress Report No. 7, 1 January to 31 March 1965, William March Rice University, Houston, Texas. The only vapor species of importance is FeF₂(g). From the vapor pressure data the third law heat of sublimation (ΔH_f⁰ 298.15) was reported as 75.6 ± 2.0 kcal. mole⁻¹. The sum of the values of ΔH_f⁰ 298.15 and ΔH_f⁰ 298.15 for FeF₂(c) is the ΔH_f⁰ 298.15 (FeF₂, g).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The Fe-F bond distance was estimated from that in FeF₂(c) reported by W. H. Baur, Acta Cryst. 11, 488 (1958). The vibrational frequencies, ω_j and ω_j, were estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The values of ω_j, electronic levels and quantum weights were estimated by comparison with those for FeCl₂(g). See FeCl₂(g) table for details. The moment of inertia is 2.04404 X 10⁻³⁹ g. cm.²

Sept. 30, 1965

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	9.216	51.319	73.890	- 92.944	- 92.944	INFINITE
200	11.449	58.427	94.522	- 93.886	- 93.886	205.178
298	13.324	63.361	103.555	- 94.770	- 94.770	103.555
300	13.324	63.361	103.555	- 94.770	- 94.770	70.073
300	13.324	63.361	103.555	- 94.770	- 94.770	69.653
400	14.673	67.482	131.031	- 95.100	- 95.100	52.697
500	15.365	70.841	154.065	- 95.100	- 95.100	42.527
600	15.647	73.072	168.186	- 95.100	- 95.100	35.748
700	15.723	74.091	174.433	- 95.100	- 95.100	30.903
800	15.744	74.814	178.614	- 95.100	- 95.100	27.256
900	15.679	75.164	180.921	- 95.100	- 95.100	24.256
1000	15.644	75.241	181.690	- 95.100	- 95.100	22.153
1100	15.617	75.179	181.968	- 95.100	- 95.100	20.276
1200	15.600	75.093	181.960	- 95.100	- 95.100	18.704
1300	15.588	75.000	181.700	- 95.100	- 95.100	17.358
1400	15.580	74.904	181.324	- 95.100	- 95.100	16.212
1500	15.580	74.806	180.850	- 95.100	- 95.100	15.225
1600	15.584	74.704	180.286	- 95.100	- 95.100	14.352
1700	15.598	74.598	179.644	- 95.100	- 95.100	13.578
1800	15.620	74.488	178.924	- 95.100	- 95.100	12.897
1900	15.642	74.374	178.126	- 95.100	- 95.100	12.307
2000	15.662	74.256	177.252	- 95.100	- 95.100	11.793
2100	15.681	74.134	176.304	- 95.100	- 95.100	11.335
2200	15.693	74.008	175.282	- 95.100	- 95.100	10.922
2300	15.700	73.878	174.186	- 95.100	- 95.100	10.552
2400	15.708	73.744	173.016	- 95.100	- 95.100	10.222
2500	15.703	73.608	171.772	- 95.100	- 95.100	9.9425
2600	15.597	73.472	170.456	- 95.100	- 95.100	9.716
2700	15.590	73.336	169.070	- 95.100	- 95.100	9.542
2800	15.582	73.199	167.624	- 95.100	- 95.100	9.412
2900	15.573	73.062	166.128	- 95.100	- 95.100	9.316
3000	15.563	72.925	164.582	- 95.100	- 95.100	9.240
3100	15.553	72.788	162.986	- 95.100	- 95.100	9.176
3200	15.542	72.651	161.340	- 95.100	- 95.100	9.122
3300	15.531	72.514	159.644	- 95.100	- 95.100	9.076
3400	15.519	72.377	157.900	- 95.100	- 95.100	9.038
3500	15.507	72.240	156.106	- 95.100	- 95.100	9.004
3600	15.495	72.103	154.262	- 95.100	- 95.100	8.972
3700	15.482	71.966	152.368	- 95.100	- 95.100	8.942
3800	15.469	71.829	150.424	- 95.100	- 95.100	8.914
3900	15.456	71.692	148.430	- 95.100	- 95.100	8.887
4000	15.443	71.555	146.386	- 95.100	- 95.100	8.861
4100	15.430	71.418	144.292	- 95.100	- 95.100	8.836
4200	15.417	71.281	142.148	- 95.100	- 95.100	8.811
4300	15.404	71.144	140.054	- 95.100	- 95.100	8.786
4400	15.391	71.007	137.910	- 95.100	- 95.100	8.761
4500	15.378	70.870	135.716	- 95.100	- 95.100	8.736
4600	15.365	70.733	133.472	- 95.100	- 95.100	8.711
4700	15.352	70.596	131.178	- 95.100	- 95.100	8.686
4800	15.339	70.459	128.834	- 95.100	- 95.100	8.661
4900	15.326	70.322	126.440	- 95.100	- 95.100	8.636
5000	15.313	70.185	124.096	- 95.100	- 95.100	8.611
5100	15.300	70.048	121.702	- 95.100	- 95.100	8.586
5200	15.287	69.911	119.258	- 95.100	- 95.100	8.561
5300	15.274	69.774	116.764	- 95.100	- 95.100	8.536
5400	15.261	69.637	114.220	- 95.100	- 95.100	8.511
5500	15.248	69.500	111.626	- 95.100	- 95.100	8.486
5600	15.235	69.363	109.082	- 95.100	- 95.100	8.461
5700	15.222	69.226	106.488	- 95.100	- 95.100	8.436
5800	15.209	69.089	103.844	- 95.100	- 95.100	8.411
5900	15.196	68.952	101.150	- 95.100	- 95.100	8.386
6000	15.183	68.815	98.406	- 95.100	- 95.100	8.361

Potassium Bifluoride (KHF₂)
(Crystal) Mol. Wt. = 78.108

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0	∞	∞	∞	∞	∞	∞	∞
100	11.680	8.458	39.618	3.654	-220.744	-220.744	INFINITE
200	16.010	18.154	26.619	1.693	-216.401	-216.401	472.920
298	18.361	23.000	23.000	0.000	-211.893	-211.893	150.566
300	18.400	25.114	25.000	.034	-221.905	-205.553	149.738
400	20.603	30.704	25.748	1.693	-222.387	-200.004	109.272
500	23.960	41.322	27.579	6.871	-219.398	-194.610	85.050
600	23.960	45.691	30.245	9.267	-218.910	-189.497	69.094
700	23.960	49.384	32.722	11.663	-218.432	-184.866	57.715
800	23.960	52.584	35.009	14.059	-217.967	-180.104	49.200
900	23.960	55.406	37.122	16.455	-217.515	-175.398	42.590
1000	23.960	57.930	39.079	18.951	-217.084	-170.743	37.314
1100	23.960	60.216	40.898	21.247	-235.580	-165.105	32.802
1200	23.960	62.299	42.598	23.643	-234.945	-158.724	28.906
1300	23.960	64.216	44.186	26.039	-234.321	-152.399	25.619
1400	23.960	65.992	45.681	28.435	-233.706	-146.119	22.809
1500	23.960	67.645	47.091	30.831	-233.101	-139.883	20.380
1600	23.960	69.191	48.424	33.227	-232.506	-133.689	18.260
1700	23.960	70.644	49.689	35.623	-231.919	-127.531	16.394
1800	23.960	72.013	50.892	38.019	-231.342	-121.409	14.740
1900	23.960	73.309	52.038	40.415	-230.773	-115.317	13.264
2000	23.960	74.538	53.132	42.811	-230.211	-109.253	11.938

F₂HK

MOL. WT. = 78.108

(CRYSTAL)

POTASSIUM BIFLUORIDE (KHF₂)

ΔH_f^o = -220.74 ± 0.35 kcal. mole⁻¹

ΔH_f^o 298.15 = -221.90 ± 0.35 kcal. mole⁻¹

ΔH_t^o = 2.671 ± 0.01 kcal. mole⁻¹

ΔH_m^o = 1.582 ± 0.003 kcal. mole⁻¹

S° 298.15 = 25.0 ± 0.1 cal. deg. mole⁻¹

T_t = 469.8°K.

T_m = 511.8°K.

Heat of Formation.

The heat of formation was obtained from the enthalpy of decomposition measurements of M. L. Davis and E. F. Westrum, J. Phys. Chem. 65, 339 (1961) who gave ΔH_d 500 = 18.82 ± 0.05 kcal. mole⁻¹ and the heats of formation of HF(g) and KF(c) in conjunction with enthalpies at 500°K. from E. F. Westrum and K. S. Pitzer, J. Am. Chem. Soc. 71, 1940 (1949). A third law analysis of the decomposition vapor pressure by Westrum and Pitzer, loc. cit. did not agree with enthalpy of decomposition measurements, giving ΔH_d 298 = 21.274 ± 0.2 kcal. mole⁻¹ as compared to Davis and Westrum's value at 298°K. of 21.505 ± 0.05 kcal. mole⁻¹. As the liquid vapor pressure data, which were not used, have a large trend in the third law heat of vaporization with temperature it was suspected that the pressure measurements were in error. This is borne out somewhat by a small trend in the values over the solid in the range 480-500°K.

Heat Capacity and Entropy.

Westrum and Pitzer, loc. cit., have measured the heat capacity from 16°K. to the melting point. Their data has been used to calculate the entropy at 298° using a T³ law extrapolation below 16°K., giving S₁₆ = 0.103 e.u.

Melting and Transition Data.

The temperatures of melting and transition and the heats of melting and transition were taken from Davis and Westrum, loc. cit.

F₂HK

Potassium Bifluoride (KHF₂)
(Liquid) Mol. Wt. = 78.108

F₂HK

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0							
100							
200							
298	18.344	32.300	32.100	0.000	-218.243	-204.168	149.652
300	18.400	32.414	32.300	-0.3%	-218.243	-204.081	149.466
400	25.000	38.817	33.112	2.282	-218.426	-199.287	108.880
500	25.000	44.396	34.832	4.782	-217.825	-194.574	85.044
600	25.000	48.934	36.817	7.282	-217.233	-189.979	69.156
700	25.000	52.808	38.893	9.782	-216.651	-185.482	57.007
800	25.000	56.156	42.775	14.782	-215.972	-181.000	47.564
900	25.000	59.080	47.065	17.282	-215.522	-177.720	40.682
1000	25.000	61.725	44.443	17.282	-214.991	-172.445	37.686
1100	25.000	64.107	46.124	19.782	-233.383	-167.101	31.216
1200	25.000	66.283	47.714	22.282	-232.644	-161.204	26.398
1300	25.000	68.284	49.134	24.782	-231.811	-155.483	22.104
1400	25.000	70.136	50.609	27.282	-231.197	-150.143	18.348
1500	25.000	71.861	52.006	29.782	-230.488	-145.395	15.021
1600	25.000	73.475	53.288	32.282	-229.789	-137.826	11.825
1700	25.000	74.990	54.550	34.782	-229.099	-132.099	10.982
1800	25.000	76.413	55.797	37.282	-228.417	-126.415	10.348
1900	25.000	77.771	56.951	39.782	-227.747	-120.747	13.848
2000	25.000	79.053	57.912	42.282	-227.079	-115.151	12.582

POTASSIUM BIFLUORIDE (KHF₂) (LIQUID) MOL. WT. = 78.108

S°_{298.15} = 32.3 cal. deg. mole⁻¹ ΔH_f<sup>o 298.15 = -218.24 ± 0.35 kcal. mole⁻¹
T_m = 511.8°K. ΔH_m<sup>o = 1.582 ± 0.003 kcal. mole⁻¹
T_{decomp.} = [751]°K.</sup></sup>

Heat of Formation.

This was calculated from the heat of formation of the crystal, the heat of melting and H°_{511.8}-H°_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The entropy was determined from that of the crystal in a manner analogous to the heat of formation. The heat capacity just above the melting point was measured by E. F. Westrum and K. S. Pitzer, J. Am. Chem. Soc. 71, 1940 (1949) and was assumed constant above the melting point. A glass type transition was assumed at 341°K. below which the heat capacity is that of the solid.

Melting.

See table for crystal.

Decomposition.

The temperature of decomposition was estimated from the free energy cross-over and is the point where the HF(g) reaches 1 atm. It should be noted that the vapor pressures over the liquid of Westrum and Pitzer, loc. cit. are apparently in error, being high by roughly 12%. A 3rd law analysis at each vapor pressure point gave an almost constant heat of reaction in the solid region but in the liquid region the value changed abruptly with temperature. The only factors which were variable were the pressure and the liquid heat capacity, a trial change of 20% in the heat capacity produced an almost negligible change in the heat of reaction. Thus the vapor pressures over the liquid appear to be in error and the decomposition point of 702°K. obtained by extrapolating to 1 atmosphere is also in error.

June 30, 1962; Dec. 31, 1963

F₂HK

Difluorosilane (SiH₂F₂)
 (Ideal Gas) Mol. Wt. = 68.106

INTERIM TABLE

T.°K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° ₂₉₈	Log K _p
0	∞	∞	∞	∞	∞
100	5.366	51.702	2.788	191.894	INFINITE
200	5.881	51.823	1.075	182.613	417.811
298	6.282	52.282	0.000	183.285	207.073
300	6.282	52.282	0.000	183.285	137.434
400	6.282	62.358	0.23	184.013	136.558
500	6.282	67.792	1.368	184.641	101.171
600	6.282	72.866	2.933	185.131	76.877
700	6.282	77.598	4.674	185.492	65.649
800	6.282	81.927	6.581	185.735	57.827
900	6.282	85.841	8.635	185.883	51.878
1000	6.282	89.354	10.835	185.953	47.116
1100	6.282	92.466	13.181	185.956	43.220
1200	6.282	95.172	15.674	185.894	39.772
1300	6.282	97.478	18.302	185.764	36.724
1400	6.282	99.384	21.059	185.574	34.069
1500	6.282	100.900	23.946	185.331	31.772
1600	6.282	102.026	26.964	185.044	29.813
1700	6.282	102.762	29.112	184.712	28.145
1800	6.282	103.108	30.397	184.344	26.724
1900	6.282	103.164	31.819	183.941	25.500
2000	6.282	102.930	33.377	183.504	24.434
2100	6.282	102.408	35.072	183.034	23.500
2200	6.282	101.592	36.904	182.531	22.684
2300	6.282	100.480	38.872	182.004	21.969
2400	6.282	99.072	40.976	181.454	21.344
2500	6.282	97.376	43.216	180.884	20.809
2600	6.282	95.304	45.592	180.294	20.354
2700	6.282	92.856	48.116	179.684	19.969
2800	6.282	90.032	50.792	179.054	19.644
2900	6.282	86.848	53.620	178.304	19.369
3000	6.282	83.312	56.600	177.434	19.134
3100	6.282	79.424	59.732	176.444	18.934
3200	6.282	75.184	63.016	175.334	18.764
3300	6.282	70.600	66.456	174.104	18.614
3400	6.282	65.672	70.056	172.754	18.474
3500	6.282	60.400	73.520	171.284	18.344
3600	6.282	54.776	76.992	169.694	18.214
3700	6.282	48.800	80.472	167.984	18.084
3800	6.282	42.472	83.960	166.154	17.954
3900	6.282	35.792	87.456	164.204	17.824
4000	6.282	28.760	90.968	162.134	17.694
4100	6.282	21.376	94.496	160.044	17.564
4200	6.282	13.640	98.040	157.934	17.434
4300	6.282	5.552	101.592	155.804	17.304
4400	6.282	-2.904	105.152	153.644	17.174
4500	6.282	-10.720	108.720	151.454	17.044
4600	6.282	-18.896	112.288	149.234	16.914
4700	6.282	-27.432	115.856	146.984	16.784
4800	6.282	-36.328	119.424	144.704	16.654
4900	6.282	-45.576	122.992	142.394	16.524
5000	6.282	-55.176	126.560	140.054	16.394
5100	6.282	-65.120	130.128	137.684	16.264
5200	6.282	-75.408	133.696	135.284	16.134
5300	6.282	-86.040	137.264	132.844	16.004
5400	6.282	-97.016	140.832	130.364	15.874
5500	6.282	-108.336	144.416	127.844	15.744
5600	6.282	-120.000	148.000	125.284	15.614
5700	6.282	-132.000	151.584	122.684	15.484
5800	6.282	-144.336	155.168	119.944	15.354
5900	6.282	-156.848	158.752	117.164	15.224
6000	6.282	-169.616	162.336	114.344	15.094

December 31, 1960.

F₂H₂Si

Difluorosilane (SiH₂F₂) (Ideal Gas)

Mol. wt. = 68.106
 ΔH_f° 298.15 = [-1.94 ± 15] kcal. mole⁻¹
 $S_{298.15}^\circ$ = [62.576] cal. deg.⁻¹ mole⁻¹
 Point Group C_{2v}
 Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies		
ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
2245 (1)	321.7 (1)	728.2 (1)
870 (1)	2250 (1)	[905] (1)
984.8 (1)	[978] (1)	[785] (1)

Moments of Inertia: I_A = 3.40 X 10⁻³⁹ g. cm.²
 I_B = 10.76 X 10⁻³⁹ g. cm.²
 I_C = 13.16 X 10⁻³⁹ g. cm.²

Heat of Formation. ΔH_f° 298.15 was estimated in G. B. Henderson and R. S. Scheffer, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were taken from G. Jenz and Y. Mikawa, Bull. Chem. Soc. Japan 34, 1485 (1961). Moments of inertia were found in Henderson and Scheffer, op. cit.

F₂H₂Si

INTERIM TABLE

(Crystal) Mol. Wt. = 238.61

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0								
100	17.4901	27.4000	27.4000	4.000	-101.000	-89.476	65.548	
200	17.5000	27.9111	27.0000	.0333	-100.963	-89.355	65.092	
300	17.5000	33.1288	28.5008	1.6444	-100.609	-85.532	46.730	
400	18.5000	37.246	29.862	3.713	-100.203	-81.809	35.757	
500	19.4000	40.778	31.398	5.428	-99.769	-78.171	28.473	
600	19.5000	43.806	32.959	7.593	-113.330	-73.037	22.802	
700	20.4000	46.896	34.886	9.608	-112.678	-67.325	18.391	
800	20.5000	48.922	35.957	11.673	-111.985	-61.656	14.981	
900	21.4000	51.155	37.357	13.788	-111.252	-56.148	12.871	
1000	21.5000	53.218	38.716	15.953	-110.476	-50.675	10.968	
1100	22.5000	55.145	40.005	18.168	-109.655	-45.274	8.245	
1200	22.5000	56.958	41.240	20.433	-108.790	-39.943	6.715	
1300	23.4000	58.673	42.475	22.748	-107.878	-34.681	5.414	
1400	23.5000	60.305	43.563	25.113	-106.921	-29.445	4.296	
1500	24.4000	61.863	44.658	27.528	-105.918	-24.357	3.327	
1600	24.5000	63.358	45.715	29.993	-104.868	-19.289	2.480	
1700	25.4000	64.795	46.735	32.508	-103.772	-14.290	1.735	
1800	25.5000	66.142	47.722	35.073	-102.627	-9.348	1.075	
1900	26.4000	67.523	48.679	37.688	-101.436	-4.468	.488	

March 31, 1952

MERCURY DIFLUORIDE (HgF₂) (Crystal)

Mol. Wt. = 238.61

 ΔH_f^0 238.15 = [-101.0 ± 10.0] kcal. mole⁻¹ $S_{298.15}^0$ = [27.800 ± 2.0] cal. deg.⁻¹ mole⁻¹ T_m = 918°K ΔH_m = [5.5 ± 1.0] kcal. mole⁻¹

Heat of Formation. Estimated by comparison of the mercurous and mercuric halides.

Heat Capacity and Entropy. The heat capacity was assumed to be a linear function of temperature and was estimated to be 7.0 cal. deg.⁻¹ per atom at the melting point. The entropy was estimated by comparison with the other mercuric and mercurous halides and use of additive entropy constants for the halogens from K. K. Kelley (Private Communication, 1950).

Melting. T_m was given by O. Ruff and G. Bahlau, Ber. 51, 1752 (1918). The heat of melting was from L. Brewer, paper 7, National Nuclear Energy Series A-153 "Thermodynamics" McGraw-Hill (1950).

Mercury Difluoride (HgF₂)
(Liquid) Mol. Wt. = 238.61

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° - (F° - H° ₂₉₈)/T cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0						
100	17.891	32.083	32.083	.000	- 86.475	63.385
200	17.900	32.194	32.083	.033	- 86.412	62.948
300	17.900	32.411	32.791	1.448	- 83.017	45.356
400	16.900	41.571	34.145	3.713	- 79.723	34.645
500	16.400	45.041	35.681	5.426	- 76.513	27.849
600	16.400	47.715	37.282	6.003	- 71.935	22.427
700	16.400	51.974	38.920	10.443	- 66.644	18.205
800	16.400	54.648	40.523	12.483	- 61.566	14.954
900	16.400	57.414	42.095	15.323	- 56.648	12.380
1000	16.400	59.744	43.595	17.743	- 51.915	10.204
1100	16.400	61.867	45.031	20.203	- 47.077	8.253
1200	16.400	63.820	46.402	22.443	- 42.426	7.132
1300	16.400	65.628	47.712	25.083	- 37.954	5.909
1400	16.400	67.312	48.963	27.523	- 33.357	4.860
1500	16.400	68.886	50.159	29.943	- 28.931	3.952
1600	16.400	70.366	51.305	32.403	- 24.565	3.152
1700	16.400	71.740	52.403	34.843	- 20.265	2.440
1800	16.400	73.060	53.457	37.283	- 16.015	1.842
1900	16.400	74.331	54.469	39.723	- 11.921	1.292

MERCURY DIFLUORIDE (HgF₂)
(Liquid)

Mol. Wt. = 238.61
ΔH_f^o 298.15 = [-96.772 ± 10.0] kcal. mole⁻¹
S° 298.15 = [32.083 ± 2.0] cal. deg⁻¹ mole⁻¹
T_m = 918°K
ΔH_m = [5.5 ± 1.0] kcal. mole⁻¹
T_b = 920°K
ΔH_v = [22.0 ± 4.0] kcal. mole⁻¹

Heat of Formation. Calculated from ΔH_f^o (crystal).

Heat Capacity and Entropy. C_p was estimated by analogy with mercuric iodide and bromide. A glass type transition was assumed at 613°K below which the heat capacity was that of HgF₂(crystal). The entropy was calculated from S°(crystal) and the estimated ΔH_m and heat capacities of crystal and liquid.

Fusion and Vaporization. T_m was given by O. Ruff and G. Bahlon, Ber. 51, 1752 (1918). T_b, ΔH_m, and ΔH_v were all taken from L. Brewer, paper 7, National Nuclear Energy Series 4-19B "Thermodynamics" McGraw-Hill (1950).

Mercury Difluoride (HgF₂)
(Ideal Gas) Mol. Wt. = 238.61

INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	3.152	-68.994	-	INFINITE
100	10.129	51.105	2.107	-69.404	-	151.674
200	11.722	58.627	1.213	-69.475	-	75.901
298	12.499	63.545	.000	-70.185	-	69.773
300	12.914	63.628	.024	-70.187	-	69.263
400	13.618	67.445	1.354	-70.288	-	50.456
500	14.018	70.530	2.737	-70.364	-	37.664
600	14.263	73.110	4.152	-70.430	-	29.980
700	14.492	75.321	5.587	-70.481	-	24.852
800	14.698	77.181	7.042	-70.521	-	20.695
900	14.878	78.670	8.515	-70.551	-	17.437
1000	15.035	80.512	9.955	-70.570	-	14.837
1100	15.170	81.911	11.423	-70.582	-	12.790
1200	15.292	83.192	12.895	-70.588	-	11.116
1300	15.403	84.366	14.366	-70.590	-	9.723
1400	15.507	85.466	15.846	-70.594	-	8.536
1500	15.603	86.486	17.325	-70.594	-	7.536
1600	15.697	87.441	18.805	-70.594	-	6.663
1700	15.787	88.337	20.289	-70.594	-	5.899
1800	15.873	89.189	21.768	-70.594	-	5.226
1900	15.955	90.000	23.251	-70.594	-	4.633
2000	16.033	90.750	24.735	-70.594	-	4.093
2100	16.107	91.474	26.219	-70.594	-	3.612
2200	16.177	92.185	27.704	-70.594	-	3.178
2300	16.243	92.887	29.192	-70.594	-	2.793
2400	16.306	93.579	30.676	-70.594	-	2.453
2500	16.366	94.264	32.162	-70.594	-	2.157
2600	16.423	94.944	33.649	-70.594	-	1.909
2700	16.477	95.619	35.135	-70.594	-	1.699
2800	16.528	96.290	36.620	-70.594	-	1.526
2900	16.576	96.957	38.106	-70.594	-	1.387
3000	16.621	97.621	39.597	-70.594	-	1.287
3100	16.663	98.283	41.095	-70.594	-	1.213
3200	16.703	98.943	42.593	-70.594	-	1.159
3300	16.741	99.601	44.092	-70.594	-	1.121
3400	16.777	100.257	45.592	-70.594	-	1.094
3500	16.811	100.911	47.096	-70.594	-	1.077
3600	16.843	101.563	48.603	-70.594	-	1.069
3700	16.873	102.213	50.115	-70.594	-	1.069
3800	16.901	102.861	51.632	-70.594	-	1.077
3900	16.927	103.507	53.155	-70.594	-	1.094
4000	16.951	104.151	54.684	-70.594	-	1.121
4100	16.973	104.793	56.219	-70.594	-	1.159
4200	16.993	105.433	57.760	-70.594	-	1.213
4300	17.011	106.071	59.307	-70.594	-	1.287
4400	17.027	106.707	60.860	-70.594	-	1.387
4500	17.041	107.341	62.419	-70.594	-	1.526
4600	17.053	107.973	63.984	-70.594	-	1.699
4700	17.063	108.603	65.555	-70.594	-	1.909
4800	17.071	109.229	67.132	-70.594	-	2.157
4900	17.077	109.853	68.715	-70.594	-	2.453
5000	17.081	110.473	70.307	-70.594	-	2.793
5100	17.083	111.090	71.906	-70.594	-	3.178
5200	17.083	111.703	73.512	-70.594	-	3.612
5300	17.081	112.313	75.125	-70.594	-	4.093
5400	17.077	112.919	76.746	-70.594	-	4.633
5500	17.071	113.521	78.374	-70.594	-	5.226
5600	17.063	114.120	80.009	-70.594	-	5.899
5700	17.053	114.715	81.651	-70.594	-	6.663
5800	17.041	115.307	83.299	-70.594	-	7.536
5900	17.027	115.896	84.954	-70.594	-	8.536
6000	17.011	116.481	86.616	-70.594	-	9.723

December 31, 1961



(IDEAL GAS)

MERCURY DIFLUORIDE (HgF₂)

MOL. WT. = 238.61

Point Group D_{2h}
ΔH_f⁰ 298.15 = [-70.2 ± 10.0] kcal mole⁻¹
S_{298.15} = 63.545 cal deg⁻¹ mole⁻¹
Vibrational Levels and Multiplicities
ω, cm⁻¹
[600] (1)
[120] (2)
[593] (1)
Hg-F distance = [1.96] Å
Moment of Inertia = [12.118 × 10⁻³⁹] g cm²
σ = 2

Heat of Formation
Estimated by comparison with the other gaseous mercuric halides and with the crystalline mercurous mercuric fluorides.

Heat Capacity and Entropy

Vibrational constants were estimated by analogy with the other mercuric halides and the mercurous halides. The bond length was estimated by assuming the mercurous bond to be 0.965 of the mercuric bond by analogy with the mercury chlorides.



Mercury Monofluoride, Dimeric (Hg_2F_2)

(Crystal) Mol. Wt. = 439.22 INTERIM TABLE

T. °K.	C _p	S° cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0							
100	24.060	38.400	38.400	.000	-116.000	-102.169	74.888
200	24.070	38.549	38.400	.044	-115.994	-102.083	74.364
300	25.070	45.499	39.355	2.498	-115.632	-97.497	53.267
400	25.910	51.280	41.190	5.045	-115.196	-93.013	40.654
500	26.490	54.075	43.281	7.676	-114.695	-88.624	32.280
600	27.070	60.241	45.413	10.380	-114.192	-81.180	25.344
700	27.950	63.935	47.502	13.147	-114.285	-72.525	19.812
800	28.830	67.235	49.515	15.666	-114.336	-63.965	15.557
900	29.710	70.273	51.282	18.831	-114.346	-55.556	12.151
1000	30.590	73.082	53.282	21.736	-114.329	-47.226	9.382
1100	31.470	75.601	55.036	24.477	-114.279	-38.990	7.101
1200	32.350	77.845	56.711	27.068	-114.205	-30.842	5.185
1300	33.230	80.199	58.310	29.644	-114.108	-22.777	3.556
1400	34.110	82.240	59.840	33.661	-113.996	-14.791	2.155



MERCURY MONOFLUORIDE, DIMERIC (Hg_2F_2) (crystal)

Mol. Wt. = 439.22
 $\Delta H_f^\circ 298.15 = [-116.0 \pm 3.0] \text{ kcal. mole}^{-1}$
 $S^\circ 298.15 = [38.4 \pm 2.0] \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 $T_{\text{sub}} = [818]^\circ \text{K (decomp.)}$

Heat of Formation. A value of $\Delta H_f^\circ 298.15$ was obtained from the cell measurements of G. G. Koerber and T. de Vries, J. Amer. Chem. Soc. 71, 5000 (1949). This was combined with ΔS_f° from the estimated entropy.

Heat Capacity and Entropy. The heat capacity was estimated by comparison with mercurous chloride. The entropy was estimated by comparison with the other mercurous and mercuric halides and use of additive entropy constants for the halogens from K. K. Kelley (Private Communication, 1960).

Sublimation. Sublimation with decomposition to $\text{Hg}_2(\text{g})$ and $\text{HF}_2(\text{g})$ was assumed at 840°K from the free energy change of the reaction.

Potassium Difluoride Uninegative Ion (KF₂⁻)
(Ideal Gas) GFW = 77.09935

T, °K	C _p ^o	S ^o	-(G ^o -H ^o)/T	H ^o -H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	log Kp
0							
100	13.627	62.561	62.561	.000	-166.000	-164.112	120.298
200							
298							
300	13.640	62.645	62.561	.027	-166.011	-164.100	119.547
400	14.130	66.645	63.103	1.417	-167.200	-163.263	99.203
500	14.386	69.828	64.141	2.684	-167.820	-162.208	70.401
600	14.537	72.466	65.315	4.291	-168.428	-161.028	46.654
700	14.631	74.714	66.501	5.749	-169.033	-159.745	29.878
800	14.693	76.672	67.652	7.216	-169.641	-158.379	18.267
900	14.736	78.405	68.753	8.687	-170.255	-156.934	9.109
1000	14.767	79.960	69.797	10.162	-170.883	-155.421	3.967
1100	14.790	81.368	70.786	11.640	-190.431	-152.821	30.363
1200	14.808	82.656	71.722	13.120	-190.842	-149.383	27.206
1300	14.822	83.842	72.609	14.602	-191.256	-145.910	24.530
1400	14.833	84.941	73.451	16.085	-191.674	-142.406	22.231
1500	14.843	85.964	74.252	17.569	-192.095	-138.871	20.234
1600	14.850	86.922	75.014	19.053	-192.520	-135.309	18.482
1700	14.856	87.823	75.741	20.538	-192.948	-131.722	16.934
1800	14.861	88.672	76.436	22.024	-193.378	-128.106	15.554
1900	14.865	89.476	77.102	23.511	-193.812	-124.471	14.317
2000	14.869	90.236	77.740	25.000	-194.250	-120.828	13.201
2100	14.872	90.966	78.352	26.484	-194.692	-117.126	12.189
2200	14.875	91.656	78.942	27.972	-195.139	-113.422	11.267
2300	14.878	92.317	79.509	29.459	-195.590	-109.690	10.424
2400	14.880	92.950	80.056	30.947	-196.047	-105.954	9.648
2500	14.882	93.558	80.584	32.435	-196.512	-102.191	8.934
2600	14.883	94.142	81.094	33.924	-196.981	-98.406	8.272
2700	14.885	94.703	81.588	35.412	-197.459	-94.608	7.658
2800	14.886	95.245	82.066	36.901	-197.945	-90.791	7.087
2900	14.887	95.767	82.529	38.389	-198.440	-86.952	6.553
3000	14.888	96.272	82.979	39.878	-198.945	-83.102	6.054
3100	14.889	96.760	83.416	41.367	-199.461	-79.230	5.586
3200	14.890	97.233	83.840	42.856	-199.989	-75.345	5.146
3300	14.891	97.691	84.253	44.345	-200.530	-71.443	4.731
3400	14.892	98.135	84.655	45.834	-201.085	-67.524	4.340
3500	14.892	98.567	85.046	47.323	-201.657	-63.585	3.970
3600	14.893	98.987	85.428	48.812	-202.246	-59.630	3.620
3700	14.893	99.395	85.800	50.302	-202.854	-55.659	3.288
3800	14.894	99.792	86.163	51.791	-203.485	-51.674	2.972
3900	14.895	100.179	86.517	53.281	-204.139	-47.674	2.672
4000	14.895	100.556	86.863	54.770	-204.818	-43.649	2.385
4100	14.895	100.928	87.202	56.260	-205.527	-39.611	2.111
4200	14.895	101.283	87.533	57.749	-206.269	-35.556	1.850
4300	14.896	101.633	87.857	59.239	-207.042	-31.482	1.600
4400	14.897	101.976	88.174	60.728	-207.857	-27.393	1.361
4500	14.897	102.310	88.484	62.218	-208.709	-23.279	1.131
4600	14.897	102.638	88.788	63.708	-209.606	-19.151	.910
4700	14.897	102.958	89.086	65.198	-210.551	-14.999	.697
4800	14.898	103.272	89.379	66.687	-211.546	-10.823	.493
4900	14.898	103.579	89.665	68.177	-212.595	-6.633	.296
5000	14.898	103.880	89.947	69.667	-213.698	-2.423	.106
5100	14.898	104.175	90.223	71.157	-214.861	1.818	-.078
5200	14.899	104.464	90.494	72.647	-216.085	6.078	-.265
5300	14.899	104.748	90.764	74.136	-217.372	10.364	-.427
5400	14.899	105.027	91.022	75.626	-218.723	14.668	-.584
5500	14.899	105.300	91.279	77.116	-220.138	19.003	-.755
5600	14.899	105.568	91.532	78.606	-221.617	23.370	-.912
5700	14.900	105.831	91.782	80.096	-223.161	27.752	-1.061
5800	14.900	106.091	92.025	81.586	-224.768	32.171	-1.212
5900	14.900	106.346	92.265	83.076	-226.437	36.615	-1.356
6000	14.900	106.596	92.502	84.566	-228.166	41.088	-1.497

Dec. 31, 1968

POTASSIUM DIFLUORIDE UNINEGATIVE ION (KF₂⁻)
(IDEAL GAS)
GFW = 77.09935
ΔH_f^o = -165 ± 10 kcal/mol
ΔH_f^o_{298.15} = -166 ± 10 kcal/mol
Point Group [D_{∞h}]
S_{298.15} = {63 ± 21 gibbs/mol
Ground State Quantum Weight = {11}

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
{350} (1)
{130} (2)
{500} (1)

Bond Distance: K-F = {2.17} Å

Bond Angle: F-K-F = {180°}

Rotational Constant: B₀ = {0.094} cm⁻¹

Heat of Formation

The heat of formation is estimated from three calculated values. The methods of calculation are described as follows. In a manner analogous to LiF₂(g), the first reaction considered is KF(g) + F⁻(g) = KF₂⁻(g) and the ΔH_f^o₂₉₈(KF₂⁻, g) is evaluated to be between 0 and 1/2(-50) = -25 kcal/mol (see LiF₂⁻(g) table for details), yielding from JANAF Tables.

The second reaction employed for estimation is K₂F₂(g) = KF₂⁻(g) + K⁺(g). The enthalpy change of this reaction is calculated as ΔH_r^o₂₉₈ = 1/2(50.0) + 138.8 = 163.8 kcal/mol where the KF₂⁻ ion is considered to be converted from K₂F₂(g) by breaking one of the two dimer association bonds (ΔH_r^o₂₉₈ = 50.0 kcal/mol) and one K⁺-F⁻ ionic bond (ΔH_r^o₂₉₈ = 138.8 kcal/mol). Using ΔH_f^o₂₉₈ = -206.2 and 122.9 kcal/mol for K₂F₂(g) and K⁺(g), we obtain the heat of formation for KF₂⁻(g) as -165 kcal/mol.

Based on an assumption that the electron affinity of KF₂(g) is similar to that of F (see LiF₂⁻(g) table for details), i.e. ΔH_r^o = 81.5 kcal/mol (1) for the reaction KF₂⁻(g) = KF₂(g) + e⁻(g), we derive ΔH_f^o₂₉₈(KF₂⁻, g) = -167.7 kcal/mol. The ΔH_f^o₂₉₈ for KF₂(g) is calculated as -84.2 kcal/mol from the value ΔH_r^o₂₉₈ = 143.3 kcal/mol for the reaction K₂F₂(g) = KF₂(g) + K(g) where the ΔH_r^o₂₉₈ value is calculated as the sum of two enthalpy changes, i.e. half of the heat of dimer dissociation into two monomers or 1/2(50.0) = 25.0 kcal/mol, and the heat of dissociation of KF(g) or 118.3 kcal/mol. The value of ΔH_f^o for KF₂⁻(g) is tentatively adopted as -166 ± 10 kcal/mol.

Heat Capacity and Entropy

The molecular structure is assumed to be linear, according to the suggestion given by Walsh (2) that molecules with not more than 16 valency electrons are linear in their ground states. The K-F bond distance is taken to be the same as that of KF(g) reported by Veazey and Gordy (3). The vibrational frequencies are estimated from the vibrational frequency of KF(g) using the method suggested by Herzberg (4). The moment of inertia is 2.971 x 10⁻³⁸ g cm². The enthalpy at 0°K is -1.293 kcal/mol.

References

1. H. O. Pritchard, Chem. Rev. 52, 529 (1953).
2. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
3. S. E. Veazey and W. Gordy, Phys. Rev. 138, A1303 (1965).
4. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945, p. 172.

F₂K⁻

Potassium Fluoride, Dimeric (K₂F₂)
(Ideal Gas) GFW = 116.2008

POTASSIUM FLUORIDE, DIMERIC (K₂F₂) (IDEAL GAS) GFW = 116.2008

$\Delta H_f^\circ = -205.1 \pm 2$ kcal/mol

$\Delta H_{298.15}^\circ = -206.2 \pm 2$ kcal/mol

Point Group D_{2h}

$S_{298.15}^\circ = 176.4 \pm 2.1$ gibbs/mol

Ground State Quantum Weight = [1]

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	1.000	INFINITE	INFINITE	4.381	-205.085	-205.085	INFINITE
100	13.560	58.214	58.214	3.797	-205.624	-205.624	19.970
200	17.768	68.484	68.484	1.855	-206.421	-206.421	150.511
298	18.768	76.484	76.484	1.000	-206.200	-205.310	
300	18.780	76.560	76.560	-0.035	-206.205	-205.325	
400	19.240	82.035	82.035	1.939	-207.699	-204.765	111.878
500	19.462	86.354	86.354	3.675	-208.056	-203.991	86.164
600	19.585	89.914	89.914	5.624	-208.387	-203.145	73.995
700	19.660	92.940	92.940	7.790	-208.704	-202.245	63.144
800	19.709	95.568	95.568	9.759	-209.029	-201.302	54.993
900	19.743	97.692	97.692	11.532	-209.356	-200.315	48.443
1000	19.767	99.373	99.373	13.107	-209.704	-199.284	43.556
1100	19.785	101.058	101.058	15.685	-210.079	-198.146	38.979
1200	19.799	102.560	102.560	17.664	-210.480	-197.187	34.875
1300	19.810	103.916	103.916	19.625	-210.904	-196.304	31.404
1400	19.818	105.165	105.165	21.684	-211.344	-195.484	28.429
1500	19.825	106.334	106.334	23.834	-211.804	-194.724	25.852
1600	19.831	107.421	107.421	26.071	-212.284	-194.024	23.598
1700	19.835	108.434	108.434	28.394	-212.784	-193.384	21.610
1800	19.839	109.371	109.371	30.804	-213.304	-192.804	19.843
1900	19.843	110.234	110.234	33.304	-213.844	-192.284	18.263
2000	19.845	111.021	111.021	35.894	-214.404	-191.824	16.840
2100	19.848	111.736	111.736	38.564	-214.984	-191.424	15.554
2200	19.850	112.371	112.371	41.314	-215.584	-191.084	14.385
2300	19.852	112.921	112.921	44.144	-216.204	-190.804	13.318
2400	19.853	113.381	113.381	47.054	-216.844	-190.584	12.339
2500	19.855	113.751	113.751	50.044	-217.504	-190.424	11.439
2600	19.856	114.031	114.031	53.114	-218.184	-190.324	10.608
2700	19.857	114.221	114.221	56.264	-218.884	-190.284	9.839
2800	19.858	114.331	114.331	59.494	-219.604	-190.304	9.125
2900	19.859	114.351	114.351	62.804	-220.344	-190.384	8.460
3000	19.860	114.271	114.271	66.194	-221.104	-190.524	7.839
3100	19.861	114.091	114.091	69.664	-221.884	-190.724	7.258
3200	19.861	113.811	113.811	73.214	-222.684	-190.984	6.713
3300	19.862	113.431	113.431	76.844	-223.504	-191.304	6.201
3400	19.863	112.951	112.951	80.554	-224.344	-191.684	5.719
3500	19.863	112.371	112.371	84.344	-225.204	-192.124	5.264
3600	19.864	111.691	111.691	88.214	-226.084	-192.624	4.834
3700	19.864	110.911	110.911	92.164	-227.004	-193.184	4.427
3800	19.864	110.031	110.031	96.194	-227.964	-193.804	4.041
3900	19.865	109.051	109.051	100.304	-228.964	-194.484	3.675
4000	19.865	108.071	108.071	104.494	-229.994	-195.224	3.325
4100	19.865	107.091	107.091	108.764	-231.054	-196.024	2.993
4200	19.865	106.111	106.111	113.114	-232.144	-196.884	2.675
4300	19.866	105.131	105.131	117.544	-233.264	-197.804	2.372
4400	19.866	104.151	104.151	122.054	-234.414	-198.784	2.082
4500	19.866	103.171	103.171	126.644	-235.594	-199.824	1.804
4600	19.867	102.191	102.191	131.314	-236.804	-200.924	1.538
4700	19.867	101.211	101.211	136.064	-238.044	-202.084	1.281
4800	19.867	100.231	100.231	140.894	-239.314	-203.304	1.035
4900	19.867	99.251	99.251	145.704	-240.614	-204.584	0.798
5000	19.867	98.271	98.271	150.594	-241.944	-205.924	0.569
5100	19.868	97.291	97.291	155.464	-243.304	-207.324	0.348
5200	19.868	96.311	96.311	160.314	-244.694	-208.784	0.134
5300	19.868	95.331	95.331	165.144	-246.114	-210.304	0.072
5400	19.868	94.351	94.351	170.004	-247.564	-211.884	0.035
5500	19.868	93.371	93.371	174.894	-249.044	-213.524	0.004
5600	19.868	92.391	92.391	179.814	-250.554	-215.224	0.000
5700	19.868	91.411	91.411	184.764	-252.094	-216.984	0.000
5800	19.868	90.431	90.431	189.744	-253.664	-218.804	0.000
5900	19.868	89.451	89.451	194.754	-255.264	-220.684	0.000
6000	19.868	88.471	88.471	199.794	-256.894	-222.624	0.000

June 30, 1961; Mar. 31, 1964; June 30, 1969

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	g
[273] (1)	[150] (1)
[150] (1)	[255] (1)
[235] (1)	[258] (1)

Bond Distance: K-F = 2.2 Å

Bond Angles: F-K-F = [90°] K-F-K = [90°]

Product of the Moments of Inertia: I_AI_BI_C = [2.240 × 10⁻¹¹³] g³ cm⁶

Heat of Formation

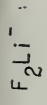
The equilibrium constants (K_c) for the reaction K₂F₂(g) = 2KF(g), in the temperature range 974-1052°K, were determined by Eisenstadt, Rothberg, and Kusch (2). Although the reported absolute values of the vapor pressures of KF(c) are not adopted for evaluation, the reported K_c values are used to calculate the enthalpy change (ΔH₂₉₈°) for the above reaction. The second law and third law values of ΔH₂₉₈° are derived as 51.0 ± 1.6 and 50.0 kcal/mol, respectively. Based on the third law ΔH₂₉₈° and ΔH₂₉₈°(KF, g) = -76.1 kcal/mol, we obtain ΔH_f° = -206.2 kcal/mol for K₂F₂(g) which is tentatively adopted.

Heat Capacity and Enthalpy

The molecular structure and K-F bond distance were determined by Akishin and Rambidi (2), using electron diffraction with sector microphotometry. The bond angles are estimated by comparison with other alkali halide dimers. The vibrational frequencies are taken from Berkowitz (3) which were calculated based on an ionic model. The three principal moments of inertia are: I_A = 3.1423 × 10⁻³⁸, I_B = 1.5267 × 10⁻³⁸, and I_C = 4.6690 × 10⁻³⁸ g cm².

References

1. M. Eisenstadt, G. M. Rothberg, and P. Kusch, J. Chem. Phys. **29**, 797 (1958).
2. P. A. Akishin and N. G. Rambidi, Z. Physik. Chem. **213**, 111 (1960).
3. J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960).



LITHIUM DIFLUORIDE UNINEGATIVE ION (LiF₂⁻) (IDEAL GAS)

GFW = 44.93635

Lithium Difluoride Uninegative Ion (LiF₂⁻) (Ideal Gas) GFW = 44.93635

Point Group [D_{∞h}]
S_{298.15} = (55 ± 2) gibbs/mol
Ground State Quantum Weight = (1)

ΔHf₀⁰ = (-169 ± 15) kcal/mol
ΔHf_{298.15}⁰ = (-170 ± 15) kcal/mol

T, K	Cp ⁰	$\frac{H^0 - H^0_{298}}{T}$	$\frac{H^0 - H^0_{298}}{T}$	ΔHf ⁰	Log Kp
0					
100	11.393	54.653	54.653	-170.000	123.403
200	11.413	54.984	54.984	-170.013	122.635
300	12.005	56.136	56.136	-170.117	121.890
400	12.922	58.219	58.219	-170.249	121.160
500	13.363	61.551	61.551	-170.407	120.432
600	13.682	65.129	65.129	-170.591	119.708
700	13.918	67.979	67.979	-170.800	119.000
800	14.095	69.129	69.129	-171.025	118.300
900	14.230	70.621	70.621	-171.268	117.610
1000	14.335	71.983	71.983	-171.528	116.930
1100	14.416	73.234	73.234	-171.800	116.260
1200	14.468	74.390	74.390	-172.080	115.600
1300	14.506	75.468	75.468	-172.368	114.950
1400	14.536	76.470	76.470	-172.660	114.310
1500	14.563	77.413	77.413	-172.960	113.680
1600	14.590	78.300	78.300	-173.270	113.050
1700	14.617	79.138	79.138	-173.590	112.430
1800	14.642	79.932	79.932	-173.920	111.810
1900	14.667	80.687	80.687	-174.260	111.200
2000	14.691	81.405	81.405	-174.610	110.600
2100	14.715	82.089	82.089	-174.970	110.010
2200	14.739	82.742	82.742	-175.340	109.430
2300	14.762	83.366	83.366	-175.720	108.860
2400	14.784	83.970	83.970	-176.110	108.300
2500	14.806	84.559	84.559	-176.510	107.750
2600	14.827	85.127	85.127	-176.920	107.210
2700	14.848	85.676	85.676	-177.340	106.680
2800	14.868	86.208	86.208	-177.770	106.160
2900	14.887	86.725	86.725	-178.210	105.650
3000	14.905	87.228	87.228	-178.660	105.150
3100	14.923	87.718	87.718	-179.120	104.660
3200	14.940	88.195	88.195	-179.590	104.180
3300	14.956	88.659	88.659	-180.070	103.710
3400	14.971	89.111	89.111	-180.560	103.250
3500	14.985	89.550	89.550	-181.060	102.800
3600	14.998	89.977	89.977	-181.570	102.360
3700	15.010	90.392	90.392	-182.090	101.930
3800	15.021	90.795	90.795	-182.620	101.510
3900	15.031	91.187	91.187	-183.160	101.100
4000	15.040	91.568	91.568	-183.710	100.700
4100	15.048	91.938	91.938	-184.270	100.310
4200	15.055	92.298	92.298	-184.840	99.930
4300	15.061	92.648	92.648	-185.420	99.560
4400	15.066	92.988	92.988	-186.010	99.200
4500	15.070	93.318	93.318	-186.610	98.850
4600	15.073	93.638	93.638	-187.220	98.510
4700	15.075	93.948	93.948	-187.840	98.180
4800	15.076	94.248	94.248	-188.470	97.860
4900	15.076	94.538	94.538	-189.110	97.550
5000	15.075	94.818	94.818	-189.760	97.250
5100	15.073	95.088	95.088	-190.420	96.960
5200	15.070	95.348	95.348	-191.090	96.680
5300	15.066	95.598	95.598	-191.770	96.410
5400	15.061	95.838	95.838	-192.460	96.150
5500	15.055	96.068	96.068	-193.160	95.900
5600	15.048	96.288	96.288	-193.870	95.660
5700	15.040	96.498	96.498	-194.590	95.430
5800	15.031	96.698	96.698	-195.320	95.210
5900	15.021	96.888	96.888	-196.060	95.000
6000	15.010	97.068	97.068	-196.810	94.800

Dec. 31, 1968

Vibrational Frequencies and Degeneracies

$\frac{w}{cm^{-1}}$
(1300) (1)
(350) (2)
(550) (1)

Bond Distance: Li-F = (1.57) Å

Bond Angle: F-Li-F = (180°)

Rotational Constant: B₀ = (0.180) cm⁻¹

Heat of Formation

Due to lack of thermal data, the heat of formation for LiF₂⁻(g) is arbitrarily selected from the following three estimated values. For the reaction (1) LiF(g) + F⁻(g) = LiF₂⁻(g), we expect the enthalpy change would be between 0 to -31 kcal/mol. Comparison with the other molecules like CO₂, BO₂, B₂F₂, etc. having 16 valence electrons leads us to assume that the isoelectronic molecule LiF₂⁻ should also be quite stable. This indicates that reaction (1) is favorable or ΔHr₂₉₈ is negative. However, the Li-F bond strength is expected to be weaker than half of the two ionic bonds between Li⁺ and F⁻ in Li₂F molecule (see Li₂F₂ (g) table for the molecular structure). In other words, the ΔHr₂₉₈ value of reaction (1) is less negative than half of the heat of dimerization (-62.4 kcal/mol). Incorporating ΔHr₂₉₈ = 0 and -31 kcal/mol, respectively, for reaction (1), with ΔHf₂₉₈⁰ = -81.45 and -62.2 kcal/mol for LiF(g) and F⁻(g), we derived the corresponding values for ΔHf₂₉₈⁰(LiF₂⁻, g) as -144 and -175 kcal/mol, which are the upper and lower limits.

The electron affinities of Li and F atoms are reported as 0.7 and 3.448 eV, respectively, by Backett and Cassidy (1). From this data we estimate that the electron affinity of LiF₂⁻(g) should be closer to that of F atom than to that of Li. Assuming ΔHr₂₉₈⁰ = electron affinity of F atom = 83.5 kcal/mol for the reaction LiF₂⁻(g) = LiF(g) + F⁻(g), we obtain the heat of formation for LiF₂⁻(g) as -177.3 kcal/mol. The ΔHf₂₉₈⁰(LiF₂⁻, g) used for calculation is derived from an estimated ΔHr₂₉₈⁰ = 169.9 kcal/mol for the decomposition of LiF dimer or LiF₂⁻(g) = LiF₂(g) + Li(g) as the sum of two enthalpy changes, namely, half of the heat of dissociation of the dimer and the heat of dissociation of the monomer.

The third estimated value for the heat of formation of LiF₂⁻(g) is calculated as follows. Based on the two heats of reaction, i.e. ΔHr₂₉₈⁰ = 62.4 kcal/mol for LiF₂(g) = LiF(g), and ΔHr₂₉₈⁰ = 183.5 kcal/mol for LiF(g) + F⁻(g), we assume the enthalpy change of the reaction LiF₂⁻(g) = LiF₂(g) + Li⁺(g) to be 1/2(62.4) + 183.5 = 714.7 kcal/mol. In other words, we consider the LiF₂⁻(g) molecule is formed by breaking half of the dimer dissociation bonds and one monomer dissociation bond to produce two ions. Using ΔHf₂₉₈⁰ = -225.33 and 164.24 kcal/mol for Li₂F₂(g) and Li⁺(g), we evaluate ΔHf₂₉₈⁰(LiF₂⁻, g) = -174.9 kcal/mol.

From the above three estimated values, we tentatively choose ΔHf₂₉₈⁰(LiF₂⁻, g) as -170 ± 15 kcal/mol.

Heat Capacity and Entropy

According to A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953), molecules with not more than 16 valence electrons are linear in their ground states. Since LiF₂⁻(g) has 16 valence electrons, we assume its molecular structure is linear. The Li-F bond distance is estimated by comparison with that of LiF(g) reported by Wharton et al. (2). The vibrational frequencies are estimated from those of the isoelectronic gaseous molecules, CO₂ and BeF₂. The moment of inertia is 1.555 × 10⁻³⁸ g cm². The enthalpy at 0°K is -2.653 kcal/mol.

References

1. C. W. Beckett and E. C. Cassidy, U. S. Natl. Bur. Std. Rept. 8628, 1 January 1965.
2. L. Wharton, W. Klumperman, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, J. Chem. Phys. 38, 1703 (1963).

(IDEAL GAS)

LITHIUM FLUORIDE, DIMERIC (Li₂F₂)

Lithium Fluoride, Dimeric (Li₂F₂)
(Ideal Gas) GFW = 51.8748

GFW = 51.8748

 $\Delta H_f^\circ = -224.20 \pm 4.0$ kcal/mol $\Delta H_f^\circ(\text{298.15}) = -225.33 \pm 4.0$ kcal/molPoint Group D_{2h} $S^\circ_{298.15} = 61.8 \pm 2$ gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

	ω, cm^{-1}	ω, cm^{-1}
	[570] (1)	301.5 (1)
	[570] (1)	571.5 (1)
	[490] (1)	658.0 (1)
Bond Distances: Li-F = 1.68 Å		F-F = 2.67 Å
Bond Angles: Li-F-Li = 74.76°		F-Li-F = 105.24°
Product of the Moments of Inertia: $I_A I_B I_C = 3.6766 \times 10^{-115} \text{ g cm}^2$		

Heat of Formation

The heat of formation (ΔH_f°) is calculated based on the adopted value $\Delta H_f^\circ(\text{1000}) = 61.4$ kcal/mol for the reaction $\text{Li}_2\text{F}_2(\text{g}) = 2\text{LiF}(\text{g})$ which is consistent with the literature values listed in the table below. Due to lack of knowledge of the fragmentation patterns, the relative ionization cross sections of the ionic species formed in the mass spectrometer, and the molecular constants of the LiF polymers, the evaluation of equilibrium constants used to calculate ΔH_f° involves considerable uncertainty. In order to solve this problem more research work seems necessary.

 $\Delta H_f^\circ(\text{1000})$, kcal/mol

Investigator

Experimental Method

1. Berkowitz et al. (1962)	61.6 ± 2	mass spectrometry with a double-oven apparatus
2. Buchler and Stauffer (1966)	61.3 ± 3	mass spectrometry with a two-piece Ni Knudsen cell
3. Eisenstadt et al. (1958)	61.2	molecular-beam velocity-selector
4. Hildenbrand et al. (1964)	60.4 ± 3	torsion effusion
5. Akishin et al. (1959)	59.5 ± 3	mass spectrometry with a double effusion chamber
6. Porter and Schoonmaker (1958)	65.0 •	mass spectrometry with a Mo Knudsen cell
• derived from reported vapor pressures of LiF(g) and Li ₂ F ₂ (g) at 1073°K.		

Heat Capacity and Entropy

The molecular structure of Li₂F₂(g) was determined as D_{2h} by Buchler et al. (12), using electric deflection and mass spectrometric detection. Akishin and Rambidi (1) studied the structure of Li₂F₂(g) by electron deflection with sector microphotography and assigned the bond distances of Li-F and F-F which are adopted. Evidence for a matrix stabilized linear structure of Li₂F₂ has been obtained by extending the spectral measurements for matrix isolated lithium fluoride into the far infrared region by Redington (8) and Abramowitz et al. (9).

Klemperer and Norris (10) observed two infrared-active vibrational frequencies, 640 and 460 cm⁻¹, and assigned them as $\nu_6(\text{F}_2)$ and $\nu_6(\text{LiF})$. The infrared absorption spectra of lithium fluoride monomer and dimer isolated in solid inert gas matrices were investigated by Linevsky (11), Shelton and Pitzer (13), and Schlick and Schnepf (14). Redington (8) obtained infrared spectra of LiF species suspended in solid Ne, O₂, CO, and CH₄ at liquid-helium temperature. The observed solvent shifts for LiF and Li₂F₂ spectra exhibit several regularities. The vibrational frequencies used for calculation are those reported by Shelton (15) who re-examined the spectrum of LiF species over the range 200 - 4000 cm⁻¹, using sample purity of 99.3%. The saturated vapor was isolated at 900°C and the superheated unsaturated vapor at 1200°C. A variety of deposition rates and matrix dilutions was tried. Based on the frequencies assigned to the isotopic species, the vibrational frequencies of the natural isotopic Li₂F₂(g) are calculated. It appears that the vibrational frequencies calculated on the basis of the potential function for an ionic model by Berkowitz (16) are too low.

The three principal moments of inertia are: $I_A = 2.3970 \times 10^{-39}$, $I_B = 1.1244 \times 10^{-38}$ and $I_C = 1.3641 \times 10^{-38} \text{ g cm}^2$.

References

1. J. Berkowitz, H. A. Tasman, and W. A. Chupka, *J. Chem. Phys.*, **36**, 2170 (1962).
2. M. Buchler and C. W. Stauffer, *Thermodynamics, Vol. 1*, Interscience, New York, 1966.
3. D. L. Hildenbrand, W. F. Hall, F. Ju, and N. D. Porter, *J. Chem. Phys.*, **40**, 2892 (1964).
4. P. A. Akishin, L. N. Gorokhov, and L. N. Sidorov, *Russ. J. Phys. Chem. (English Transl.)*, **33**, 648 (1959).
5. R. F. Porter and R. C. Schoonmaker, *J. Chem. Phys.*, **29**, 1070 (1958).
6. P. A. Akishin and N. G. Rambidi, *Z. Physik. Chem.*, **213**, 111 (1960).
7. S. P. Akishin, *Thermodynamics, Vol. 1*, Interscience, New York, 1966.
8. S. P. Akishin, *Thermodynamics, Vol. 1*, Interscience, New York, 1966.
9. S. P. Akishin, *Thermodynamics, Vol. 1*, Interscience, New York, 1966.
10. S. P. Akishin, *Thermodynamics, Vol. 1*, Interscience, New York, 1966.
11. M. J. Linevsky, *J. Chem. Phys.*, **34**, 587 (1961); **35**, 658 (1963).
12. A. Buchler, J. L. Stauffer, and W. Klemperer, *J. Am. Chem. Soc.*, **88**, 4544 (1966).
13. A. Shelton and K. S. Pitzer, *J. Phys. Chem.*, **67**, 882 (1963).
14. A. Schlick and W. Schnepf, *J. Chem. Phys.*, **37**, 83 (1962).
15. A. Schlick, *Thermodynamics, Vol. 1*, Interscience, New York, 1966.
16. J. Berkowitz, *J. Chem. Phys.*, **32**, 1519 (1960).

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Dec. 31, 1968

T, °K.	C _p ^a	S ^a	-(F ^a -H ₂₉₈)/T	H ^a -H ₂₉₈	ΔH _f ^a	ΔF _f ^a	Log K _p
0	0.000	0.000	INFINITE	-2.370	-267.764	-267.764	INFINITE
100	5.193	2.552	24.476	-2.452	-267.805	-267.805	24.476
200	11.472	6.835	11.472	-2.452	-267.805	-267.805	24.476
298	14.720	13.683	13.683	-2.452	-267.805	-267.805	24.476
300	14.790	13.775	13.775	-2.452	-267.805	-267.805	24.476
400	16.390	18.265	14.785	-2.452	-267.805	-267.805	24.476
500	17.310	22.028	15.468	-2.452	-267.805	-267.805	24.476
600	17.830	25.232	16.835	-2.452	-267.805	-267.805	24.476
700	18.250	28.013	18.237	-2.452	-267.805	-267.805	24.476
800	18.600	30.473	19.616	-2.452	-267.805	-267.805	24.476
900	18.930	32.683	20.947	-2.452	-267.805	-267.805	24.476
1000	19.250	34.693	22.223	-2.452	-267.805	-267.805	24.476
1100	19.520	36.535	23.441	-2.452	-267.805	-267.805	24.476
1200	19.800	38.250	24.605	-2.452	-267.805	-267.805	24.476
1300	20.080	39.846	25.717	-2.452	-267.805	-267.805	24.476
1400	20.350	41.344	26.780	-2.452	-267.805	-267.805	24.476
1500	20.610	42.757	27.799	-2.452	-267.805	-267.805	24.476
1600	20.860	44.096	28.776	-2.452	-267.805	-267.805	24.476
1700	21.140	45.369	29.715	-2.452	-267.805	-267.805	24.476
1800	21.400	46.585	30.612	-2.452	-267.805	-267.805	24.476
1900	21.660	47.749	31.489	-2.452	-267.805	-267.805	24.476
2000	21.920	48.867	32.331	-2.452	-267.805	-267.805	24.476
2100	22.175	49.942	33.144	-2.452	-267.805	-267.805	24.476
2200	22.430	50.980	33.931	-2.452	-267.805	-267.805	24.476
2300	22.686	51.982	34.694	-2.452	-267.805	-267.805	24.476
2400	22.943	52.953	35.435	-2.452	-267.805	-267.805	24.476
2500	23.200	53.895	36.155	-2.452	-267.805	-267.805	24.476

Dec. 31, 1960; June 30, 1964; Mar. 31, 1966

$S_{298.15}^{\circ} = 13.68 \pm 0.07$ cal. deg.⁻¹ mole⁻¹
 $T_m = 1536^{\circ}\text{K.}$
 $\Delta H_f^{\circ} 0 = -267.8 \pm 0.3$ kcal. mole⁻¹
 $\Delta H_f^{\circ} 298.15 = -268.7 \pm 0.3$ kcal. mole⁻¹
 $\Delta H_m^{\circ} = 13.90$ kcal. mole⁻¹
 $\Delta H_g^{\circ} 298.15 = 95.5 \pm 1.5$ kcal. mole⁻¹

Heat of Formation.

The value of $\Delta H_f^{\circ} 298.15$ for MgF₂(c) was obtained from E. Rudzitis and W. N. Hubbard, Argonne National Laboratory, Argonne, Illinois, private communication, dated June 18, 1964. This value was determined by fluorine bomb calorimetry which is considered as comparatively the best method available at the present time. The heats of reaction involving MgF₂(c) were measured by many early investigators. However, the $\Delta H_f^{\circ} 298.15$ (MgF₂, c) values derived are in reasonable agreement. The results are presented as follows.

Investigator	Chemical Reaction	$\Delta H_f^{\circ} 298.15^{\circ}$, kcal. mole ⁻¹	$\Delta H_f^{\circ} 298.15^{\circ}$, kcal. mole ⁻¹
Domange (1)	MgF ₂ (c) + H ₂ O(g) → 2HF(g) + MgO(c)	+51.76 ± 1.2(1)	-267.3 ± 1.3
Wartenberg (2)	Mg(c) + 2(HF·80H ₂ O) → MgF ₂ (c) + H ₂ (g) + 160H ₂ O(l)	-109.5 ± 0.7	-262.1 ± 0.8
Torgeson, et al. (3)	Mg(OH) ₂ (c) + 2HF(sol.) → MgF ₂ (c) + 2H ₂ O(l)	-29.09	-266.5 ± 0.8
Gross, et al. (4)	Mg(c) + PbF ₂ (c) → MgF ₂ (c) + Pb(c)	-109.5 ± 1.5	-269.1 ± 1.8
(1) L. Domange, Ann. chim. phys. 7(11)225 (1937). The ΔH_f° value was calculated by the third law method.			
(2) H. V. Wartenberg, Z. anorg. allgem. Chem. 249, 100 (1942).			
(3) D. R. Torgeson and T. G. Sahara, J. Am. Chem. Soc. 70, 2156 (1948).			
(4) P. Gross, C. Hayman and D. L. Levi, Trans. Faraday Soc. 50, 477 (1954).			

Heat Capacity and Entropy.

The low temperature heat capacities, 54.22-296.5°K., were measured by S. S. Todd, J. Am. Chem. Soc. 71, 4115 (1949). The high temperature heat capacities, 298-1536°K., were obtained from the heat content measurements determined by B. P. Naylor, J. Am. Chem. Soc. 67, 150 (1945). These two sets of data were joined smoothly at 298°K. $S_{298.15}$ was obtained from C_p data reported by S. S. Todd, loc. cit., using $S_{298.15}^{\circ}$ (extrap.) = 0.537 cal. deg.⁻¹ mole⁻¹.

Melting Data.

T_m and ΔH_m° were taken from B. P. Naylor, loc. cit.

Heat of Sublimation.

The vapor pressure of MgF₂(c) has been measured by seven investigators. Using the reported data, the respective $\Delta H_g^{\circ} 298.15$ for MgF₂(c) were calculated (see MgF₂(g) table for detail). The adopted value was selected to be 95.5 ± 1.5 kcal. mole⁻¹.

Magnesium Difluoride (MgF₂)

(Liquid) Mol. Wt. = 62.3088



MOL. WT. = 62.3088

(LIQUID)

MAGNESIUM DIFLUORIDE (MgF₂)

T, °K. C_p S° - (F° - H₂₉₈°)/T kcal. mole⁻¹ ΔH_f⁰ ΔF_f⁰ Log K_p

S_{298.15}⁰ = 15.290 cal. deg.⁻¹ mole⁻¹
T_m = 1536°K.
T_b = [2499]°K.
ΔH_f⁰ 298.15 = -259.557 kcal. mole⁻¹
ΔH_m⁰ = 13.90 kcal. mole⁻¹
ΔH_v⁰ = [63.48] kcal. mole⁻¹

Heat of Formation.

ΔH_f⁰ 298.15(l) was obtained from ΔH_f⁰ 298.15(c) by adding ΔH_m⁰ and the difference between H_m⁰ - H_l⁰ 298.15 for crystal and liquid.

Heat Capacity and Entropy.

Heat capacity (1691-1800°K.) was reported by B. F. Naylor, J. Am. Chem. Soc. 67, 150 (1945). The same value was used for other temperatures. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and ΔH_m⁰ were obtained from B. F. Naylor, loc. cit.

Vaporization Data.

T_b was obtained from equilibrium calculation between the species MgF₂(l), MgF₂(g), and (MgF₂)₂(g), i.e., the temperature at which the sum of the partial pressures of MgF₂(g) and (MgF₂)₂(g) equals one atmosphere. From the difference between the heats of formation of MgF₂(l) and MgF₂(g) at the boiling point, the heat of vaporization was calculated. At the boiling point the amount of dimeric species is negligible in comparison with that of the monomeric species.

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100						
200						
298						
2250	15.290	15.290	-0.000	-259.557	-247.341	181.297
22570	15.430	15.290	+0.042	-259.540	-247.266	180.124
22570	21.923	16.176	2.299	-258.667	-243.308	132.931
22570	26.959	17.847	4.556	-257.859	-239.563	104.708
22570	31.074	19.719	6.813	-257.103	-235.976	85.950
22570	34.553	21.596	9.470	-256.390	-232.511	72.590
22570	37.567	23.408	11.327	-255.724	-229.147	62.597
22570	40.225	25.132	13.584	-255.104	-225.862	54.844
22570	42.603	26.763	15.841	-254.651	-222.463	48.617
22570	44.754	28.302	18.008	-254.088	-219.073	43.524
22570	46.718	29.756	20.355	-253.555	-215.731	39.288
22570	48.525	31.131	22.612	-253.054	-212.432	35.711
22570	50.197	32.434	24.869	-252.584	-209.174	32.577
22570	51.755	33.671	27.126	-252.146	-205.956	29.616
22570	53.211	34.847	29.383	-251.734	-202.774	26.833
22570	54.580	35.968	31.640	-251.342	-199.626	24.260
22570	55.870	37.038	33.897	-250.967	-196.512	21.887
22570	57.090	38.062	36.154	-250.607	-193.432	19.614
22570	58.248	39.042	38.411	-250.260	-190.385	17.441
22570	59.349	39.983	40.668	-249.926	-187.370	15.365
22570	60.399	40.888	42.925	-249.604	-184.385	13.389
22570	61.402	41.758	45.182	-249.294	-181.430	11.512
22570	62.363	42.596	47.439	-248.996	-178.504	9.735
22570	63.284	43.406	49.696	-248.710	-175.607	8.058
22570	64.160	44.187	51.953	-248.436	-172.738	6.481
22570	65.021	44.943	54.210	-248.172	-169.896	5.004
22570	65.842	45.675	56.467	-247.919	-167.081	3.627
22570	66.634	46.384	58.724	-247.676	-164.292	2.350
22570	67.399	47.072	60.981	-247.442	-161.528	1.173
22570	68.139	47.740	63.238	-247.218	-158.790	0.096
22570	68.856	48.388	65.495	-246.994	-156.077	-0.981
22570	69.550	49.019	67.752	-246.779	-153.389	-2.158
22570	70.224	49.633	70.009	-246.572	-150.726	-3.435
22570	70.878	50.231	72.266	-246.372	-148.088	-4.812
22570	71.514	50.813	74.523	-246.178	-145.474	-6.289
22570	72.132	51.381	76.780	-245.989	-142.884	-7.866
22570	72.734	51.935	79.037	-245.804	-140.318	-9.543
22570	73.321	52.476	81.294	-245.624	-137.776	-11.320
22570	73.892	53.004	83.551	-245.448	-135.258	-13.197



MAGNESIUM DIFLUORIDE (MgF₂) (IDEAL GAS)

MOL. WT. = 62.3088

$$\Delta H_f^0 = -172.0 \pm 1.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = -173.2 \pm 1.5 \text{ kcal. mole}^{-1}$$

Point Group C_{2v}

$$S_{298.15}^0 = 61.734 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

 $\omega_e, \text{ cm.}^{-1}$

478 (1)

241 (1)

834 (1)

Bond Distances: Mg-F = 1.77 ± 0.02 Å

Bond Angle: F-Mg-F = 150 ± 5°

Product of the Moments of Inertia: $I_A I_B I_C = 1.80832 \times 10^{-115} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation

The vapor pressure of MgF₂(g) over MgF₂(c) and MgF₂(l) has been measured by many investigators using different methods. Based on the reported vapor pressure data, the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K.	Method*	Second Law Value	Third Law Value	Drift
Ruff and Boucher ¹	1394 - 2129	a	99.49 ± 2.56	98.19	-1.86 ± 1.31
Quenther ²	1284 - 1550	b	95.06 ± 0.50	95.64	0.45 ± 0.33
Hammer ³	1451 - 1533	b	93.68 ± 2.67	96.21	1.62 ± 1.73
	1588 - 1613	b	94.17 ± 6.00	96.21	1.28 ± 4.16
	1413 - 1518	b	95.75 ± 2.89	96.19	0.22 ± 2.08
	1539 - 1614	c	96.81 ± 4.35	96.09	-0.51 ± 2.74
Berkowitz and Marquart ⁴	1450	c	—	94.68	—
Farber, et al. ⁵	1273 - 1513	c	80.72 ± 1.11	91.58	7.75 ± 0.80
Hildenbrand, et al. ⁶	1328 - 1527	c	91.80 ± 1.11	93.40	1.12 ± 0.78
	1544 - 1604	c	94.49 ± 5.00	93.95	-0.39 ± 3.17
	1455 - 1533	c	104.79 ± 1.00	95.75	-8.14 ± 0.65
	1540 - 1608	c	102.81	95.48	—
Margrave, et al. ⁷	1200 - 1550	c	94.0	—	—
	1241 - 1492	b	93.77 ± 2.5	93.07	1.89 ± 0.08

*a = Monometric method; b = Knudsen effusion method; and c = Torsion effusion method

1 O. Ruff and L. LeBoucher, Z. anorg. allgem. Chem. 219, 378 (1934).

2 K. O. Quenther, Oesterr. Ber. 31, 9 (1959).

3 R. R. Hamner, Ph.D. Thesis, University of California, 1961. Also see R. R. Hamner and J. A. Peek, J. Am. Ceram. Soc. 47, 284 (1964).

4 J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962). The value, 91.38 kcal. mole⁻¹, was converted from the reported value 88 kcal. mole⁻¹ at 1350°K.5 M. A. Greenbaum, R. C. McRae, and M. Farber, J. Phys. Chem. 68, 985 (1964), whose reported ΔH_f⁰ 298.15 value was derived using different values of free energy functions for MgF₂(c) and MgF₂(g) from those used here.6 Data of Hildenbrand, et al., and Hildenbrand, et al., J. Phys. Chem. 68, 985 (1964), whose reported ΔH_f⁰ 298.15 value was derived using different values of free energy functions for MgF₂(c) and MgF₂(g) from those used here.

7 J. W. Green, G. D. Blue, T. C. Ehlers, and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).

When vapor pressure data were determined above melting point, 1536°K., the heat of sublimation was derived from the heat of vaporization obtained incorporating heat of melting. All data were carefully examined and some inconsistent vapor pressure points were discarded. The heat value of ΔH_f⁰ 298.15 for MgF₂(c) was selected as 95.5 ± 1.5 kcal. mole⁻¹. The heat of formation for MgF₂(g) was calculated from the heats of formation and sublimation for MgF₂(c).

Heat Capacity and Entropy

The molecular structure of MgF₂(g) has been reported to be linear by A. Büchler, J. L. Steuffer and W. Klemperer, Interim Technical Report No. 7, June 30, 1964, A. D. Little, Inc., and bent by M. J. Linevsky, First Quarterly Report, Nov. 1, 1963 - Jan. 31, 1964, General Electric Company. An intensive investigation of the matrix spectrum of MgF₂(g) has been made recently by D. E. Mann and O. V. Calder, National Bureau of Standards Report 8919, July 1, 1965. The final results were presented by D. E. Mann at the ICRP Working Group on Thermochemistry meeting on Mar. 17, 1968. The vibrational frequencies, bent structure and bond angle were confirmed by use of isotopic substitution, and were adopted here. The Mg-F bond distance was reported by P. A. Aikshin, V. P. Spiridonov, O. A. Sobolev and V. A. Naumov, Zh. Fiz. Khim. 32, 463 (1957). The three principal moments of inertia are: I_A = 5.1680 × 10⁻⁴⁰, I_B = 1.8442 × 10⁻³⁸ and I_C = 1.8959 × 10⁻³⁸ g. cm.²

T, °K.	C _p	S°	-(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	INFINITE	-2.878	-172.772	-172.772	INFINITE
100	6.942	50.059	171.232	-2.059	-172.602	-173.571	370.340
200	10.468	67.319	62.764	-1.089	-173.094	-174.342	190.512
298	11.621	61.734	-0.000	-0.000	-173.200	-174.832	128.155
300	11.638	61.806	0.022	-173.203	-174.842	-174.842	127.372
400	12.304	65.052	1.245	-173.548	-175.815	-175.815	70.657
500	12.615	66.073	2.468	-173.579	-175.833	-175.833	30.168
600	13.103	70.437	3.782	-173.777	-176.267	-176.267	64.205
700	13.295	72.472	5.182	-174.000	-176.664	-176.664	55.157
800	13.427	74.236	6.439	-174.255	-177.028	-177.028	46.362
900	13.522	75.844	7.617	-174.544	-177.359	-177.359	38.068
1000	13.592	77.272	8.643	-174.862	-177.652	-177.652	30.168
1100	13.644	78.570	10.505	-175.207	-177.506	-177.506	35.267
1200	13.685	79.759	12.187	-175.682	-177.506	-177.506	32.328
1300	13.717	80.856	13.742	-176.067	-177.476	-177.476	29.636
1400	13.743	81.874	15.135	-176.385	-177.407	-177.407	27.021
1500	13.764	82.832	16.390	-176.678	-177.354	-177.354	24.447
1600	13.782	83.711	17.537	-176.943	-177.337	-177.337	23.545
1700	13.796	84.547	18.576	-177.186	-177.308	-177.308	22.643
1800	13.808	85.336	19.512	-177.408	-177.266	-177.266	21.741
1900	13.818	86.083	20.346	-177.608	-177.212	-177.212	20.839
2000	13.827	86.792	21.080	-177.786	-177.148	-177.148	19.937
2100	13.835	87.467	21.723	-177.943	-177.075	-177.075	19.035
2200	13.841	88.111	22.276	-178.086	-177.000	-177.000	18.133
2300	13.846	88.726	22.740	-178.216	-176.915	-176.915	17.231
2400	13.850	89.311	23.116	-178.334	-176.820	-176.820	16.329
2500	13.853	89.861	23.402	-178.440	-176.716	-176.716	15.427
2600	13.856	90.425	23.608	-178.534	-176.604	-176.604	14.525
2700	13.858	90.948	23.784	-178.616	-176.486	-176.486	13.623
2800	13.860	91.432	23.932	-178.686	-176.362	-176.362	12.721
2900	13.861	91.886	24.056	-178.744	-176.234	-176.234	11.819
3000	13.862	92.316	24.156	-178.792	-176.102	-176.102	10.917
3100	13.863	92.726	24.236	-178.830	-175.966	-175.966	10.015
3200	13.864	93.116	24.296	-178.858	-175.826	-175.826	9.113
3300	13.865	93.486	24.336	-178.876	-175.682	-175.682	8.211
3400	13.866	93.836	24.356	-178.886	-175.534	-175.534	7.309
3500	13.867	94.166	24.366	-178.886	-175.382	-175.382	6.407
3600	13.868	94.476	24.366	-178.876	-175.226	-175.226	5.505
3700	13.868	94.766	24.356	-178.856	-175.066	-175.066	4.603
3800	13.869	95.036	24.336	-178.826	-174.902	-174.902	3.701
3900	13.869	95.286	24.306	-178.786	-174.734	-174.734	2.800
4000	13.870	95.516	24.266	-178.736	-174.562	-174.562	1.900
4100	13.870	95.726	24.216	-178.676	-174.386	-174.386	1.000
4200	13.871	95.916	24.156	-178.606	-174.206	-174.206	0.100
4300	13.871	96.086	24.086	-178.526	-174.022	-174.022	-0.800
4400	13.872	96.236	24.006	-178.436	-173.836	-173.836	-1.700
4500	13.873	96.366	23.916	-178.336	-173.642	-173.642	-2.600
4600	13.874	96.476	23.816	-178.226	-173.446	-173.446	-3.500
4700	13.875	96.566	23.706	-178.106	-173.246	-173.246	-4.400
4800	13.876	96.636	23.586	-177.976	-173.042	-173.042	-5.300
4900	13.877	96.686	23.456	-177.836	-172.836	-172.836	-6.200
5000	13.878	96.716	23.316	-177.686	-172.626	-172.626	-7.100
5100	13.879	96.726	23.166	-177.526	-172.412	-172.412	-8.000
5200	13.880	96.716	23.006	-177.356	-172.196	-172.196	-8.900
5300	13.881	96.686	22.836	-177.176	-171.976	-171.976	-9.800
5400	13.882	96.636	22.656	-176.986	-171.752	-171.752	-10.700
5500	13.883	96.566	22.466	-176.786	-171.516	-171.516	-11.600
5600	13.884	96.476	22.266	-176.576	-171.266	-171.266	-12.500
5700	13.885	96.366	22.056	-176.356	-170.996	-170.996	-13.400
5800	13.886	96.236	21.836	-176.126	-170.716	-170.716	-14.300
5900	13.887	96.086	21.606	-175.886	-170.426	-170.426	-15.200
6000	13.888	95.916	21.366	-175.646	-170.126	-170.126	-16.100

Dec. 31, 1960; June 30, 1964; Mar. 31, 1966

Nitrogen Difluoride (NF_2)					
(Ideal Gas)	Mol. wt. = 52.008				
		$\Delta H_f^\circ = 10.7 \pm 2.0 \text{ kcal. mole}^{-1}$			
		Point Group = C_{2v}			
		$S_{298.15}^\circ = 59.72 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$			
		$\Delta H_f^\circ 298.15 = 10.1 \pm 2.0 \text{ kcal. mole}^{-1}$			
					F_2^N

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ke ₁ , mole ⁻¹	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞	∞
100	7.995	50.345	0.000	INFINITE	-2.528	10.718	10.718	10.718	INFINITE
200	7.985	46.467	0.7667	-1.732	-1.732	10.476	10.476	10.476	24.951
300	7.980	43.074	1.5175	-0.906	-0.906	10.251	10.251	10.251	13.604
400	7.975	40.571	2.1775	-0.506	-0.506	10.044	10.044	10.044	9.942
500	7.970	38.622	2.7575	-0.318	-0.318	9.856	9.856	9.856	8.065
600	7.965	36.944	3.2775	-0.184	-0.184	9.686	9.686	9.686	6.793
700	7.960	35.425	3.7475	-0.108	-0.108	9.532	9.532	9.532	5.925
800	7.955	34.025	4.1775	-0.064	-0.064	9.392	9.392	9.392	5.335
900	7.950	32.725	4.5775	-0.036	-0.036	9.264	9.264	9.264	4.874
1000	7.945	31.500	4.9475	-0.020	-0.020	9.148	9.148	9.148	4.484
1100	7.940	30.340	5.2875	-0.012	-0.012	9.044	9.044	9.044	4.153
1200	7.935	29.240	5.5975	-0.007	-0.007	8.952	8.952	8.952	3.866
1300	7.930	28.190	5.8775	-0.004	-0.004	8.872	8.872	8.872	3.612
1400	7.925	27.190	6.1375	-0.002	-0.002	8.804	8.804	8.804	3.388
1500	7.920	26.240	6.3775	-0.001	-0.001	8.748	8.748	8.748	3.193
1600	7.915	25.340	6.5975	-0.000	-0.000	8.704	8.704	8.704	3.025
1700	7.910	24.490	6.7975	-0.000	-0.000	8.672	8.672	8.672	2.880
1800	7.905	23.690	6.9775	-0.000	-0.000	8.650	8.650	8.650	2.756
1900	7.900	22.940	7.1375	-0.000	-0.000	8.638	8.638	8.638	2.651
2000	7.895	22.240	7.2875	-0.000	-0.000	8.634	8.634	8.634	2.564
2100	7.890	21.590	7.4275	-0.000	-0.000	8.636	8.636	8.636	2.494
2200	7.885	20.990	7.5575	-0.000	-0.000	8.642	8.642	8.642	2.436
2300	7.880	20.440	7.6775	-0.000	-0.000	8.652	8.652	8.652	2.389
2400	7.875	19.940	7.7875	-0.000	-0.000	8.666	8.666	8.666	2.352
2500	7.870	19.490	7.8875	-0.000	-0.000	8.684	8.684	8.684	2.324
2600	7.865	19.090	7.9775	-0.000	-0.000	8.706	8.706	8.706	2.304
2700	7.860	18.740	8.0575	-0.000	-0.000	8.732	8.732	8.732	2.290
2800	7.855	18.440	8.1275	-0.000	-0.000	8.762	8.762	8.762	2.282
2900	7.850	18.190	8.1875	-0.000	-0.000	8.796	8.796	8.796	2.284
3000	7.845	17.990	8.2375	-0.000	-0.000	8.834	8.834	8.834	2.294
3100	7.840	17.840	8.2775	-0.000	-0.000	8.876	8.876	8.876	2.310
3200	7.835	17.740	8.3175	-0.000	-0.000	8.922	8.922	8.922	2.332
3300	7.830	17.680	8.3575	-0.000	-0.000	8.972	8.972	8.972	2.360
3400	7.825	17.660	8.3975	-0.000	-0.000	9.026	9.026	9.026	2.394
3500	7.820	17.680	8.4375	-0.000	-0.000	9.084	9.084	9.084	2.436
3600	7.815	17.740	8.4775	-0.000	-0.000	9.146	9.146	9.146	2.484
3700	7.810	17.840							

Dec. 31, 1982; Mar. 31, 1964

Dec. 31, 1962: Mar. 31, 1964

DIFLUORODIAZINE, Cis-(N₂F₂) (IDEAL GAS) MOL. WT. = 66.0102

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹ S ^o - (C _p ^o - II ₂₉₈)/T	cal. mole ⁻¹ II ^o - II ₂₉₈	ΔII ₂₉₈ ^o	ΔF ₂₉₈ ^o	Log K _p
0	-0.000	INFINITE	-2.725	17.857	17.857	INFINITE
100	8.646	51.787	1.125	17.857	17.857	-25.000
200	20.644	77.787	1.060	16.733	22.887	-25.000
298	11.941	62.071	0.000	16.400	25.584	-19.046
300	11.982	62.071	0.022	16.395	26.043	-18.972
400	15.900	65.867	1.521	16.227	29.290	-16.003
500	15.306	69.124	2.785	16.181	32.562	-14.232
600	16.318	72.014	4.367	16.221	35.837	-13.053
700	17.053	74.587	6.039	16.317	39.100	-12.207
800	17.595	76.902	7.773	16.437	42.345	-11.568
900	18.002	78.999	9.584	16.583	45.576	-11.067
1000	18.313	80.917	11.370	16.740	48.788	-10.662
1100	18.555	82.669	13.214	16.904	51.985	-10.328
1200	18.746	84.292	15.080	17.072	55.168	-10.047
1300	18.900	85.799	16.962	17.251	58.336	-9.807
1400	19.025	87.234	18.859	17.400	61.489	-9.598
1500	19.127	88.521	20.766	17.576	64.633	-9.417
1600	19.213	89.758	22.684	17.743	67.765	-9.256
1700	19.284	90.925	24.608	17.906	70.887	-9.113
1800	19.345	92.029	26.540	18.067	73.997	-8.984
1900	19.397	93.076	28.477	18.227	77.103	-8.868
2000	19.442	94.072	30.419	18.384	80.198	-8.763
2100	19.481	95.022	32.365	18.538	83.281	-8.667
2200	19.514	95.929	34.315	18.689	86.361	-8.579
2300	19.540	96.797	36.268	18.838	89.434	-8.498
2400	19.570	97.630	38.224	18.985	92.499	-8.423
2500	19.595	98.444	40.182	19.127	95.560	-8.353
2600	19.614	99.239	42.143	19.268	98.614	-8.289
2700	19.632	100.003	44.105	19.406	101.667	-8.229
2800	19.649	100.653	46.069	19.542	104.707	-8.172
2900	19.664	101.362	48.035	19.676	107.752	-8.120
3000	19.677	102.034	50.002	19.805	110.783	-8.070
3100	19.690	102.655	51.970	19.933	113.810	-8.023
3200	19.701	103.280	53.940	20.058	116.838	-7.979
3300	19.711	103.886	55.910	20.179	119.862	-7.938
3400	19.720	104.475	57.882	20.300	122.881	-7.898
3500	19.729	105.057	59.854	20.416	125.896	-7.861
3600	19.736	105.633	61.827	20.530	128.908	-7.825
3700	19.744	106.143	63.801	20.642	131.920	-7.792
3800	19.750	106.670	65.776	20.751	134.926	-7.760
3900	19.756	107.183	67.751	20.857	137.928	-7.729
4000	19.762	107.683	69.727	20.961	140.929	-7.700
4100	19.767	108.171	90.683	21.062	143.926	-7.672
4200	19.772	108.648	91.105	21.160	146.920	-7.645
4300	19.777	109.113	91.518	21.257	149.918	-7.619
4400	19.781	109.568	91.923	21.349	152.905	-7.594
4500	19.785	110.012	92.320	21.439	155.895	-7.571
4600	19.789	110.447	92.710	21.528	158.884	-7.548
4700	19.792	110.873	93.092	21.613	161.866	-7.526
4800	19.796	111.290	93.466	21.696	164.851	-7.505
4900	19.799	111.698	93.834	21.775	167.830	-7.485
5000	19.802	112.098	94.196	21.852	170.812	-7.466
5100	19.804	112.490	94.551	21.927	173.784	-7.447
5200	19.807	112.875	94.899	22.000	176.767	-7.429
5300	19.809	113.252	95.243	22.068	179.743	-7.411
5400	19.812	113.622	95.579	22.134	182.714	-7.394
5500	19.814	113.986	95.910	22.197	185.690	-7.378
5600	19.816	114.343	96.236	22.258	188.662	-7.363
5700	19.818	114.694	96.557	22.315	191.634	-7.347
5800	19.820	115.038	96.873	22.371	194.608	-7.333
5900	19.822	115.377	97.183	22.423	197.571	-7.318
6000	19.823	115.710	97.489	22.473	200.541	-7.304

Dec. 31, 1965

Point Group C_{2v}

S_{298.15} = 62.1 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH_f^o 0 = 17.9 ± 1.2 kcal. mole⁻¹

ΔH_f^o 298.15 = 16.4 ± 1.2 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

W, cm. ⁻¹	W, cm. ⁻¹
896 (1)	952 (1)
1524 (1)	573 (1)
552 (1)	737 (1)

Bond Distance: N-F = 1.384 Å N-N = 1.214 Å

Bond Angle: F-N-N = 114.5 ± 0.5°

Product of the Moments of Inertia: I_AI_BI_C = 6.53821 X 10⁻¹¹⁵ g.³ cm.⁶

σ = 2

Heat of Formation.

The heat of formation was derived from the heat of reaction N₂F₂(g) + 8/5 NH₃(g) = 2NH₄F(c) + 4/5 N₂(g) which was measured calorimetrically by G. T. Armstrong and S. Marantz¹. There are two isomers, the trans and the active form of difluorodiazine. The heats of formation were determined to be 19.4 and 16.4 kcal. mole⁻¹ for the trans and the active isomers respectively. The active form of N₂F₂ has been interpreted here as the cis isomer which will be discussed later. The heat of isomerization has also been reported as 3.0 kcal. mole⁻¹ by Armstrong and Marantz. The value, ΔH_f^o 298 (cis N₂F₂, g) = 16.4 kcal. mole⁻¹, is adopted in the tabulation.

A. V. Pankratov et al.² have measured the enthalpy of reaction N₂F₂(g) + 3KI = 2KF + N₂ + KI₃ in acidic solution (pH = 3), and reported ΔH_f^o 298 (active N₂F₂, g) = 25.3 ± 2.0 kcal. mole⁻¹.

The "heat of isomerization" has been reported as 27.5 ± 5.0 kcal. mole⁻¹ by C. B. Colburn et al.⁹. The derivation of this value is unknown. The authors observed three values of the equilibrium constant for the isomerization reaction. Third law analysis of their data gives ΔH_f^o 298 = 2.52 ± 0.05 kcal. mole⁻¹ for the reaction cis N₂F₂(g) → trans N₂F₂(g) which is in good agreement with Armstrong and Sidney's data.

Heat Capacity and Entropy.

Although the infrared spectrum^{7,8} of the active form of N₂F₂(g) has been interpreted as favoring the 1,1-difluorodiazine over the cis-configuration^{3,4}, n.m.r.⁵ and microwave studies definitely indicate the latter. The vibrational frequencies⁷ previously assigned to the 1,1-difluorodiazine have been adopted here for the cis isomer. The selected bond distances and angle were taken from the isotopic nitrogen microwave studies⁶. The principal moments of inertia were: I_A = 4.2438 X 10⁻³⁹, I_B = 10.5129 X 10⁻³⁹ and I_C = 14.7567 X 10⁻³⁹ g. cm.²

See the trans N₂F₂(g) table for the comparison of the different physical properties between trans and cis isomers.

References:

- (1) G. T. Armstrong and S. Marantz, *J. Chem. Phys.* **36**, 169 (1963).
- (2) A. V. Pankratov, A. N. Zhercheninov, O. G. Talakin, O. M. Sokolov, and N. A. Knyazeva, *Zh. Fiz. Khim.* **57**, 1399 (1963).
- (3) R. Ettinger, F. A. Johnson, and C. B. Colburn, *J. Chem. Phys.* **34**, 2187 (1961).
- (4) J. T. Herron and V. H. Dibeler, *J. Res. Natl. Bur. Std.* **55A**, 405 (1961).
- (5) J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, *J. Chem. Phys.* **37**, 182 (1962).
- (6) R. L. Kuczkowski and E. B. Wilson, Jr., *J. Chem. Phys.* **39**, 1030 (1963).
- (7) R. H. Sanborn, *J. Chem. Phys.* **35**, 2185 (1961).
- (8) R. H. Sanborn, *J. Chem. Phys.* **35**, 2188 (1961).
- (9) C. B. Colburn, F. A. Johnson, K. Kennedy, K. McCallum, L. C. Metzger and C. O. Parker, *J. Am. Chem. Soc.* **81**, 6397 (1959).

Di fluorodiazine, Trans-(N₂F₂)

(Ideal Gas) Mol. wt. = 66.0102

F₂N₂

MOL. WT. = 66.0102

(IDEAL GAS)

DIFLUORODIAZINE, Trans-(N₂F₂)

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.453	51.506	2.923	20.659	20.659	INFINITE
200	10.774	58.062	6.860	22.813	22.813	49.856
298	12.779	62.752	10.000	25.733	25.733	28.118
300	12.812	62.832	10.024	25.733	25.733	21.096
400	14.392	66.744	13.87	28.439	28.439	17.486
500	15.583	70.090	18.289	32.006	32.006	15.379
600	16.473	73.014	22.916	35.362	35.362	13.973
700	17.139	75.482	27.766	38.346	38.346	12.828
800	17.641	77.498	32.816	40.928	40.928	11.866
900	18.026	79.029	37.951	43.166	43.166	11.066
1000	18.323	81.945	43.166	45.004	45.004	10.360
1100	18.528	85.302	48.543	46.488	46.488	9.728
1200	18.724	89.098	54.098	47.662	47.662	9.150
1300	18.895	93.332	59.832	48.571	48.571	8.614
1400	19.049	98.002	65.746	49.262	49.262	8.112
1500	19.121	103.117	71.839	49.771	49.771	7.640
1600	19.206	108.680	78.111	50.131	50.131	7.194
1700	19.277	114.692	84.562	50.362	50.362	6.766
1800	19.338	121.154	91.194	50.482	50.482	6.352
1900	19.390	128.066	97.996	50.502	50.502	5.950
2000	19.435	135.428	104.968	50.432	50.432	5.560
2100	19.474	143.240	112.098	50.282	50.282	5.182
2200	19.509	151.502	119.370	50.052	50.052	4.826
2300	19.538	159.214	126.782	49.752	49.752	4.482
2400	19.565	166.376	134.334	49.382	49.382	4.150
2500	19.588	173.988	142.026	48.942	48.942	3.830
2600	19.609	182.050	149.858	48.432	48.432	3.520
2700	19.628	190.562	157.830	47.852	47.852	3.220
2800	19.645	199.524	165.942	47.202	47.202	2.930
2900	19.660	208.936	174.194	46.482	46.482	2.650
3000	19.673	218.798	182.586	45.702	45.702	2.380
3100	19.686	229.110	191.118	44.862	44.862	2.120
3200	19.697	239.872	199.790	43.972	43.972	1.870
3300	19.707	251.084	208.602	43.032	43.032	1.630
3400	19.717	262.746	217.554	42.052	42.052	1.400
3500	19.726	274.858	226.656	41.032	41.032	1.180
3600	19.733	287.420	235.908	40.002	40.002	0.970
3700	19.741	299.432	245.310	39.002	39.002	0.770
3800	19.748	311.894	254.862	38.032	38.032	0.580
3900	19.754	324.806	264.564	37.082	37.082	0.400
4000	19.760	338.168	274.416	36.152	36.152	0.230
4100	19.765	351.980	284.418	35.242	35.242	0.070
4200	19.770	366.242	294.570	34.352	34.352	-0.080
4300	19.775	380.954	304.872	33.482	33.482	-0.240
4400	19.779	396.116	315.324	32.632	32.632	-0.410
4500	19.783	411.728	325.926	31.802	31.802	-0.580
4600	19.787	427.790	336.678	30.992	30.992	-0.760
4700	19.791	444.302	347.580	30.202	30.202	-0.940
4800	19.794	461.264	358.632	29.432	29.432	-1.130
4900	19.797	478.676	369.834	28.682	28.682	-1.320
5000	19.800	496.538	381.186	27.952	27.952	-1.520
5100	19.803	514.850	392.698	27.242	27.242	-1.720
5200	19.805	533.612	404.370	26.552	26.552	-1.930
5300	19.808	552.824	416.192	25.882	25.882	-2.140
5400	19.810	572.486	428.164	25.232	25.232	-2.360
5500	19.813	592.598	440.286	24.602	24.602	-2.580
5600	19.815	613.160	452.558	24.002	24.002	-2.810
5700	19.817	634.172	464.980	23.432	23.432	-3.040
5800	19.819	655.634	477.552	22.882	22.882	-3.280
5900	19.820	677.546	490.274	22.352	22.352	-3.520
6000	19.822	699.908	503.146	21.842	21.842	-3.770

Dec. 31, 1965

Point Group C_{2h}

S_{298.15} = 62.75 cal. mole⁻¹ deg.⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

W, cm. ⁻¹	W, cm. ⁻¹
1010 (1)	989 (1)
1636 (1)	421 (1)
592 (1)	360 (1)

Bond Distance: N-F = 1.44 Å

Bond Angle: F-N-F = 115°

Product of the Moments of Inertia: I_AI_BI_C = 432.6784 X 10⁻¹¹⁷ g.³ cm.⁶

σ = 2

Heat of Formation.

G. T. Armstrong and S. Marantz, J. Chem. Phys. **39**, 169 (1963) have measured calorimetrically the enthalpy of reaction N₂F₂(g) + 8/5 NH₃(g) = 2NH₄F(c) + 4/5 N₂(g), and reported ΔH_f° 298 (trans N₂F₂, g) = 19.4 ± 1.2 kcal. mole⁻¹ which is adopted in this tabulation.

Heat Capacity and Entropy.

The bond distances and bond angle were obtained from S. H. Bauer, J. Am. Chem. Soc. **69**, 3104 (1947), by electron diffraction. The fundamental vibrational frequencies were obtained from R. H. Sanborn, J. Chem. Phys. **33**, 1855 (1960) by infrared spectroscopy. The three principal moments of inertia are I_A = 0.919 X 10⁻³⁹, I_B = 21.2433 X 10⁻³⁹ and I_C = 22.1823 X 10⁻³⁹ g. cm.²

As pointed out by R. Ettinger, F. A. Johnson and C. B. Colburn, J. Chem. Phys. **34**, 2187 (1961), the trans N₂F₂ is the less active isomer which is different from the active isomer by its (1) vapor pressure (2) boiling point (3) heat of vaporization (4) critical temperature (5) melting point (6) mass spectral cracking pattern (7) NMR spectrum (8) infrared spectrum (9) heat of isomerization (10) reactivity with mercury and glass.

F₂N₂



SODIUM DIFLUORIDE UNINEGATIVE ION (NaF_2^-)

(IDEAL GAS)

Point Group $[\text{D}_{\infty h}]$

Sodium Difluoride Uninegative Ion (NaF_2^-)
(Ideal Gas) $\text{GFW} = 60.98715$

$\Delta H_f^\circ = -159 \pm 10 \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = -160 \pm 10 \text{ kcal/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies
 ω, cm^{-1}

Bond Distance: $\text{Na}-\text{F} = [1.93] \text{ \AA}$
Bond Angle: $\text{F}-\text{Na}-\text{F} = [180^\circ]$
Rotational Constant: $B_0 = [0.119] \text{ cm}^{-1}$
 $\sigma = [2]$

Heat of Formation

The heat of formation for $\text{NaF}_2^-(g)$ is estimated from three calculated values. The methods of calculation are described as follows. The first reaction we take into consideration is $\text{NaF}(g) + \text{F}^-(g) = \text{NaF}_2^-(g)$. In a manner analogous to $\text{LiF}_2^-(g)$ molecule (see $\text{LiF}_2^-(g)$ table for details), we assume $\text{NaF}_2^-(g)$ is stable and ΔH_f° for the reaction $\text{NaF}(g) + \text{F}^-(g) = \text{NaF}_2^-(g)$ is somewhere between 0 to $1/2(-84) = -42 \text{ kcal/mol}$ where the value -84 kcal/mol is the heat of dimerization. Based on $\Delta H_f^\circ = 0$ and -28 kcal/mol , respectively, with JANAF ΔH_f° values for the species involved, we obtain $\Delta H_f^\circ(\text{NaF}_2^-, g) = -112$ and -164 kcal/mol as the upper and lower limits.

The heat of formation, calculated based on the reaction $\text{NaF}_2^-(g) = \text{NaF}_2(g) + e^-(g)$, is -165.8 kcal/mol , using ΔH_f° for $\text{NaF}_2(g)$ estimated as 83.6 and -82.3 kcal/mol , respectively. The ΔH_f° value is obtained from an assumption that the enthalpy change for removing an electron from $\text{NaF}_2^-(g)$ is comparable to that from $\text{F}^-(g)$. Due to the fact that the Na atom has smaller electronegativity (0.9) than that of the F atom (4.0), we expect that there is less possibility that the electron will associate with Na atom in the NaF_2^- molecule. Therefore we adopt the electron affinity of $\text{F}(g)$ reported by H. O. Pritchard, Chem. Rev. 53, 529 (1963), or $\Delta H_f^\circ = 83.6 \text{ kcal/mol}$ for the reaction $\text{F}^-(g) = \text{F}(g) + e^-(g)$ as the ΔH_f° for $\text{NaF}_2^-(g) = \text{NaF}_2(g) + e^-(g)$. The value of ΔH_f° for $\text{NaF}_2(g)$ is calculated using the enthalpy change for the reaction $\text{Na}_2\text{F}_2(g) = \text{NaF}_2(g) + \text{Na}(g)$ as 145.8 kcal/mol which is derived from the sum of two enthalpy changes, namely, half of the ΔH_f° value for the dimer dissociation reaction $\text{Na}_2\text{F}_2(g) = 2\text{NaF}(g)$, and the ΔH_f° for the monomer dissociation reaction $\text{NaF}(g) = \text{Na}(g) + \text{F}(g)$.

Employing $\Delta H_f^\circ = 63.5 \text{ kcal/mol}$ for $\text{Na}_2\text{F}_2(g) = 2\text{NaF}(g)$ and 153.0 kcal/mol for $\text{NaF}(g) = \text{Na}(g) + \text{F}(g)$, we estimate $\Delta H_f^\circ = 1/2(63.5) + 153.0 = 180.7 \text{ kcal/mol}$ for the reaction $\text{NaF}_2(g) = \text{NaF}_2(g) + \text{Na}(g)$, which leads to $\Delta H_f^\circ = 163.4 \text{ kcal/mol}$ for $\text{NaF}_2^-(g)$. For all calculations the ΔH_f° values of the chemical species involved are taken from JANAF Thermochemical Tables.

The value of ΔH_f° for $\text{NaF}_2^-(g)$ is tentatively adopted as $-160 \pm 10 \text{ kcal/mol}$.

Heat Capacity and Entropy

The molecular structure is assumed to be linear, according to the suggestion by A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953) that molecules with not more than 16 valence electrons are linear in their ground state. The Na-F bond distance is estimated by comparison with that of $\text{NaF}(g)$ reported by S. E. Veazey and W. Gordy, Phys. Rev. 138, A1303 (1965). The vibrational frequencies are estimated from those for the isoelectronic molecule $\text{SiO}_2(g)$. The moment of inertia is $2.350 \times 10^{-38} \text{ g cm}^2$. The enthalpy at 0°K is -3.117 kcal/mol .

Dec. 31, 1960



Sodium Fluoride, Dimeric (Na₂F₂)
(Ideal Gas) GFW = 83.9764SODIUM FLUORIDE, DIMERIC (Na₂F₂)

(IDEAL GAS)

GFW = 83.9764

Point Group [D_{2h}] $\Delta H_f^\circ = [-200.8 \pm 3] \text{ kcal/mol}$ $S_{298.15}^\circ = [68.7 \pm 4] \text{ gibbs/mol}$ $\Delta H_f^\circ = [-202.3 \pm 3] \text{ kcal/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	$\frac{\omega, \text{cm}^{-1}}{\omega, \text{cm}^{-1}}$
[420] (1)	[200] (1)
[400] (1)	[425] (1)
[350] (1)	[500] (1)

Bond Distance: Na-F = 2.02 Å

Bond Angle: Na-F-Na = [85°]

Product of the Moments of Inertia: $I_{AB} = [5.613 \times 10^{-114}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

Although the absolute values of the vapor pressure measurements are not used for evaluation, the ratios of the numbers of dimeric and monomeric NaF molecules that effuse from the oven at the temperatures 1115 - 1191°K determined by Eisenstadt, Rothberg, and Kusch (1) by use of the electron-beam velocity-selector method are used. Based on the reported equilibrium data we evaluate the enthalpy change of the reaction (A) $\text{Na}_2\text{F}_2(\text{g}) = 2\text{NaF}(\text{g})$ by the second and third law methods. The results are presented in the table below.

Porter and Schoonmaker (2) analyzed the vapor effusing from a Knudsen cell at 1121°K mass spectrometrically and derived the partial pressures of NaF(g) and Na₂F₂(g) at that temperature. Using these reported partial pressures we calculate, by the third law method, the value $\Delta H_{298}^\circ = 64.1 \text{ kcal/mol}$ for reaction (A).

Sidorov et al. (3) studied the NaF - ZrF₄ system by the mass spectrometric method and derived the partial pressures of NaF(g) and Na₂F₂(g) as a function of composition and temperature. Employing the data points reported at 1074° and 1167°K we obtain the third law value $\Delta H_{298}^\circ = 62.0 \pm 1.6 \text{ kcal/mol}$ for the same reaction.

The ΔH_{298}° (Na₂F₂, g) is calculated based on the adopted third law value $\Delta H_{298}^\circ = 63.5 \text{ kcal/mol}$ for the reaction $\text{Na}_2\text{F}_2(\text{g}) = 2\text{NaF}(\text{g})$, using ΔH_f° (NaF, g) = -69.5 kcal/mol. Brewer and Brackett (3) reported $\Delta H_{1000}^\circ = 56.9 \text{ kcal/mol}$ for the above reaction. According to our tables the ΔH_{1000}° value is 62.5 kcal/mol.

Investigator	Temperature, °K	No. of Points	ΔH_{298}° , kcal/mol	Drift, kcal/mol	ΔH_{298}° , kcal/mol
1. Eisenstadt et al. (1958)	1115 - 1191	6	58.1 ± 2.9	4.7 ± 2.5	-202.4
2. Porter and Schoonmaker (1958)	1121	1	64.1	---	-203.0
3. Sidorov et al. (1964)	1074 - 1167	8	62.0 ± 1.6	---	-200.9

Heat Capacity and Entropy

The Na₂F₂ molecule is assumed to have a rhombic structure with D_{2h} (h) symmetry (4, 5). The Na-F bond distance is reported by Akishin and Rambidi (5), who studied the molecular structure of alkali halide vapors by electron diffraction with sector microphotometry. The bond angle is estimated by comparison with those of the other alkali halides. Berkowitz (4, 5) has calculated the vibration frequencies of Na₂F₂ based on an ionic model. By comparison of the calculated frequencies of Li₂F₂ (5) with those of the observed ones (see Li₂F₂(g) table for details) we reestimate the vibrational frequencies for Na₂F₂(g) to be higher than the ones reported by Berkowitz (5). Bauer et al. (7) used a pseudo-electrostatic model, similar to the one suggested by O'Konski and Higuchi (8), to calculate the entropies of dimerization for a number of gaseous alkali halides and estimated the six vibrational frequencies as 477, 318, 291, 477, 291, and 291 cm⁻¹. Bauer et al. calculated $\Delta S_{1146}^\circ = -32.5 \text{ eu}$ for the reaction $2\text{NaF}(\text{g}) = \text{Na}_2\text{F}_2(\text{g})$, in reasonable agreement with the value -33.5 eu which is derived using JANAF Silus values for NaF(g) and Na₂F₂(g).

The three principal moments of inertia are: $I_A = 1.399 \times 10^{-38}$, $I_B = 1.422 \times 10^{-38}$, and $I_C = 2.821 \times 10^{-38} \text{ g cm}^2$.

References

1. M. Eisenstadt, G. M. Rothberg, and P. Kusch, J. Chem. Phys. **23**, 797 (1958).
2. R. F. Porter and R. C. Schoonmaker, J. Chem. Phys. **23**, 1070 (1958).
3. L. N. Sidorov, P. A. Akishin, V. I. Belousov, and V. V. Shol'ts, Russ. J. Phys. Chem. (English Transl.) **38**, 641 (1964).
4. J. Berkowitz, J. Chem. Phys. **23**, 1306 (1958).
5. P. A. Akishin and N. G. Rambidi, Z. Physik. Chem. **213**, 111 (1960).
6. J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960).
7. S. H. Bauer, R. M. Diner, and R. F. Porter, J. Chem. Phys. **23**, 991 (1958).
8. C. T. O'Konski and W. I. Higuchi, J. Chem. Phys. **23**, 1175 (1955).
9. L. Brewer and E. Brackett, Chem. Rev. **51**, 475 (1961).

June 30, 1984; Dec. 31, 1968

Thionyl Difluoride (SOF₂)

(Ideal Gas) Mol. Wt. = 86.0602

F₂O₈

THIONYL DIFLUORIDE (SOF₂) (IDEAL GAS)

MOL. WT. = 86.0602

Point Group C_{2v}
 $\Delta H_f^\circ 0 = -134 \pm 10$ kcal. mole⁻¹
 $\Delta H_f^\circ 298.15 = -135 \pm 10$ kcal. mole⁻¹
 $\Delta H_f^\circ 298.15 = 66.965$ cal. deg.⁻¹ mole⁻¹
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies	
ω , cm. ⁻¹	ω , cm. ⁻¹
1308 (1)	393 (1)
801 (1)	721 (1)
526 (1)	326 (1)

Bond Distances: O-S = 1.412 Å S-F = 1.585 Å
 Bond Angle: O-S-F = 106° 49' F-S-F = 92° 49'
 Product of the Moments of Inertia: I_AI_BI_C = 1.65545 X 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation.

From the enthalpy change, $\Delta H_f^\circ 298.15 = 131.03$ kcal. mole⁻¹, for the reaction SO₂F₂(g) = SOF₂(g) + O(g), the value of $\Delta H_f^\circ 298.15$ for SOF₂(g) was calculated to be -133.5 kcal. mole⁻¹, using $\Delta H_f^\circ 298.15 = -203.0$ and 59.56 kcal. mole⁻¹ for SO₂F₂(g) and O(g), respectively. The value of $\Delta H_f^\circ 298.15$ was assumed to be the same as that for the reaction SO₂(g) = SO(g) + O(g) which was calculated based on $\Delta H_f^\circ 298.15 = -70.95$, 0.52 and 59.56 kcal. mole⁻¹ for SO₂(g), SO(g) and O(g), respectively. Using $\Delta H_f^\circ 298.15 = 127.86$ kcal. mole⁻¹ for the reaction SO₂F₂(g) = SOF₂(g) + O(g), the value of $\Delta H_f^\circ 298.15$ (SOF₂, g) was evaluated as -136.7 kcal. mole⁻¹ where the $\Delta H_f^\circ 298.15$ value was assumed to be the same as the S-O bond energy in SO₂(g). The value of $\Delta H_f^\circ 298.15$ (SOF₂, g) adopted is -135 ± 10 kcal. mole⁻¹.

Heat Capacity and Entropy.

The bond distances and angles were obtained from R. C. Ferguson, J. Am. Chem. Soc. 76, 850 (1954). The vibrational frequencies were taken from R. J. Gillespie and E. A. Robinson, Can. J. Chem. 39, 2171 (1961). The assignment of these vibrational frequencies was based on the previous measurements of the infrared and Raman spectra reported by J. K. O'Loane and M. K. Wilson, J. Chem. Phys. 23, 1313 (1955), P. Bender and J. M. Wood, J. Chem. Phys. 23, 1316 (1955) and D. M. Vost, Proc. Indian Acad. Sci. B, 333 (1958). The fundamental assignment reported by J. K. O'Loane and M. K. Wilson, loc. cit., was 1333, 808, 530, (410), 748 and 390 cm.⁻¹. The three principal moments of inertia are: I_A = 1.0034 X 10⁻³⁸, I_B = 9.7421 X 10⁻³⁹ and I_C = 1.6935 X 10⁻³⁸ g. cm.².

The heat capacities of thionyl fluoride (SOF₂) have been measured, from 12° to 230°K., by E. L. Pace and B. F. Turnbull, J. Chem. Phys. 43, 1953 (1965), for a sample of 99.97% mole % purity. Incorporating them with the measured $\Delta H_f^\circ 1.506$ kcal. mole⁻¹ at T₀ = 143.25°K., and $\Delta H_f^\circ 5.091$ kcal. mole⁻¹ at T₀ = 228.84°K., which was derived from the measured vapor pressure of SOF₂(l), the entropy of SOF₂(g) at 228.84°K. was evaluated as 63.56 e.u. This value is in excellent agreement with the corresponding value, 63.522 e.u., calculated using the adopted molecular constants. This indicates the fact that the molecular constants used for the calculation of the tabulated thermodynamic functions are adequate. Hence the new vibrational frequencies suggested by Pace and Turnbull, loc. cit., were not used.

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f ° kcal. mole ⁻¹	ΔF _f ° kcal. mole ⁻¹	Log K _p
0	0.000	0.000	INFINITE	-133.862	-133.862	INFINITE
100	8.650	55.063	77.606	-133.862	-133.862	291.386
1100	11.514	68.160	1.254	-134.269	-134.269	291.386
298	14.833	68.965	0.000	-134.697	-134.697	164.480
300	14.833	68.965	0.000	-135.000	-135.000	95.978
300	13.870	67.051	0.026	-135.005	-130.916	95.367
400	15.508	71.280	67.531	-135.755	-129.497	70.750
500	16.622	74.868	68.649	-136.256	-127.873	55.800
600	17.389	77.971	69.950	-136.619	-126.160	45.951
700	17.928	80.694	71.294	-136.892	-124.369	38.828
800	18.317	83.115	72.623	-137.093	-122.504	33.828
900	18.605	85.290	73.912	-137.243	-120.550	29.272
1000	18.821	87.262	75.150	-137.352	-118.511	25.630
1100	18.989	89.064	76.334	-137.426	-116.402	22.654
1200	19.120	90.722	77.465	-137.463	-114.225	20.175
1300	19.224	92.257	78.544	-137.463	-112.079	18.079
1400	19.309	93.684	79.575	-137.432	-110.046	16.285
1500	19.378	95.019	80.561	-137.372	-108.115	14.732
1600	19.435	96.271	81.504	-137.287	-106.273	13.373
1700	19.483	97.451	82.408	-137.173	-104.518	12.176
1800	19.524	98.566	83.275	-137.035	-102.843	11.113
1900	19.559	99.623	84.108	-136.868	-101.243	10.163
2000	19.588	100.627	84.909	-136.673	-99.718	9.308
2100	19.614	101.583	85.680	-136.453	-98.262	8.536
2200	19.637	102.496	86.424	-136.202	-96.876	7.834
2300	19.656	103.369	87.142	-135.923	-95.558	7.194
2400	19.674	104.206	87.836	-135.618	-94.299	6.607
2500	19.689	105.010	88.507	-135.289	-93.098	6.068
2600	19.703	105.782	89.156	-134.937	-91.942	5.571
2700	19.715	106.526	89.786	-134.558	-90.824	5.111
2800	19.726	107.243	90.397	-134.153	-89.743	4.684
2900	19.735	107.935	90.980	-133.725	-88.691	4.286
3000	19.744	108.605	91.546	-133.275	-87.660	3.916
3100	19.752	109.252	92.126	-132.802	-86.656	3.570
3200	19.760	109.874	92.671	-132.307	-85.676	3.245
3300	19.766	110.488	93.202	-131.792	-84.719	2.941
3400	19.772	111.078	93.719	-131.258	-83.783	2.654
3500	19.778	111.651	94.223	-130.705	-82.866	2.384
3600	19.783	112.208	94.715	-130.132	-81.967	2.128
3700	19.788	112.750	95.195	-129.540	-81.082	1.887
3800	19.792	113.276	95.664	-128.929	-80.211	1.659
3900	19.796	113.787	96.122	-128.300	-79.354	1.443
4000	19.800	114.284	96.570	-127.653	-78.509	1.237
4100	19.804	114.762	97.008	-127.000	-77.674	1.041
4200	19.807	115.260	97.437	-126.332	-76.843	0.855
4300	19.810	115.726	97.857	-125.649	-76.014	0.678
4400	19.813	116.161	98.269	-124.951	-75.186	0.508
4500	19.815	116.627	98.672	-124.238	-74.351	0.347
4600	19.818	117.062	99.067	-123.511	-73.509	0.192
4700	19.820	117.488	99.454	-122.770	-72.661	0.044
4800	19.822	117.906	99.834	-122.015	-71.806	-0.088
4900	19.824	118.314	100.207	-121.245	-70.946	-0.235
5000	19.826	118.715	100.575	-120.460	-70.081	-0.365
5100	19.828	119.108	100.933	-119.662	-69.211	-0.490
5200	19.830	119.493	101.286	-118.849	-68.336	-0.611
5300	19.831	119.870	101.633	-118.022	-67.456	-0.728
5400	19.833	120.241	101.974	-117.181	-66.571	-0.839
5500	19.834	120.605	102.310	-116.327	-65.681	-0.947
5600	19.835	120.962	102.640	-115.460	-64.786	-1.051
5700	19.837	121.313	102.964	-114.580	-63.886	-1.151
5800	19.838	121.658	103.284	-113.686	-62.981	-1.248
5900	19.839	121.998	103.598	-112.778	-62.071	-1.341
6000	19.840	122.331	103.907	-111.855	-61.156	-1.432

Dec. 31, 1960; Sept. 30, 1965

F₂O₈

Silicon Oxide Difluoride (SiOF₂)F₂Osi

(Ideal Gas) Mol. Wt. = 82.09

SILICON OXIDE DIFLUORIDE (SiOF₂)

(IDEAL GAS)

MOL. WT. = 82.09

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.205	53.862	2.409	- 479.953	- 479.953	INFINITE
200	10.471	60.167	2.407	- 230.270	- 230.270	501.370
298	12.032	64.806	1.168	- 230.668	- 228.412	249.885
300	12.032	64.806	∞	- 231.000	- 227.723	166.557
300	12.032	64.806	0.024	- 231.006	- 227.208	165.513
400	14.656	68.847	1.405	- 231.258	- 225.602	123.421
500	15.922	72.261	2.938	- 231.448	- 224.540	98.142
600	16.818	75.448	4.737	- 231.501	- 223.145	81.276
700	17.462	77.891	6.253	- 231.727	- 221.727	69.223
800	17.932	80.255	7.0176	- 231.801	- 220.296	60.179
900	18.284	82.489	7.816	- 231.887	- 218.852	53.142
1000	18.551	84.630	8.612	- 231.968	- 217.399	47.510
1100	18.758	86.108	9.4759	- 232.045	- 215.940	44.003
1200	18.921	87.147	10.2857	- 232.120	- 214.471	39.059
1300	19.052	87.967	11.0508	- 232.195	- 212.997	35.806
1400	19.158	88.683	11.7813	- 232.269	- 211.518	33.018
1500	19.245	89.308	12.4819	- 232.344	- 210.033	30.600
1600	19.317	89.852	13.1576	- 232.421	- 208.543	28.484
1700	19.378	90.421	13.8124	- 232.498	- 207.048	26.621
1800	19.429	90.924	14.4434	- 232.576	- 205.548	24.985
1900	19.471	91.366	15.0544	- 232.654	- 204.043	23.556
2000	19.505	91.744	15.6414	- 232.732	- 202.534	21.885
2100	19.534	92.064	16.2094	- 232.810	- 201.020	20.612
2200	19.559	92.324	16.7634	- 232.888	- 199.502	20.612
2300	19.580	92.524	17.2984	- 232.966	- 197.978	18.196
2400	19.598	92.674	17.8184	- 233.044	- 196.448	17.427
2500	19.614	92.784	18.3284	- 233.122	- 194.914	16.535
2600	19.628	92.854	18.8284	- 233.200	- 193.378	15.711
2700	19.641	92.894	19.3184	- 233.278	- 191.840	14.944
2800	19.653	92.914	19.7984	- 233.356	- 190.298	14.240
2900	19.665	92.924	20.2684	- 233.434	- 188.754	13.580
3000	19.676	92.934	20.7284	- 233.512	- 187.208	12.964
3100	19.686	92.944	21.1784	- 233.590	- 185.662	12.387
3200	19.696	92.954	21.6184	- 233.668	- 184.116	11.847
3300	19.706	92.964	22.0484	- 233.746	- 182.570	11.339
3400	19.716	92.974	22.4684	- 233.824	- 181.024	10.860
3500	19.726	92.984	22.8784	- 233.902	- 179.478	10.410
3600	19.736	92.994	23.2784	- 233.980	- 177.932	9.976
3700	19.746	93.004	23.6684	- 234.058	- 176.386	9.566
3800	19.756	93.014	24.0484	- 234.136	- 174.840	9.176
3900	19.766	93.024	24.4184	- 234.214	- 173.294	8.806
4000	19.776	93.034	24.7784	- 234.292	- 171.748	8.456
4100	19.786	93.044	25.1284	- 234.370	- 170.202	8.126
4200	19.796	93.054	25.4684	- 234.448	- 168.656	7.816
4300	19.806	93.064	25.7984	- 234.526	- 167.110	7.526
4400	19.816	93.074	26.1184	- 234.604	- 165.564	7.252
4500	19.826	93.084	26.4284	- 234.682	- 164.018	6.996
4600	19.836	93.094	26.7284	- 234.760	- 162.472	6.756
4700	19.846	93.104	27.0184	- 234.838	- 160.926	6.536
4800	19.856	93.114	27.2984	- 234.916	- 159.380	6.336
4900	19.866	93.124	27.5684	- 234.994	- 157.834	6.156
5000	19.876	93.134	27.8284	- 235.072	- 156.288	5.996
5100	19.886	93.144	28.0784	- 235.150	- 154.742	5.856
5200	19.896	93.154	28.3184	- 235.228	- 153.196	5.736
5300	19.906	93.164	28.5484	- 235.306	- 151.650	5.636
5400	19.916	93.174	28.7684	- 235.384	- 150.104	5.556
5500	19.926	93.184	28.9784	- 235.462	- 148.558	5.496
5600	19.936	93.194	29.1784	- 235.540	- 147.012	5.456
5700	19.946	93.204	29.3684	- 235.618	- 145.466	5.436
5800	19.956	93.214	29.5484	- 235.696	- 143.920	5.436
5900	19.966	93.224	29.7184	- 235.774	- 142.374	5.456
6000	19.976	93.234	29.8784	- 235.852	- 140.828	5.496

Sept. 30, 1983

Point Group [C_{2v}] $\Delta H_f^o = [-230 \pm 6] \text{ kcal. mole}^{-1}$ $S_{298.15}^o = [64.806] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^o = [-231 \pm 6] \text{ kcal. mole}^{-1}$ Ground State Quantum Weight $\tau(1)$

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
[440] (1)	[760] (1)
[490] (1)	[980] (1)
[610] (1)	[1420] (1)

Bond Distance: Si-O = [1.60] Å Si-F = [1.54] Å $\sigma = 2$

Bond Angle: P-Si-O = [120]° P-Si-F = [120]°

Product of the Moments of Inertia: $I_{A,B,C} = 2.56608 \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

 ΔH_f^o was estimated by comparison with those for SiF₄(g) and SiO₂(g).

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for COF₂(g) and TiOF₂(g). The vibrational frequencies for COF₂(g) and TiOF₂(g) were obtained from R. J. Lovell, C. V. Stephenson, and E. A. Jones, J. Chem. Phys. 22, 1953 (1954), and J. S. Gordon, private communication, May 12, 1961, respectively. The bond distances of Si-O and Si-F were assumed to be the same as those for SiO(g) and SiF₄(g), respectively. Point group, ground state multiplicity, and bond angles were estimated.

F₂Osi

T, °K.	C _p	S° - (F° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	0	0	0	INFINITE
100	12.527	52.1529	64.314	-210.986	-210.986	2.000
200	15.005	68.016	88.016	-210.986	-210.986	2.000
298	15.005	68.016	88.016	-210.986	-210.986	2.000
300	15.042	68.104	88.104	-210.986	-210.986	2.000
400	16.625	72.627	102.627	-210.986	-210.986	2.000
500	17.368	74.494	104.494	-210.986	-210.986	2.000
600	18.195	76.758	107.258	-210.986	-210.986	2.000
700	18.973	79.497	110.497	-210.986	-210.986	2.000
800	19.700	82.732	114.232	-210.986	-210.986	2.000
900	19.372	86.464	118.464	-210.986	-210.986	2.000
1000	19.000	90.696	123.196	-210.986	-210.986	2.000
1100	18.584	95.428	128.428	-210.986	-210.986	2.000
1200	18.125	100.660	134.160	-210.986	-210.986	2.000
1300	17.625	106.392	140.392	-210.986	-210.986	2.000
1400	17.084	112.624	147.124	-210.986	-210.986	2.000
1500	16.500	119.356	154.356	-210.986	-210.986	2.000
1600	15.875	126.588	162.088	-210.986	-210.986	2.000
1700	15.210	134.320	170.320	-210.986	-210.986	2.000
1800	14.500	142.552	179.052	-210.986	-210.986	2.000
1900	13.750	151.284	188.284	-210.986	-210.986	2.000
2000	13.000	160.516	198.016	-210.986	-210.986	2.000
2100	12.250	170.248	208.248	-210.986	-210.986	2.000
2200	11.500	180.480	218.480	-210.986	-210.986	2.000
2300	10.750	191.212	229.212	-210.986	-210.986	2.000
2400	10.000	202.444	240.444	-210.986	-210.986	2.000
2500	9.250	214.176	252.176	-210.986	-210.986	2.000
2600	8.500	226.408	264.408	-210.986	-210.986	2.000
2700	7.750	239.140	277.140	-210.986	-210.986	2.000
2800	7.000	252.372	290.372	-210.986	-210.986	2.000
2900	6.250	266.104	304.104	-210.986	-210.986	2.000
3000	5.500	280.336	318.336	-210.986	-210.986	2.000
3100	4.750	295.068	333.068	-210.986	-210.986	2.000
3200	4.000	310.300	348.300	-210.986	-210.986	2.000
3300	3.250	326.032	364.032	-210.986	-210.986	2.000
3400	2.500	342.264	380.264	-210.986	-210.986	2.000
3500	1.750	359.096	397.096	-210.986	-210.986	2.000
3600	1.000	376.428	414.428	-210.986	-210.986	2.000
3700	0.250	394.160	432.160	-210.986	-210.986	2.000
3800	-0.500	412.392	450.392	-210.986	-210.986	2.000
3900	-1.250	431.124	469.124	-210.986	-210.986	2.000
4000	-2.000	450.356	488.356	-210.986	-210.986	2.000
4100	-2.750	470.088	508.088	-210.986	-210.986	2.000
4200	-3.500	490.320	528.320	-210.986	-210.986	2.000
4300	-4.250	511.052	549.052	-210.986	-210.986	2.000
4400	-5.000	532.284	570.284	-210.986	-210.986	2.000
4500	-5.750	554.016	592.016	-210.986	-210.986	2.000
4600	-6.500	576.248	614.248	-210.986	-210.986	2.000
4700	-7.250	599.080	637.080	-210.986	-210.986	2.000
4800	-8.000	622.512	660.512	-210.986	-210.986	2.000
4900	-8.750	646.544	684.544	-210.986	-210.986	2.000
5000	-9.500	671.276	709.276	-210.986	-210.986	2.000
5100	-10.250	696.608	734.608	-210.986	-210.986	2.000
5200	-11.000	722.540	760.540	-210.986	-210.986	2.000
5300	-11.750	749.072	787.072	-210.986	-210.986	2.000
5400	-12.500	776.204	814.204	-210.986	-210.986	2.000
5500	-13.250	803.936	841.936	-210.986	-210.986	2.000
5600	-14.000	832.268	870.268	-210.986	-210.986	2.000
5700	-14.750	861.100	899.100	-210.986	-210.986	2.000
5800	-15.500	890.432	928.432	-210.986	-210.986	2.000
5900	-16.250	920.264	958.264	-210.986	-210.986	2.000
6000	-17.000	950.596	989.056	-210.986	-210.986	2.000

Sept. 30, 1963

TITANIUM OXIDE DIFLUORIDE (TiOF₂)

(IDEAL GAS)

MOL. WT. = 101.9

Point Group [C_{2v}]
 $\Delta H_f^0 = [-220] \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = [68.016] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta F_f^0 = [-221] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
[553] (1)	[718] (1)
[888] (1)	[300] (1)
[350] (1)	[452] (1)

ε = 2

Bond Distances: Ti-O = [1.62] Å Ti-F = [1.74] Å

Bond Angle: O-Ti-F = [120°]

Product of Moments of Inertia: $I_A I_B I_C = [4.34 \times 10^{-11}] \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

ΔH_f^0 was estimated as -220 kcal. mole⁻¹ by J. S. Gordon, Astrostatem, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. ΔH_f^0 298.15 was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. The principal moments of inertia are:
 $I_A = 14.3274 \times 10^{-39} \text{ g. cm.}^2$, $I_B = 11.6632 \times 10^{-39} \text{ g. cm.}^2$, and $I_C = 25.9907 \times 10^{-39} \text{ g. cm.}^2$

Sulfuryl Difluoride (SO₂F₂)
(Ideal Gas) Mol. Wt. = 102.066

F₂O₂S

MOL. WT. = 102.066

(IDEAL GAS)

SULFURYL DIFLUORIDE (SO₂F₂)

Point Group C_{2v}
ΔH_f⁰ = -203 kcal. mole⁻¹
S_{298.15} = 68.883 cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ 298.15 = -205 kcal. mole⁻¹
Oscillator Strength Multiplicity = [1]

Vibrational Frequencies and Degeneracies			
ν, cm. ⁻¹	ν, cm. ⁻¹	ν, cm. ⁻¹	ν, cm. ⁻¹
1269 (1)	274 (1)	539 (1)	
848 (1)	360 (1)	885 (1)	
553 (1)	1502 (1)	386 (1)	

Bond Distance: S-O = 1.405 ± 0.003 Å S-F = 1.530 ± 0.003 Å
Bond Angle: O-S-O = 123° 58' ± 12' F-S-F = 98° 7' ± 10' σ⁻ = 2

Product of the Moments of Inertia: I_AI_BI_C = 4.4673 × 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation.

The heat of formation was reported by R. M. Reese, V. H. Dibeler and J. L. Franklin, J. Chem. Phys. 29, 880 (1958). The value was calculated from the appearance potential of the SO₂⁺ ion obtained from electron impact studies of SO₂ and SO₂P₂.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from O. R. Hunt, and M. K. Wilson, Spectrochim. Acta, 16, 570 (1960). The bond distances and bond angles were reported by D. R. Lide, Jr., D. E. Mann, and R. M. Friarom, J. Chem. Phys., 26, 734 (1957). The entropy of sulfuryl fluoride gas has been calculated from the calorimetric data and the third law of thermodynamics to be 62.66 cal. deg.⁻¹ mole⁻¹ at 217.78°K. by P. J. Bockhoff, R. V. Petrella, and E. L. Pace, J. Chem. Phys. 32, 799 (1960). The discrepancy between entropy value calculated from calorimetric data and that calculated from molecular and spectroscopic data (1 atm., 217.78°K) is attributed to randomness in the solid at 0°K by P. J. Bockhoff and E. L. Pace, J. Chem. Phys. 34, 3502 (1962). The vibrational frequencies reported by M. D. Perkins and M. Kent Wilson, J. Chem. Phys. 20, 1791 (1952) were 1269 (1), 848 (1), 544 (1), [500] (1), [385] (1), 1502 (1), 553 (1), 885 (1), and 539 (1) cm.⁻¹. The three principal moments of inertia are: 1.6567 × 10⁻³⁶, 1.6567 × 10⁻³⁶, and 1.6349 × 10⁻³⁶ g. cm.².

F₂O₂S

Dec. 31, 1960 Mar. 31, 1963

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	ΔH _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞
100	9.213	55.351	-203.169	INFINITE
200	13.238	62.984	-203.910	439.124
298	16.356	68.883	-204.567	216.009
300	16.406	68.985	-205.000	142.351
300	16.406	68.985	-205.007	161.425
400	18.698	74.036	-205.825	104.053
500	20.355	78.396	-206.344	81.535
600	21.556	82.219	-206.689	66.490
700	22.453	85.617	-206.917	55.722
800	23.154	88.583	-207.023	47.134
900	23.572	91.400	-207.023	41.312
1000	23.947	93.904	-207.023	35.075
1100	24.239	96.200	-207.023	31.612
1200	24.470	98.320	-207.023	27.981
1300	24.653	100.280	-207.023	24.791
1400	24.807	102.119	-207.023	22.293
1500	24.931	103.835	-207.023	20.009
1600	25.034	105.447	-207.023	18.021
1700	25.118	106.967	-207.023	16.269
1800	25.184	108.400	-207.023	14.713
1900	25.238	109.769	-207.023	13.323
2000	25.312	111.066	-207.023	12.073
2100	25.359	112.302	-207.023	10.944
2200	25.400	113.483	-207.023	9.918
2300	25.436	114.613	-207.023	8.994
2400	25.468	115.696	-207.023	8.152
2500	25.496	116.736	-207.023	7.339
2600	25.521	117.737	-207.023	6.614
2700	25.543	118.700	-207.023	5.942
2800	25.563	119.627	-207.023	5.319
2900	25.581	120.527	-207.023	4.740
3000	25.598	121.395	-207.023	4.200
3100	25.612	122.234	-207.023	3.695
3200	25.626	123.048	-207.023	3.222
3300	25.639	123.833	-207.023	2.778
3400	25.650	124.592	-207.023	2.356
3500	25.660	125.346	-207.023	1.958
3600	25.669	126.086	-207.023	1.587
3700	25.678	126.772	-207.023	1.246
3800	25.686	127.413	-207.023	0.914
3900	25.693	128.010	-207.023	0.592
4000	25.700	128.575	-207.023	0.300
4100	25.707	129.109	-207.023	0.016
4200	25.713	130.029	-207.023	-0.254
4300	25.719	130.924	-207.023	-0.512
4400	25.725	131.794	-207.023	-0.758
4500	25.728	132.634	-207.023	-0.993
4600	25.733	133.444	-207.023	-1.217
4700	25.737	134.223	-207.023	-1.432
4800	25.741	134.972	-207.023	-1.637
4900	25.745	135.694	-207.023	-1.835
5000	25.748	136.394	-207.023	-2.024
5100	25.752	137.075	-207.023	-2.205
5200	25.755	137.738	-207.023	-2.380
5300	25.758	138.384	-207.023	-2.548
5400	25.761	139.014	-207.023	-2.710
5500	25.763	139.627	-207.023	-2.866
5600	25.766	140.224	-207.023	-3.016
5700	25.768	140.800	-207.023	-3.160
5800	25.770	141.358	-207.023	-3.300
5900	25.772	141.899	-207.023	-3.435
6000	25.774	142.422	-207.023	-3.566

Phosphorus Difluoride (PF₂)
(Ideal Gas) Mol. Wt. = 68.975

INTERIM TABLE

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔF°	Log K _p
0	0.000	INFINITE	0.000	INFINITE	-2.668	-104.696	INFINITE
100	8.216	52.151	1.189	1.045	-1.189	-104.696	1.189
200	9.437	58.201	63.143	0.889	-0.889	-106.628	116.512
298	10.677	62.207	62.207	0.000	0.000	-107.478	78.779
300	10.698	62.273	62.207	0.020	-105.003	-107.493	78.305
400	11.548	65.468	62.639	1.140	-105.186	-108.294	59.166
500	12.249	68.138	63.483	2.337	-105.367	-109.632	47.664
600	12.687	70.434	64.457	3.686	-105.551	-109.772	39.984
700	12.970	72.412	65.455	4.870	-105.751	-110.459	34.485
800	13.169	74.158	66.436	6.178	-106.392	-116.428	31.805
900	13.312	75.718	67.382	7.602	-106.380	-115.183	27.969
1000	13.415	77.126	68.287	8.639	-126.367	-115.940	24.900
1100	13.499	78.409	69.150	10.185	-126.354	-112.699	22.390
1200	13.562	79.586	69.971	11.458	-126.341	-111.458	20.298
1300	13.612	80.674	70.753	12.897	-126.329	-110.217	18.528
1400	13.652	81.684	71.498	14.269	-126.318	-108.978	17.011
1500	13.684	82.627	72.209	15.627	-126.305	-107.758	15.697
1600	13.711	83.511	72.888	16.997	-126.300	-106.502	14.547
1700	13.733	84.343	73.538	18.369	-126.294	-105.264	13.532
1800	13.752	85.129	74.160	19.743	-126.290	-104.024	12.630
1900	13.768	85.870	74.767	21.117	-126.287	-102.791	11.823
2000	13.782	86.579	75.351	22.497	-126.286	-101.555	11.097
2100	13.793	87.252	75.883	23.876	-126.287	-100.319	10.440
2200	13.804	87.894	76.414	25.255	-126.292	-99.082	9.842
2300	13.813	88.508	76.927	26.636	-126.297	-97.845	9.297
2400	13.821	89.096	77.422	28.018	-126.305	-96.609	8.797
2500	13.828	89.660	77.900	29.400	-126.315	-95.370	8.330
2600	13.834	90.202	78.363	30.783	-126.328	-94.133	7.912
2700	13.839	90.725	78.811	32.167	-126.342	-92.893	7.519
2800	13.844	91.228	79.245	33.551	-126.358	-91.655	7.154
2900	13.848	91.714	79.666	34.936	-126.376	-90.413	6.813
3000	13.853	92.184	80.077	36.321	-126.398	-89.175	6.490
3100	13.856	92.638	80.474	37.707	-126.420	-87.933	6.199
3200	13.860	93.078	80.861	39.092	-126.447	-86.692	5.921
3300	13.863	93.504	81.238	40.478	-126.474	-85.449	5.659
3400	13.866	93.916	81.605	41.863	-126.504	-84.205	5.412
3500	13.868	94.320	81.963	43.252	-126.536	-82.959	5.180
3600	13.870	94.711	82.311	44.639	-126.570	-81.714	4.960
3700	13.873	95.091	82.652	46.026	-126.607	-80.468	4.753
3800	13.875	95.461	82.984	47.413	-126.646	-79.218	4.556
3900	13.877	95.826	83.310	48.801	-126.686	-77.971	4.369
4000	13.878	96.173	83.628	50.188	-126.732	-76.722	4.192
4100	13.880	96.515	83.936	51.576	-126.778	-75.472	4.023
4200	13.881	96.850	84.239	52.964	-126.827	-74.221	3.864
4300	13.882	97.177	84.536	54.352	-126.877	-72.966	3.708
4400	13.883	97.498	84.827	55.740	-126.930	-71.709	3.562
4500	13.885	97.808	85.112	57.129	-126.986	-70.456	3.422
4600	13.886	98.113	85.392	58.518	-127.042	-69.201	3.288
4700	13.887	98.412	85.666	59.906	-127.103	-67.942	3.159
4800	13.888	98.704	85.934	61.295	-127.165	-66.680	3.036
4900	13.889	98.991	86.198	62.684	-127.229	-65.417	2.918
5000	13.890	99.271	86.456	64.073	-127.296	-64.156	2.804
5100	13.891	99.546	86.710	65.462	-127.366	-62.897	2.695
5200	13.891	99.816	86.960	66.851	-127.437	-61.624	2.590
5300	13.892	100.080	87.205	68.240	-127.511	-60.361	2.489
5400	13.893	100.340	87.446	69.629	-127.588	-59.099	2.392
5500	13.893	100.595	87.682	71.019	-127.665	-57.836	2.298
5600	13.894	100.845	87.915	72.408	-127.747	-56.556	2.207
5700	13.895	101.091	88.144	73.798	-127.830	-55.282	2.120
5800	13.895	101.333	88.370	75.187	-127.915	-54.010	2.035
5900	13.895	101.564	88.594	76.576	-128.001	-52.736	1.953
6000	13.896	101.804	88.810	77.966	-128.085	-51.460	1.874

June 30, 1962

Phosphorus Difluoride (PF₂) (Ideal Gas)

Mol. Wt. = 68.975

ΔH_f 298.15 = [-105 ± 15] kcal. mole⁻¹

S_{298.15} = [62.2 ± 3] cal. deg.⁻¹ mole⁻¹

Ground State Multiplicity = 2

Point Group C_{2v}

Vibrational Levels and Multiplicities
(U, cm.⁻¹)
(376) (1)
(775) (1)
(890) (1)

I_{AB}C = [1.9059 × 10⁻¹¹] g.³ cm.⁶ σ = 2

Heat of Formation. ΔH_f 298.15 was estimated by C. B. Henderson and R. S. Scheffer, "Atlantic Research Corp., Alexandria, Virginia, "Survey of Thermochemical Data," January, 1960. For their estimation they assumed certain bond energies for the dissociation of PF₃(g). Bond one was assumed 20% greater than bond two and three which were assumed to be equal. ΔH_f 298.18 was corrected for the change in phosphorus reference state (white α → red V).

Heat Capacity and Entropy. Molecular constants and vibrational levels were estimated by J. S. Gordon, Thiokol Chemical Corp., Reaction Motors Division, Denver, N. J., "Thermodynamic Data for Combustion Products," January, 1960.

Lead Difluoride (PbF₂)

GFW = 245.1868

T, °K	Cp	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0							
100							
200							
298	17.770	27.000	27.000	-0.000	-161.800	-150.790	110.431
300	17.750	27.110	27.000	-0.033	-161.793	-150.791	100.800
400	19.290	32.427	27.715	1.865	-161.813	-150.829	69.762
500	20.830	36.897	28.115	3.691	-160.837	-151.586	62.761
600	22.370	40.831	30.726	6.051	-160.199	-150.190	51.044
700	23.810	45.394	32.549	8.974	-159.093	-136.810	42.712
800	24.300	49.529	34.443	12.053	-158.505	-133.623	36.504
900	24.300	52.391	36.299	14.483	-157.665	-129.594	27.806
1000	24.300	54.925	38.103	16.511	-156.603	-127.594	21.806
1100	24.300	57.267	39.663	19.343	-155.987	-124.715	24.778
1200	24.300	59.362	41.238	21.773	-155.185	-121.907	27.202
1300	24.300	61.377	42.709	24.203	-154.304	-119.171	20.035
1400	24.300	63.126	44.104	26.633	-153.466	-116.511	16.761
1500	24.300	64.804	45.429	29.063	-152.631	-113.808	10.593
1600	24.300	66.372	46.689	31.493	-151.803	-111.333	15.207
1700	24.300	67.845	47.881	33.923	-150.980	-108.828	13.991
1800	24.300	69.234	49.038	36.353	-150.166	-106.375	17.916
1900	24.300	70.548	50.134	38.783	-149.358	-103.868	11.107
2000	24.300	71.795	51.184	41.213	-148.558	-101.594	

Mar. 31, 1962; Dec. 31, 1963; Dec. 31, 1965; June 30, 1969

(Crystal)

S°_{298.15} = [27.0 ± 2] gibbs/molT°₂ = 613°KT°₁ = 725°K

Tm = 1099°K

ΔH°_{298.15} = 88.5 kcal/mol

Heat of Formation

The heats of formation at 298.15°K derived from the enthalpy changes of different chemical reactions are listed below. The adopted one is the average of the last three ΔH°_{298.15} values, which is also in reasonable agreement with the ΔH°_{298.15} values evaluated from (1) and (5).

Reference	Chemical Reaction	ΔH° _{298.15} Kcal/mol	ΔH° _{298.15} Kcal/mol
1	PbF ₂ (c) + H ₂ (g) = Pb(l) + 2 HF(g)	32.0 ± 0.56*	-161.3 ± 0.6
2	PbF ₂ (c) + H ₂ O(g) = PbO(c) + 2 HF(g)	29.6 ± 2.1**	-154.5 ± 4.0
3	Pb(c) + F ₂ (g) = PbF ₂ (c)	-159.7 ± 0.5	-159.7 ± 0.5
4	PbO(c) + 2 HF(40% aq) = PbF ₂ (c) + H ₂ O(l)	-22.9 ± 0.3	-159.0 ± 0.5
5	PbF ₂ (c) + 2 Na(c) = Pb(c) + 2 NaF(aq)	-112.2 ± 0.2	-162.2 ± 0.4
6	PbF ₂ (c) + Mg(c) = Pb(c) + MgF ₂ (c)	-109.5 ± 1.5	-159.2 ± 2.0
7	3/2 PbF ₂ (c) + Al(c) = 3/2 Pb(c) + AlF ₃ (c)	-128.5 ± 0.1	-161.5 ± 1.0
8	3/2 PbF ₂ (c) + Al(c) = 3/2 Pb(c) + AlF ₃ (c)	-117.7 ± 0.6	-162.1 ± 1.0
9	1/2 PbF ₂ (c) + 1/3 Al(c) = 1/2 Pb(c) + 1/3 AlF ₃ (c)	-38.3 ± 0.8	-161.8 ± 1.0

* This is the third law value. The second law value is 32.4 ± 0.9 kcal/mol. The entropy drift is -0.5 ± 1.2 eu.
 ** This is the third law value. The second law value is 39.6 ± 0.7 kcal/mol. The entropy drift is -10.9 ± 0.8 eu.

Heat Capacity and Entropy

Banashek, Patsukova, and Rassonskaya (10) measured the high temperature enthalpies (H°-H°_{298.15}) for PbF₂(c) in the temperature range 670-1165°K. Based on their enthalpy measurements the heat capacity of PbF₂(c) at temperatures 725-1099°K is derived as 24.3 ± 0.2 gibbs/mol by the least square method. The heat capacities below 725°K are estimated using their reported enthalpies at 670-725°K, which are based on a mixture of β and γ, as a guide.

The S°_{298.15} is estimated to be 25 eu by the method suggested by Kubaschewski and Evans (11), and adjusted to 27 eu so that the second and third law ΔH°_{298.15} values derived from the equilibrium data reported by Jellinek and Rudat (1) are in good agreement.

Transition Data

The transition temperatures are obtained from Banashek, Patsukova, and Rassonskaya (10). The β + γ transition at 613°K was reported as either slow or irreversible and the γ + β transition at 725°K was reversible. The polymorphism of PbF₂(c) has been studied by many other investigators. However, the relations between the temperature and the character of polymorphic transformation are not consistent (10).

The enthalpy difference at 725°K for PbF₂(γ) and PbF₂(β) is ΔH°₁. The value of ΔH°₂ is estimated such that the generated functions yield reasonable agreement among the derived ΔH°₂₉₈ values (see the above table).

Melting Data

See PbF₂(l) table.

Heat of Sublimation

The difference between ΔH°_{298.15} for PbF₂(g) and PbF₂(c) is ΔH°_{298.15}.

References

1. K. Jellinek and A. Rudat, Z. Anorg. Chem. 175, 281 (1928).
2. M. L. Domange, Compt. Rend. 200, 2180 (1935).
3. W. Jahn-Held and K. Jellinek, Z. Elektrochem. 48, 401 (1936).
4. H. W. Martenberg, Z. Anorg. Allgem. Chem. 244, 337 (1940).
5. W. Martenberg, D. Anorg. Chem. 244, 337 (1940).
6. P. Gross, C. Hayman, and D. L. Levi, Trans. Faraday Soc. 50, 477 (1954).
7. P. Gross, C. Hayman, and D. L. Levi, Physical Chemistry of Process Metallurgy, Part 2, Interscience Publishers, Inc., New York, 1961.
8. V. P. Kolesov, A. M. Martynov, and S. M. Skuratov, Russ. J. Inorg. Chem. 8, 1326 (1961).
9. E. J. Heus and J. J. Egan, Z. Phys. Chem. 43, S. 38 (1966).
10. E. J. Heus and J. J. Egan, Z. Phys. Chem. 43, S. 38 (1966).
11. O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, Pergamon Press, New York, 1958.



GFW = 245.1868

(LIQUID)

LEAD DIFLUORIDE (PbF_2)

Lead Difluoride (PbF_2)

(Liquid) GFW = 245.1868

$\Delta H_f^{298.15} = -158.722$ kcal/mol

$\Delta H_m^* = 2.98$ kcal/mol

$T_m = 1099^\circ K$

Heat of Formation

$\Delta H_f^{298.15}(l)$ is obtained from $\Delta H_f^{298.15}(c)$ by adding ΔH_m^* and the difference between $H_m^* - H_m^{298.15}$ for crystal and liquid.

Heat Capacity and Entropy

The enthalpies ($H_m^* - H_m^{298.15}$) of $PbF_2(l)$ in the temperature range 1104-1165°K were determined by Banashek, Patsukova, and Rassonskaya (1). Based on their reported results the heat capacity of $PbF_2(l)$ is evaluated to be 24 ± 2 gibbs/mol by the least square method. This Cp value is adopted and extended to 298 and 2500°K, respectively.

The entropy ($S_{298.15}^*$) is calculated in a manner analogous to that of the heat of formation.

Melting Data

T_m is taken from Banashek, Patsukova, and Rassonskaya (1). The enthalpy difference at T_m for $PbF_2(l)$ and $PbF_2(s)$ is ΔH_m^* .

Other values of T_m (°K) reported are 1091 (2, 11), 1097 (3, 4, 5) and 1128 (6). Using the freezing point data of binary systems PbF_2-PbBr_2 (5), PbF_2-PbCl_2 (5, 7), PbF_2-PbI_2 (5, 8), PbF_2-PbO (9), and PbF_2-NaF (10), Kelley (3) evaluated the corresponding values of ΔH_m^* (kcal/mol) as 1.70, 1.96, 3.87, and 2.47. Other reported values of ΔH_m^* are 3.00 (1) and 4.16 (2) kcal/mol.

Vaporization Data

From mass spectroscopic study on the vapor species in PbF_2 , Zmbov, Hastie, and Margrave (4) have shown that molten PbF_2 vaporizes partly as molecular PbF_2 . There is considerable disproportionation, and at 715°K the vapor composition is approximately 66% PbF_2 , 25% PbF , 21% Pb , and 71% Pb (4, 12). T_b has been reported as 1565°K (11) where the vapor is expected to be a mixture of the above species.

References

1. E. I. Banashek, N. N. Patsukova, and I. S. Rassonskaya, Izvest. Sektora Fiz. Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk SSSR 27, 223 (1956).
2. M. Blanc, Diplôme d'Études Supérieures, Paris, 1956, quoted by M. Blanc and G. Perit, Compt. Rend. 248, 1305 (1959).
3. K. K. Kelley, U. S. Bur. Mines Bull. 393, 1936.
4. K. Zmbov, J. W. Hastie, and J. L. Margrave, Trans. Faraday Soc. 64, 861 (1968).
5. C. Sandonini, Gazz. Chim. Ital. 41, II 144 (1911).
6. Amadori, Gazz. Chim. Ital. 49, I 38 (1919).
7. C. Sandonini, Atti Acad. Lincei, Ser. 5, 20, I 172 (1911).
8. C. Sandonini, Atti Acad. Lincei, Ser. 5, 20, I 253 (1911).
9. C. Sandonini, Atti Acad. Lincei, Ser. 5, 23, I 959 (1914).
10. N. A. Puschin and A. B. Baskov, J. Russ. Phys. Chem. Soc. 45, 82 (1913); Z. Anorg. Chem. 81, 347 (1913).
11. H. V. Wartenberg and O. Bosse, Z. Elektrochem. 28, 384 (1922).
12. R. H. Hauge, J. W. Hastie, and J. L. Margrave, J. Phys. Chem. 72, 3510 (1968).

T, K	Cp	$S^* - (C^* - H_{298}^*)/T$	$H^* - H_{298}^*$	ΔG^*	Log Kp
100					
200					
298					
300	24.000	28.687	24.687	-148.202	108.635
400	24.000	28.786	26.688	-158.704	107.914
500	24.000	35.700	29.589	-157.724	79.095
600	24.000	41.036	31.367	-154.804	61.907
700	24.000	45.431	33.357	-155.926	50.514
800	24.000	49.131	35.353	-156.249	42.361
900	24.000	52.336	37.260	-155.434	36.279
1000	24.000	55.143	39.113	-154.424	31.573
1100	24.000	57.691	40.847	-153.417	27.827
1200	24.000	59.979	42.484	-153.004	24.779
1300	24.000	62.067	44.030	-152.194	22.252
1400	24.000	63.988	45.482	-151.395	20.125
1500	24.000	65.766	46.878	-150.577	18.312
1600	24.000	67.422	48.193	-149.772	16.749
1700	24.000	68.971	49.443	-148.974	15.389
1800	24.000	70.426	50.635	-148.181	14.195
1900	24.000	71.788	51.773	-147.397	13.140
2000	24.000	73.096	52.862	-146.614	12.200
2100	24.000	74.327	53.904	-145.844	11.349
2200	24.000	75.498	54.905	-145.077	10.481
2300	24.000	76.614	55.867	-144.321	9.555
2400	24.000	77.681	56.792	-143.564	8.751
2500	24.000	78.702	57.684	-142.804	8.016
		79.682	58.544	-142.042	7.344



LEAD DIFLUORIDE (PbF₂) (IDEAL GAS) GFW = 245.1868

Point Group C_{2v}

S_{298.15}^o = {71 ± 2} gibbs/mol

ΔHf₀^o = -102.7 ± 1 kcal/mol

ΔHf_{298.15}^o = -103.3 ± 1 kcal/mol

Ground State Quantum Weight = {1}

Lead Difluoride (PbF₂)

(Ideal Gas) GFW = 245.1868

T, °K	C _p ^o	S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	ΔHf ^o	ΔGf ^o	Log Kp
0	-0.000	-0.000	INFINITE	-3.1134	-102.644	-102.644	INFINITE
100	9.766	46.829	91.449	-2.265	-103.929	-103.862	226.991
200	11.549	46.186	72.152	-1.193	-103.160	-104.494	114.805
298	12.603	47.027	71.027	-0.000	-103.300	-105.416	77.272
300	12.616	71.105	71.027	.023	-101.303	-105.429	76.405
400	13.115	74.811	71.599	1.313	-103.435	-106.117	57.940
500	13.379	77.768	72.491	2.639	-103.549	-106.772	46.647
600	13.532	80.222	73.581	3.985	-103.745	-107.391	39.117
700	13.622	82.316	74.783	5.343	-105.124	-107.749	33.653
800	13.692	84.140	75.793	6.709	-105.349	-108.155	29.587
900	13.737	85.756	76.777	8.081	-105.567	-108.493	26.346
1000	13.769	87.205	77.748	9.456	-105.741	-108.806	23.740
1100	13.793	88.518	78.669	10.835	-105.895	-109.099	21.474
1200	13.812	89.719	79.580	12.215	-106.023	-109.370	19.191
1300	13.826	90.826	80.366	13.597	-106.140	-109.626	16.830
1400	13.838	91.851	81.151	14.980	-106.241	-109.866	14.410
1500	13.847	92.806	81.896	16.364	-106.330	-110.049	12.040
1600	13.854	93.700	82.606	17.749	-106.407	-110.200	10.046
1700	13.861	94.500	83.281	19.135	-106.476	-110.329	8.382
1800	13.866	95.332	83.931	20.521	-106.538	-110.439	7.069
1900	13.871	96.092	84.551	21.904	-106.593	-110.531	6.015
2000	13.874	96.793	85.146	23.296	-106.642	-110.608	5.273
2100	13.878	97.470	85.717	24.693	-106.676	-109.603	4.804
2200	13.881	98.133	86.268	26.095	-106.706	-108.675	4.404
2300	13.883	98.733	86.794	27.498	-106.732	-107.721	4.075
2400	13.885	99.324	87.304	28.848	-106.754	-106.745	3.805
2500	13.887	99.891	87.796	30.236	-106.774	-105.715	3.555
2600	13.889	100.436	88.272	31.625	-106.791	-104.629	3.322
2700	13.892	100.962	88.732	33.003	-106.806	-103.486	3.102
2800	13.893	101.465	89.178	34.382	-106.819	-102.292	2.895
2900	13.894	101.953	89.610	35.762	-106.830	-101.045	2.705
3000	13.894	102.424	90.030	37.142	-106.840	-99.745	2.535
3100	13.895	102.879	90.437	38.571	-106.848	-98.395	2.385
3200	13.895	103.320	90.827	40.000	-106.855	-96.995	2.255
3300	13.896	103.748	91.217	41.431	-106.860	-95.545	2.145
3400	13.896	104.163	91.592	42.840	-106.864	-94.045	2.055
3500	13.896	104.566	91.957	44.230	-106.867	-92.495	1.985
3600	13.897	104.957	92.313	45.520	-106.869	-90.895	1.935
3700	13.897	105.337	92.659	46.810	-106.870	-89.245	1.895
3800	13.900	105.709	92.999	48.100	-106.870	-87.545	1.865
3900	13.901	106.070	93.329	49.490	-106.869	-85.795	1.845
4000	13.901	106.422	93.652	51.080	-106.867	-84.005	1.835
4100	13.902	106.765	93.967	52.470	-106.864	-82.165	1.835
4200	13.902	107.107	94.278	53.860	-106.860	-80.275	1.845
4300	13.902	107.447	94.578	55.251	-106.855	-78.335	1.865
4400	13.903	107.747	94.878	56.641	-106.849	-76.345	1.895
4500	13.903	108.059	95.163	58.031	-106.841	-74.305	1.935
4600	13.903	108.365	95.447	59.421	-106.830	-72.215	1.985
4700	13.904	108.655	95.722	60.810	-106.816	-70.075	2.045
4800	13.904	108.937	95.988	62.202	-106.800	-67.885	2.115
4900	13.904	109.213	96.245	63.593	-106.781	-65.645	2.195
5000	13.904	109.524	96.527	64.983	-106.760	-63.355	2.285
5100	13.905	109.769	96.785	66.373	-106.735	-61.015	2.385
5200	13.905	110.009	97.031	67.763	-106.706	-58.625	2.495
5300	13.905	110.236	97.264	69.154	-106.674	-56.185	2.615
5400	13.905	110.598	97.530	70.545	-106.639	-53.695	2.745
5500	13.905	110.849	97.770	71.935	-106.600	-51.155	2.885
5600	13.906	111.100	98.006	73.326	-106.557	-48.565	3.035
5700	13.906	111.349	98.226	74.716	-106.511	-45.925	3.195
5800	13.906	111.586	98.466	76.107	-106.461	-43.235	3.365
5900	13.906	111.826	98.690	77.498	-106.408	-40.495	3.545
6000	13.906	112.059	98.911	78.888	-106.402	-37.705	3.735

Mar. 31, 1962; Dec. 31, 1963; Dec. 31, 1965; June 30, 1969

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹
[450] (1)
[120] (1)
[450] (1)

Bond Distance: Pb-F = 2.13 ± 0.02 Å

Bond Angle: F-Pb-F = {95°}

Product of the Moments of Inertia: I_AI_BI_C = {4.5690 × 10⁻¹¹⁴} g³ cm⁶ σ = 2

Heat of Formation

Vapor pressure data for PbF₂ have previously been interpreted on the assumption that PbF₂ was the only species present in the gas phase (1, 2). Zmbov, Hastie, and Margrave (3) have studied the vapor species over PbF₂(c, l) mass spectrometrically and shown that PbF₂ vaporizes only partly as molecular PbF₂ and there is considerable disproportionation. The vapor composition at 988°K is approximately 66% PbF₂, 25% PbF, and 7% Pb (3, 4). From extrapolation of the ion intensity data from 1043 to 988°K to the temperature region in which Nemeyanov and Iofa (2) measured the saturated vapor pressures of PbF₂(c), 792-988°K, by Knudsen effusion method, the partial pressure of PbF₂(c), at 988°K was calculated to be 0.0435 ± 0.005 torr. Based on this calculated vapor pressure, the heat of sublimation (ΔH_{sub})₂₉₈^o of PbF₂(c) is derived as 58.50 kcal/mol by the third law method, yielding ΔHf₂₉₈^o(PbF₂, g) = -103.3 ± 1 kcal/mol.

Due to lack of data on vapor compositions over PbF₂(c, l) at various temperatures, the total pressure measurements reported by Wartenberg and Bosc (1), using boiling point method, and those of Nemeyanov and Iofa (2) are not used for evaluation.

Heat Capacity and Entropy

The bond distance was determined by Akishin, Spiridonov, and Khodchenkova (5). The bond angle is assumed to be the same as that in PbX₂(g) where X = Cl, Br or I (6). The vibrational frequencies are calculated by valence force method (10) using force constants estimated by comparison with those for PbF (7), CaF₂ (8), HgF₂ (9), and HgF₂ (9). The value of ν₂ is in fair agreement with the value, 145 cm⁻¹, estimated by (4). The three principal moments of inertia are: I_A = 1.5559 × 10⁻³⁸, I_B = 1.1040 × 10⁻³⁸, and I_C = 2.6599 × 10⁻³⁸ g cm².

References

1. H. V. Wartenberg and O. Bosc, Z. Elektrochem. 28, 384 (1922).
2. A. N. Nemeyanov and B. Z. Iofa, Zh. Neorg. Khim. 2, 486 (1955).
3. K. Zmbov, J. W. Hastie, and J. L. Margrave, Trans. Faraday Soc. 64, 861 (1968).
4. R. H. Hauge, J. W. Hastie, and J. L. Margrave, J. Phys. Chem. 72, 3510 (1968).
5. P. A. Akishin, V. P. Spiridonov, and A. N. Khodchenkova, Zh. Fiz. Khim. 32, 1679 (1958).
6. H. Lister and L. E. Sutton, Trans. Faraday Soc. 37, 406 (1941).
7. G. Herzberg, 'Spectra of Diatomic Molecules,' D. Van Nostrand Co., Inc., New York, 1950.
8. G. V. Calder, Natl. Bur. Std. Rept. 9389, July 1966.
9. JANAF HgF₂(g) table, Mar. 31, 1966.
10. G. Herzberg, 'Infrared and Raman Spectra,' D. Van Nostrand Co., Inc., New York, 1945.

Silicon Difluoride (SiF₂)

(Ideal Gas) GFW = 66.0828

SILICON DIFLUORIDE (SiF₂)

(IDEAL GAS)

GFW = 66.0828

Point Group (C_{2v})

$$\Delta H_f^\circ = -140.3 \pm 3 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 61.30 \pm 0.05 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = -140.5 \pm 3 \text{ kcal/mol}$$

Electronic Levels and Quantum Weights

 $\epsilon_i, \text{ cm}^{-1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$
 $\frac{g_i}{1}$

T, K

Op°

S°

-(G°-H°)/T

H°-H°₂₉₈

kcal/mol

ΔH°

ΔG°

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

T, K

Op°

S°

-(G°-H°)/T

H°-H°₂₉₈

kcal/mol

ΔH°

ΔG°

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

T, K

Op°

S°

-(G°-H°)/T

H°-H°₂₉₈

kcal/mol

ΔH°

ΔG°

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

T, K

Op°

S°

-(G°-H°)/T

H°-H°₂₉₈

kcal/mol

ΔH°

ΔG°

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

T, K

Op°

S°

-(G°-H°)/T

H°-H°₂₉₈

kcal/mol

ΔH°

ΔG°

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

T, K

Op°

S°

-(G°-H°)/T

H°-H°₂₉₈

kcal/mol

ΔH°

ΔG°

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Log Kp

Titanium Difluoride (TiF₂)

(Ideal Gas) GFW = 85.8968

Point Group {D_{2h}} $\Delta H_f^\circ = -164.1 \pm 10 \text{ kcal/mol}$ $S_{298.15}^\circ = 61.1 \pm 1.5 \text{ gibbs/mol}$ $\Delta H_f^\circ = -164.5 \pm 10 \text{ kcal/mol}$

Ground State Quantum Weight = 3

T, °K	C _p ^a	$-\log_{10} S^\circ$	$-(C_p^\circ - T^\circ)_{298.15}^\circ$	ΔH_f°	Log K _p
0	0.000	INFINITE	-2.071	-164.109	INFINITE
100	0.238	89.695	71.156	-164.213	360.896
200	0.476	81.151	62.652	-164.316	121.782
298	0.638	61.081	42.000	-164.500	121.782
300	12.659	61.159	-0.23	-164.502	120.999
400	13.466	66.927	61.569	-166.610	91.032
500	13.942	67.990	62.573	-167.111	73.044
600	14.213	70.857	63.495	-167.593	61.066
700	14.367	72.762	64.637	-168.059	52.070
800	14.504	74.692	65.951	-168.509	46.035
900	14.590	76.405	67.019	-168.940	41.024
1000	14.660	77.946	68.036	-169.354	37.012
1100	14.722	79.346	69.001	-169.745	33.725
1200	14.784	80.630	69.918	-170.113	30.976
1300	14.850	81.816	70.746	-170.469	28.635
1400	14.923	82.919	71.615	-170.819	26.635
1500	15.002	83.951	72.404	-171.156	24.896
1600	15.089	84.922	73.156	-171.479	23.373
1700	15.181	85.840	73.875	-171.785	22.028
1800	15.278	86.710	74.564	-172.072	20.831
1900	15.378	87.539	75.226	-172.341	19.758
2000	15.479	88.330	75.861	-172.592	18.775
2100	15.579	89.088	76.473	-172.849	17.876
2200	15.678	89.815	77.063	-173.069	17.056
2300	15.773	90.514	77.633	-173.261	16.310
2400	15.868	91.187	78.184	-173.427	15.624
2500	15.956	91.837	78.717	-173.567	15.001
2600	16.040	92.464	79.234	-173.689	14.407
2700	16.120	93.071	79.735	-173.794	13.865
2800	16.194	93.659	80.222	-173.884	13.362
2900	16.264	94.228	80.695	-173.962	12.902
3000	16.330	94.781	81.155	-174.025	12.454
3100	16.391	95.317	81.604	-174.076	12.044
3200	16.449	95.836	82.040	-174.114	11.659
3300	16.503	96.345	82.466	-174.141	11.296
3400	16.554	96.839	82.882	-174.159	10.955
3500	16.602	97.319	83.287	-174.167	10.633
3600	16.648	97.788	83.684	-174.166	10.313
3700	16.692	98.244	84.071	-174.156	9.996
3800	16.733	98.690	84.450	-174.137	9.686
3900	16.773	99.125	84.821	-174.110	9.382
4000	16.811	99.550	85.184	-174.077	9.078
4100	16.848	99.966	85.539	-174.037	8.778
4200	16.884	100.372	85.887	-173.990	8.485
4300	16.918	100.770	86.229	-173.937	8.195
4400	16.952	101.160	86.564	-173.877	7.909
4500	16.984	101.541	86.892	-173.812	7.627
4600	17.016	101.914	87.215	-173.743	7.347
4700	17.046	102.281	87.532	-173.670	7.070
4800	17.075	102.640	87.843	-173.593	6.796
4900	17.104	102.992	88.148	-173.512	6.525
5000	17.131	103.338	88.446	-173.428	6.256
5100	17.157	103.678	88.744	-173.342	5.990
5200	17.183	104.011	89.034	-173.254	5.726
5300	17.207	104.339	89.320	-173.164	5.464
5400	17.230	104.660	89.601	-173.072	5.203
5500	17.251	104.977	89.878	-172.978	4.943
5600	17.272	105.288	90.150	-172.882	4.685
5700	17.291	105.594	90.418	-172.784	4.428
5800	17.309	105.895	90.683	-172.684	4.172
5900	17.325	106.191	90.943	-172.581	3.916
6000	17.341	106.487	91.200	-172.476	3.660

Dec. 31, 1960; June 30, 1964; Dec. 31, 1967; June 30, 1968; Dec. 31, 1968

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	(3)
(7000)	(6)
(17000)	(6)
(22000)	(15)

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹
(473) (1)
(203) (2)
(633) (1)

Bond Distance: Ti-F = (1.95) Å

Bond Angle: F-Ti-F = (180°)

Rotational Constant: B₀ = (0.1167) cm⁻¹

Heat of Formation

Zhbov and Margrave (1) have reported ion intensities and the corresponding equilibrium constants for the reaction $\text{Ca(g)} + \text{TiF}_3(\text{g}) = \text{CaF(g)} + \text{TiF}_2(\text{g})$. Second and third law analyses of their data give a second law ΔH_{298}° of 7.0 kcal/mol, a third law ΔH_{298}° of 11.76 kcal/mol and a third law drift of 3.1 ± 3.8 au. The heat of formation, ΔH_{298}° , of $\text{TiF}_2(\text{g})$ is calculated from the third law ΔH_{298}° , above, and the JANAF heat of formation of $\text{TiF}_3(\text{g})$, CaF(g) and Ca(g) .

Heat Capacity and Entropy

The interatomic distances are estimated from those of TiCl_2 , TiCl_4 , and TiF_4 . The vibrational frequencies are estimated from a valence force field model.

The electronic levels are assumed to be the same as $\text{TiCl}_2(\text{g})$. The levels of $\text{TiCl}_2(\text{g})$ are estimated by assuming they correspond to the inverted states of $\text{NiCl}_2(\text{g})$ (2). The linear configuration is assumed because experimental evidence (3) indicates that other transition metal difluorides, viz. those of Mn, Co, Ni, Cu, and Zn, are linear.

References

1. K. F. Zhbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
2. C. W. DeKock and D. H. Gruen, J. Chem. Phys. **44**, 4387 (1966).
3. A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. **40**, 3471 (1964).

GF_W = 129.2168

(CRYSTAL)

ZIRCONIUM DIFLUORIDE (ZrF₂)Zirconium Difluoride (ZrF₂)GF_W = 129.2168

(Crystal)

 $\Delta H_f^\circ = \text{Unknown}$ $\Delta H_f^\circ_{298.15} = [-230 \pm 15] \text{ kcal/mol}$ $\Delta H_m^\circ = [9 \pm 2] \text{ kcal/mol}$ $\Delta H_s^\circ_{298.15} = [96.6] \text{ kcal/mol}$ $S^\circ_{298.15} = [18 \pm 2] \text{ gibbs/mol}$ $T_m = [1175 \pm 150]^\circ \text{K}$

Heat of Formation

More recent thermal data related to the heat of formation of ZrF₂(c) is unavailable. The adopted ΔH_f° (ZrF₂, c) value is taken from (1) which was estimated by Brewer (2).

Heat Capacity and Entropy

The heat capacities in the temperature range 298-2000°K are estimated by comparison with those of ZrF₄(c) and Zr(c). The S°_{298} is calculated as 17.2 and 17.0 eu based on the assumptions that $S(\text{ZrF}_2) = 1/2[S(\text{ZrF}_4) + S(\text{Zr})]$ and $S(\text{ZrF}_2) = S(\text{ZrF}_2) - S(\text{Zn}) + S(\text{Zr})$. Using the additive entropy constants $S^\circ_{298} = 12.1$ and 4.7 eu for Zr and F suggested by Kubaschewski and Evans (3), we obtain $S^\circ_{298}(\text{ZrF}_2, c) = 12.1 + 2(4.7) = 21.5$ eu. Based on $S^\circ_{298} = 11.5$ and 3.9 eu for Zr⁴⁺ and F⁻ recommended by Kelley (4), the value $S^\circ_{298}(\text{ZrF}_2, c)$ is derived as 19.3 eu. The entropy at 298°K for ZrF₂(c) is tentatively adopted as 18 ± 2 eu.

Melting Data

Both T_m and ΔH_m° are estimated. The derived entropy of melting, 2.55 eu/atom, is the same as that of ZrF₄(c) which was obtained from experimental measurements (5). Therefore these estimated values are tentatively adopted.

Heat of Sublimation

The difference between ΔH_f° for ZrF₂(g) and ZrF₂(c) is $\Delta H_s^\circ_{298}$.

References

1. U. S. Natl. Bur. Std. Circ. 500, 1952.
2. L. Brewer, unpublished data. University of California, Berkeley, California.
3. O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.
4. K. K. Kelley, private communication, June 1960.
5. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).

T, °K	Cp*	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG°	Log Kp
0							
100	15.760	18.000	18.000	0.000	-230.000	-218.145	159.805
200							
298	15.760	18.098	18.000	0.029	-229.99A	-218.072	158.8A5
300	16.700	22.766	18.631	1.65A	-229.76A	-218.130	116.095
400	17.500	26.580	19.850	3.365	-229.511	-210.252	91.801
500							
600	18.200	29.83A	21.050	5.151	-229.235	-206.42A	75.190
700	18.800	32.687	22.68A	7.002	-228.941	-202.687	63.2A9
800	19.270	35.228	24.096	8.906	-228.63A	-198.912	54.3A0
900	19.700	37.523	25.462	10.855	-228.325	-195.215	47.405
1000	20.080	39.619	26.775	12.86A	-228.010	-191.553	41.86A
1100	20.380	41.587	28.031	14.86A	-227.695	-187.923	37.337
1200	20.650	43.332	29.233	16.919	-227.377	-184.269	33.5A0
1300	20.890	44.995	30.382	18.997	-227.05A	-180.62A	30.36A
1400	21.100	46.551	31.482	21.097	-226.72A	-177.01A	27.433
1500	21.230	48.011	32.536	23.213	-226.399	-173.443	25.271
1600							
1700	21.350	49.386	33.546	25.343	-226.072	-169.905	23.208
1800	21.420	50.682	34.517	27.481	-225.740	-166.39A	21.301
1900	21.480	51.909	35.449	29.627	-225.406	-162.91A	19.7A1
2000	21.500	53.071	36.346	31.777	-225.071	-159.459	18.3A2
2100	21.500	54.17A	37.210	33.927	-224.740	-156.027	17.050

(LIQUID)

ZIRCONIUM DIFLUORIDE (ZrF₂)

GFW = 129.2168

S_{298.15}^o = [24.103] gibbs/mol $\Delta H_f^{\circ}{}_{298.15}$ = [-222.502] kcal/molT_m = [1175 ± 150]*K ΔH_m° = [9 ± 2] kcal/molT_b = [2529]*K ΔH_v° = [169.0] kcal/mol

Heat of Formation

The $\Delta H_{f298}^{\circ}(\ell)$ is obtained from $\Delta H_{f298}^{\circ}(c)$ by adding ΔH_m° and the difference between $H_{1175}^{\circ} - H_{298}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated from those of ZrF₄(ℓ), CaF₂(ℓ), Zr(ℓ), and Ca(ℓ), and is assumed to be constant in the temperature range 800-1000°K. A glass transition temperature is assumed at 800°K. The Cp values below 800°K are adopted from the ZrF₂(c) table.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

Both T_m and ΔH_m° are estimated. The derived entropy of melting, 2.55 eu/atom, is the same as that of ZrF₄(c) which was obtained from experimental measurements (1). Therefore these estimated values are tentatively adopted.

Vaporization Data

T_b is the temperature at which the Gibbs energy change of the process ZrF₂(ℓ) = ZrF₂(g) approaches zero. The difference between ΔH_f° for ZrF₂(ℓ) and ZrF₂(g) at T_b is ΔH_v° .

References

1. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).

Zirconium Difluoride (ZrF₂)

GFW = 129.2168

(Liquid)

T, °K	Cp ^o	S ^o gibbs/mol	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	ΔH ^o kcal/mol	ΔG ^o	Log Kp
0							
100							
200							
298	15.760	24.103	24.103	.000	-222.502	-212.467	155.742
300	15.760	24.201	24.103	.029	-222.498	-212.405	154.737
400	16.750	25.683	25.683	1.416	-222.498	-207.075	141.232
500	17.500	26.683	26.683	3.365	-222.013	-205.806	89.958
600	18.200	35.937	27.353	5.151	-221.737	-202.589	73.783
700	18.800	36.780	28.787	7.002	-221.443	-199.421	62.262
800	24.000	41.332	30.199	8.907	-221.137	-196.296	53.626
900	24.000	44.148	31.488	10.807	-219.848	-192.002	41.542
1000	24.000	46.688	32.981	12.707	-219.449	-190.261	41.542
1100	24.000	48.975	34.333	14.607	-218.958	-187.356	37.224
1200	24.000	51.063	35.681	16.507	-218.151	-184.461	33.595
1300	24.000	52.984	36.902	20.907	-216.388	-181.602	30.530
1400	24.000	54.768	38.015	23.707	-214.787	-178.603	25.452
1500	24.000	56.419	39.281	25.707	-217.787	-174.603	25.452
1600	24.000	57.968	40.401	28.107	-216.030	-173.374	23.642
1700	24.000	59.423	41.478	30.507	-215.284	-170.729	21.949
1800	24.000	60.795	42.513	32.907	-214.558	-168.132	20.418
1900	24.000	62.102	43.510	35.307	-213.848	-165.585	18.945
2000	24.000	63.323	44.470	37.707	-213.182	-163.088	17.417
2100	24.000	64.484	45.386	40.107	-212.455	-160.562	16.710
2200	24.000	65.611	46.269	42.507	-211.785	-157.930	15.649
2300	24.000	66.697	47.153	44.907	-211.120	-155.267	14.754
2400	24.000	67.746	48.036	47.307	-210.460	-152.567	13.968
2500	24.000	68.679	48.796	49.707	-210.034	-150.034	13.116
2600	24.000	69.620	49.579	52.107	-210.142	-147.456	12.395
2700	24.000	70.526	50.336	54.507	-210.467	-144.902	11.729
2800	24.000	71.399	51.075	56.907	-210.438	-142.375	11.113
2900	24.000	72.241	51.781	59.307	-210.438	-139.875	10.548
3000	24.000	73.054	52.465	61.707	-210.537	-137.389	10.009

Dec. 31, 1960; June 30, 1961; June 30, 1969



GFV = 129.2168

(IDEAL GAS)

ZIRCONIUM DIFLUORIDE (ZrF_2)

$\Delta H_f^\circ = -132.0 \pm 5$ kcal/mol

ΔH_f° 298.15 = -133.4 $\pm$ 5 kcal/mol

Point Group C_{2v}

$S^\circ_{298.15} = 167.7 \pm 2$ gibbs/mol

Ground State Quantum Weight = {3}

Zirconium Difluoride (ZrF_2)
(Ideal Gas)

GFV = 129.2168

T, °K	C_p°	gibbs/mol S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	.000	.000	INFINITE	-2.027	-132.796	-132.796	INFINITE
100	8.509	56.898	77.099	2.020	-132.966	-132.966	293.253
200	10.249	83.336	86.741	.000	-133.161	-133.161	147.906
298	11.626	87.715	87.715	.000	-133.400	-133.400	99.960
300	11.647	87.787	87.787	.022	-133.403	-136.366	99.357
400	12.437	91.257	88.183	1.229	-133.569	-137.352	75.045
500	12.896	94.086	89.090	2.498	-133.778	-138.272	60.439
600	13.176	96.444	90.126	3.803	-133.983	-139.151	50.466
700	13.357	98.509	91.181	5.130	-134.213	-139.995	43.708
800	13.481	100.302	92.211	6.472	-134.470	-140.804	38.466
900	13.572	101.895	93.200	7.825	-134.755	-141.579	34.380
1000	13.646	103.329	94.143	9.186	-135.068	-142.371	31.104
1100	13.711	104.632	95.038	10.554	-135.409	-143.030	28.417
1200	13.776	105.828	95.888	11.928	-135.768	-143.655	26.163
1300	13.844	106.934	96.696	13.309	-136.144	-144.231	24.247
1400	13.918	107.962	97.464	14.697	-136.536	-144.791	22.603
1500	13.999	108.925	98.196	16.093	-136.943	-145.334	21.175
1600	14.086	109.831	98.896	17.497	-137.368	-145.863	19.924
1700	14.180	110.688	99.564	18.910	-137.811	-146.375	18.814
1800	14.277	111.501	100.205	20.333	-138.270	-146.875	17.833
1900	14.378	112.276	100.820	21.766	-138.742	-147.359	16.950
2000	14.479	113.016	101.411	23.209	-139.228	-147.829	16.154
2100	14.581	113.725	101.981	24.662	-139.728	-148.289	15.433
2200	14.684	114.406	102.530	26.125	-140.242	-148.758	14.778
2300	14.777	115.061	103.061	27.598	-140.770	-149.242	14.185
2400	14.870	115.691	103.574	29.080	-141.311	-149.731	13.643
2500	14.959	116.300	104.071	30.572	-141.863	-150.230	13.156
2600	15.043	116.888	104.553	32.072	-142.425	-150.746	12.729
2700	15.123	117.458	105.020	33.580	-143.000	-151.278	12.267
2800	15.198	118.009	105.474	35.096	-143.587	-151.822	11.776
2900	15.268	118.543	105.916	36.620	-144.186	-152.376	11.264
3000	15.334	119.062	106.346	38.150	-144.797	-152.941	10.748
3100	15.395	119.566	106.764	39.684	-145.420	-153.516	10.224
3200	15.453	120.056	107.172	41.229	-146.054	-154.100	9.693
3300	15.507	120.532	107.569	42.777	-146.700	-154.692	9.156
3400	15.559	120.996	107.957	44.330	-147.356	-155.292	8.613
3500	15.607	121.447	108.336	45.888	-148.022	-155.900	8.063
3600	15.653	121.888	108.707	47.451	-148.697	-156.516	7.508
3700	15.696	122.317	109.069	49.019	-149.381	-157.139	6.948
3800	15.738	122.736	109.423	50.591	-150.072	-157.768	6.383
3900	15.778	123.146	109.770	52.166	-150.770	-158.402	5.813
4000	15.816	123.546	110.109	53.746	-151.474	-159.040	5.238
4100	15.853	123.937	110.442	55.330	-152.184	-159.688	4.658
4200	15.889	124.319	110.767	56.917	-152.900	-160.346	4.073
4300	15.924	124.693	111.087	58.507	-153.622	-161.012	3.483
4400	15.957	125.060	111.401	60.100	-154.350	-161.686	2.888
4500	15.990	125.419	111.708	61.699	-155.082	-162.366	2.288
4600	16.021	125.771	112.010	63.299	-155.818	-163.050	1.683
4700	16.051	126.115	112.306	64.903	-156.558	-163.738	1.073
4800	16.081	126.454	112.598	66.510	-157.300	-164.430	0.458
4900	16.109	126.786	112.884	68.119	-158.046	-165.126	-0.158
5000	16.137	127.111	113.165	69.731	-158.796	-165.826	-0.768
5100	16.164	127.431	113.442	71.346	-159.548	-166.530	-1.373
5200	16.188	127.745	113.714	72.964	-160.302	-167.238	-1.973
5300	16.212	128.054	113.981	74.584	-161.058	-167.948	-2.568
5400	16.235	128.357	114.245	76.206	-161.816	-168.658	-3.158
5500	16.257	128.655	114.504	77.831	-162.576	-169.368	-3.743
5600	16.277	128.948	114.759	79.458	-163.338	-170.078	-4.323
5700	16.297	129.237	115.011	81.086	-164.102	-170.788	-4.898
5800	16.314	129.520	115.259	82.717	-164.868	-171.498	-5.468
5900	16.331	129.799	115.503	84.349	-165.636	-172.208	-6.033
6000	16.346	130.074	115.743	85.983	-166.406	-172.918	-6.593

Bond Distance: $Zr-F = (1.92) \text{ \AA}$
Bond Angle: $F-Zr-F = (125^\circ)$
Product of the Moments of Inertia: $I_{AB}^2 C = (1.3968 \times 10^{-114}) \text{ g cm}^6$
 $\sigma = 2$

Heat of Formation

Murad and Hildenbrand (1) studied the gaseous equilibria involving ZrF_4 , ZrF_3 , ZrF_2 , Ca , and CaF , mass-spectrometrically. Ion intensities were measured 3 eV above threshold over the temperature range 1665-1747°K, and the equilibrium constants for the reaction $2 Ca(g) + ZrF_4(g) = 2 CaF(g) + ZrF_2(g)$ were calculated. Using the reported equilibrium constants, the enthalpy changes (ΔH_f°) of this reaction are evaluated by the second and third law methods to be 15.4 and 50.9 kcal/mol, respectively. The drift in third law values is 70.4 ± 17.6 eu. Based on the third law ΔH_f° value and ΔH_f° 298 = 42.85 $\pm$ 0.3, -65.0 $\pm$ 2, and -400.0 $\pm$ 0.5 kcal/mol for $Ca(g)$, $CaF(g)$, and $ZrF_4(g)$, respectively, we obtain ΔH_f° (ZrF_2, g) = -133.4 $\pm$ 5 kcal/mol, which is adopted.
Using Gibbs energy functions derived from different molecular constants for the reactants and products, Murad and Hildenbrand (1) derived a third law ΔH_f° 298 = 42.6 $\pm$ 5 and ΔH_f° (ZrF_2, g) = -141 $\pm$ 5 kcal/mol, which are in fair agreement with the adopted values.

Heat Capacity and Entropy

According to the correlations of Charkin and Dyatkina (2), the $ZrF_2(g)$ molecule has an angular configuration. The $F-Zr-F$ angle is estimated as 125° , which is similar to the value reported by Hastie, Hauge, and Margrave (3) for $TiF_2(g)$. The $F-Zr$ bond distance is estimated from that of $ZrF_6(g)$. The vibrational frequencies are calculated based on the method suggested by Herzberg (3). The value ν_1 is calculated from the vibrational frequency (ν) of $ZrF(g)$ by use of the relation $\nu_1 = \nu \sqrt{\frac{M_{Zr}}{M_{Ti}}}$, where Zr and F are gram atomic weights of zirconium and fluorine. ν_3 is derived from ν_1 using the formula $\nu_3 = \nu_1 \sqrt{\frac{M_{Zr}}{M_{Ti}}}$, where the value 0.44 ν_3 where the value 0.44 is estimated by comparison with the ratios of ν_2/ν_3 for other related compounds. Ground state quantum weight is taken to be the same as that of $TiF_2(g)$. The three principal moments of inertia are: $I_A = 1.830 \times 10^{-38}$, $I_B = 3.502 \times 10^{-39}$ and $I_C = 2.180 \times 10^{-38} \text{ g cm}^2$. The electronic levels and quantum weights are estimated to be the same as those of $TiF_2(g)$.

References

1. E. Murad and D. L. Hildenbrand, J. Chem. Phys. **45**, 4751 (1966).
2. O. P. Charkin and M. E. Dyatkina, Russ. J. Struct. Chem. (English Transl.) **5**, 550 (1965).
3. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945.
4. J. V. Hastie, R. H. Hauge, and J. L. Margrave, J. Chem. Phys. **51**, 2648 (1969).



T, °K.	C _p	S° - (F° - H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	Log K _p
0					
100	21.750	23.500	0.000	-249.000	170.341
200	21.900	23.635	0.040	-248.962	169.215
300	21.900	23.635	0.040	-248.962	168.215
400	21.900	23.635	0.040	-248.962	167.215
500	22.805	35.584	4.711	-247.088	96.709
600	23.140	39.778	28.092	-216.104	78.745
700	23.140	43.267	30.024	-210.969	65.864
800	23.140	46.756	31.462	-205.781	56.214
900	24.040	49.330	33.672	-200.544	48.712
1000	24.340	51.879	35.371	-195.267	42.712
1100	24.640	54.212	36.979	-190.049	37.701
1200	24.940	56.369	38.506	-185.084	33.701
1300	25.240	58.352	39.952	-180.267	30.237
1400	25.540	60.259	41.322	-175.595	27.211
1500	25.840	62.031	42.663	-171.065	24.704
1600	26.140	63.708	43.926	-166.602	22.462
1700	26.440	65.302	45.137	-162.305	20.485
1800	26.740	66.822	46.309	-158.167	18.730
1900	27.040	68.272	47.450	-154.187	17.159
2000	27.340	69.670	48.547	-150.361	15.766

Sept. 30, 1965

IRON TRIFLUORIDE (FeF₃)

(CRYSTAL)

 $\Delta H_f^0 =$ Unknown ΔH_f^0 298.15 = -249 ± 3 kcal. mole⁻¹ ΔH_g^0 298.15 = [52.8] kcal. mole⁻¹ $S_{298.15}^0 = [23.5 \pm 2]$ cal. deg.⁻¹ mole⁻¹ $T_g = [1200]^{\circ}\text{K.}$

Heat of Formation.

The equilibrium pressures for the reaction $2\text{FeF}_3(\text{c}) + \text{H}_2(\text{g}) = 2\text{FeF}_2(\text{c}) + 2\text{HF}(\text{g})$ have been measured at temperatures 623, 723 and 823°K. by K. Jellinek and A. Rudat, Z. anorg. allgem. Chem. 175, 281 (1928). Using the reported data, the enthalpy change of the reaction was evaluated as 37.9 and 31.3 kcal. mole⁻¹ by the third and second law methods, respectively. The corresponding ΔH_f^0 298.15 (FeF₃, c) values are calculated to be -252.4 and -249.2 kcal. mole⁻¹. The equilibrium constants for the reaction $2\text{FeF}_3(\text{c}) + 3\text{H}_2\text{O}(\text{g}) = \text{Fe}_2\text{O}_3(\text{c}) + 6\text{HF}(\text{g})$ were determined by L. Domange, Ann. Chim., 7, 225 (1937). Based on the third law value of ΔH_f^0 298.15, 62.0 kcal. mole⁻¹, the ΔH_f^0 298.15 (FeF₃, c) was calculated as -237.4 kcal. mole⁻¹. The value of ΔH_f^0 298.15 for FeF₃(c) is selected to be -249 ± 3 kcal. mole⁻¹.

Heat Capacity and Entropy.

The heat capacities of FeF₃(c) at temperatures 100-450°K. were determined by H. Bizette, R. Mainard and J. Picard, Comp. rend. 5508 (1965). The results were presented graphically by plotting C_p vs. T. The C_p curve shows a peak at 367°K. An antiferromagnetic transition at about 394°K. was reported by E. O. Mollan, H. R. Child, W. C. Koshler and M. K. Wilkinson, Phys. Rev. 112, 1132 (1958). The heat capacities above 450°K. and $S_{298.15}^0$ were estimated by comparison with those for FeCl₃(c) AlCl₃(c) and AlF₃(c).

Sublimation Data.

The phenomenon that FeF₃(c) sublimates without fusion at temperatures near 1000°C has been observed and reported by Poulenc, Ann. Chim. phys. (7), 2, 1 (1894). Based on this data the value of T_m was estimated. The value of heat of sublimation (ΔH_{sub}^0 298.15) was calculated using an estimated entropy of sublimation, $\Delta S_{\text{sub}}^0 = 40$ e.u. In order to have $\Delta H_{\text{sub}}^0 = 0$ for the reaction $\text{FeF}_3(\text{c}) = \text{FeF}_3(\text{g})$ at 1200°K.

Iron Trifluoride (FeF₃)

(Ideal Gas) Mol. wt. = 112.8422



MOL. WT. = 112.8422

IRON TRIFLUORIDE (FeF₃) (IDEAL GAS)

Point Group [D_{3h}]
 $S^{\circ}_{298.15} = [72.7] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = [1]

$\Delta H^{\circ}_f 0 = [-195.5 \pm 5] \text{ kcal. mole}^{-1}$
 $\Delta H^{\circ}_f 298.15 = [-196.2 \pm 5] \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies
 $\omega, \text{ cm.}^{-1}$

[600] (1) [800] (2)
 [250] (1) [220] (2)

Bond Distance: Fe-F = [1.9] cm.⁻¹
 Bond Angle: F-Fe-F = [120]°
 Product of the Moments of Inertia: $I_A I_B I_C = [9.96723 \times 10^{-114}] \text{ g.}^3 \text{ cm.}^6$
 $\sigma = [6]$

Heat of Formation.

The value of $\Delta H^{\circ}_f 298.15$ (FeF₃, g) was calculated from $\Delta H^{\circ}_f 298.15$ and $\Delta H^{\circ}_f 298.15$ for FeF₃(c). The value $\Delta H^{\circ}_f 298.15 = 65.5 \text{ kcal. mole}^{-1}$ was derived from $\Delta H^{\circ}_f 1200$ (see FeF₃(c) table for details).

Heat Capacity and Entropy.

The molecular structure, bond distance and angle were estimated by comparison with those for AlF₃(g). The vibrational frequencies were estimated by comparison with those for AlF₃(g), TlF₃(g) and ZrF₃(g). The three principal moments of inertia are: $I_A = I_B = 1.7081 \times 10^{-38}$ and $I_C = 3.4182 \times 10^{-38} \text{ g. cm.}^2$.

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	-0.000	0.000	INFINITE	3.539	-195.499	-195.499	INFINITE
100	10.557	58.479	85.163	2.668	-195.774	-195.371	426.963
200	13.644	66.840	74.063	1.445	-196.022	-194.867	212.930
298	15.666	72.690	72.690	0.000	-196.200	-194.259	142.389
300	15.697	72.787	72.690	0.029	-196.203	-194.247	141.502
400	17.027	77.500	73.423	1.670	-196.343	-193.573	105.758
500	17.858	81.396	76.560	3.418	-196.481	-192.866	84.298
600	18.389	84.702	75.982	5.232	-196.644	-192.128	69.979
700	18.782	87.525	75.483	7.045	-196.822	-191.356	59.742
800	19.086	90.084	74.883	8.977	-197.014	-190.532	51.855
900	19.310	92.331	80.237	10.885	-197.214	-189.713	46.066
1000	19.488	94.357	81.569	12.807	-197.426	-188.820	41.264
1100	19.625	96.206	82.709	14.741	-197.655	-187.851	37.321
1200	19.730	97.900	83.760	16.683	-197.897	-186.821	34.045
1300	19.810	99.450	84.727	18.633	-198.151	-185.731	31.405
1400	19.866	100.898	85.613	20.587	-198.415	-184.604	28.631
1500	19.905	102.250	87.219	22.546	-198.687	-183.450	26.749
1600	19.937	103.516	88.199	24.508	-198.965	-182.288	24.925
1700	19.963	104.702	90.032	26.440	-199.247	-181.130	23.313
1800	19.985	105.832	90.032	28.440	-199.522	-180.000	21.865
1900	19.704	106.897	90.891	30.410	-199.795	-178.807	20.567
2000	19.720	107.908	91.717	32.381	-200.067	-177.568	19.383
2100	19.734	108.870	92.511	34.354	-200.340	-176.346	18.310
2200	19.744	109.789	93.279	36.328	-200.609	-175.142	17.332
2300	19.757	110.667	94.023	38.302	-200.875	-173.962	16.451
2400	19.767	111.508	94.725	40.279	-201.137	-172.812	15.615
2500	19.775	112.315	95.412	42.257	-201.397	-171.686	14.857
2600	19.782	113.091	96.077	44.234	-201.654	-170.584	14.155
2700	19.788	113.831	96.714	46.211	-201.907	-169.504	13.503
2800	19.794	114.537	97.324	48.188	-202.157	-168.444	12.931
2900	19.800	115.212	97.911	50.172	-202.403	-167.404	12.431
3000	19.804	115.852	98.479	52.152	-202.645	-166.384	11.981
3100	19.809	116.572	99.110	54.133	-202.883	-165.384	11.584
3200	19.813	117.271	100.207	56.114	-203.117	-164.404	11.244
3300	19.816	117.941	100.773	58.095	-203.347	-163.444	10.951
3400	19.819	118.403	101.246	60.077	-203.572	-162.504	10.707
3500	19.822	118.977	101.746	62.059	-203.792	-161.584	10.507
3600	19.825	119.536	102.177	64.041	-204.007	-160.684	10.344
3700	19.828	120.079	102.711	66.023	-204.217	-159.804	10.204
3800	19.830	120.608	103.177	68.007	-204.422	-158.944	10.084
3900	19.832	121.123	103.672	69.990	-204.622	-158.104	9.984
4000	19.834	121.625	104.135	71.973	-204.817	-157.284	9.907
4100	19.836	122.115	104.577	73.957	-205.007	-156.484	9.844
4200	19.838	122.593	105.000	75.941	-205.192	-155.704	9.794
4300	19.839	123.060	105.416	77.924	-205.372	-154.944	9.754
4400	19.841	123.516	105.835	79.908	-205.547	-154.204	9.724
4500	19.842	123.962	106.253	81.893	-205.717	-153.484	9.694
4600	19.844	124.398	106.666	83.877	-205.882	-152.784	9.664
4700	19.846	124.825	107.071	85.861	-206.042	-152.104	9.634
4800	19.848	125.242	107.466	87.846	-206.197	-151.444	9.604
4900	19.849	125.650	107.851	89.831	-206.347	-150.804	9.574
5000	19.850	126.046	108.226	91.815	-206.492	-150.184	9.544
5100	19.852	126.431	108.593	93.800	-206.632	-149.584	9.514
5200	19.853	126.806	108.951	95.784	-206.767	-148.994	9.484
5300	19.854	127.172	109.300	97.769	-206.897	-148.424	9.454
5400	19.855	127.529	109.641	99.754	-207.022	-147.874	9.424
5500	19.856	127.876	109.976	101.740	-207.142	-147.344	9.394
5600	19.857	128.214	110.306	103.726	-207.257	-146.834	9.364
5700	19.858	128.542	110.631	105.711	-207.367	-146.344	9.334
5800	19.859	128.861	110.951	107.696	-207.472	-145.874	9.304
5900	19.860	129.171	111.266	109.681	-207.572	-145.424	9.274
6000	19.861	129.472	111.576	111.667	-207.667	-144.984	9.244

Trifluorosilane (SiHF₃)
(Ideal Gas) Mol. Wt. = 86.098

T, °K	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _f
0	∞	∞	∞	∞	∞	∞	∞	∞
100	12.146	53.100	INFINITE	3.249	-281.316	INFINITE	INFINITE	INFINITE
200	17.453	60.668	7.773	1.112	-281.316	281.316	281.316	0.000
298	18.153	66.317	6.317	0.000	-281.316	281.316	281.316	0.000
300	18.153	66.317	6.317	0.000	-281.316	281.316	281.316	0.000
400	17.453	71.102	1.664	1.028	-281.316	281.316	281.316	0.000
500	16.153	75.190	3.499	3.499	-281.316	281.316	281.316	0.000
600	14.453	78.401	6.964	5.482	-281.316	281.316	281.316	0.000
700	12.146	80.927	7.120	7.576	-281.316	281.316	281.316	0.000
800	10.453	82.973	7.282	9.753	-281.316	281.316	281.316	0.000
900	9.247	84.575	7.428	11.997	-281.316	281.316	281.316	0.000
1000	8.153	85.953	7.571	14.292	-281.316	281.316	281.316	0.000
1100	7.153	87.219	7.710	16.628	-281.316	281.316	281.316	0.000
1200	6.153	88.471	7.849	18.998	-281.316	281.316	281.316	0.000
1300	5.153	89.702	7.978	21.396	-281.316	281.316	281.316	0.000
1400	4.153	90.914	8.107	23.816	-281.316	281.316	281.316	0.000
1500	3.153	92.103	8.236	26.255	-281.316	281.316	281.316	0.000
1600	2.153	93.261	8.361	28.711	-281.316	281.316	281.316	0.000
1700	1.153	94.417	8.486	31.179	-281.316	281.316	281.316	0.000
1800	0.153	95.573	8.611	33.660	-281.316	281.316	281.316	0.000
1900	0.153	96.729	8.736	36.150	-281.316	281.316	281.316	0.000
2000	0.153	97.885	8.861	38.644	-281.316	281.316	281.316	0.000
2100	0.153	99.041	8.986	41.155	-281.316	281.316	281.316	0.000
2200	0.153	100.197	9.111	43.666	-281.316	281.316	281.316	0.000
2300	0.153	101.353	9.236	46.176	-281.316	281.316	281.316	0.000
2400	0.153	102.509	9.361	48.686	-281.316	281.316	281.316	0.000
2500	0.153	103.665	9.486	51.196	-281.316	281.316	281.316	0.000
2600	0.153	104.821	9.611	53.706	-281.316	281.316	281.316	0.000
2700	0.153	105.977	9.736	56.216	-281.316	281.316	281.316	0.000
2800	0.153	107.133	9.861	58.726	-281.316	281.316	281.316	0.000
2900	0.153	108.289	9.986	61.236	-281.316	281.316	281.316	0.000
3000	0.153	109.445	10.111	63.746	-281.316	281.316	281.316	0.000
3100	0.153	110.601	10.236	66.256	-281.316	281.316	281.316	0.000
3200	0.153	111.757	10.361	68.766	-281.316	281.316	281.316	0.000
3300	0.153	112.913	10.486	71.276	-281.316	281.316	281.316	0.000
3400	0.153	114.069	10.611	73.786	-281.316	281.316	281.316	0.000
3500	0.153	115.225	10.736	76.296	-281.316	281.316	281.316	0.000
3600	0.153	116.381	10.861	78.806	-281.316	281.316	281.316	0.000
3700	0.153	117.537	10.986	81.316	-281.316	281.316	281.316	0.000
3800	0.153	118.693	11.111	83.826	-281.316	281.316	281.316	0.000
3900	0.153	119.849	11.236	86.336	-281.316	281.316	281.316	0.000
4000	0.153	121.005	11.361	88.846	-281.316	281.316	281.316	0.000
4100	0.153	122.161	11.486	91.356	-281.316	281.316	281.316	0.000
4200	0.153	123.317	11.611	93.866	-281.316	281.316	281.316	0.000
4300	0.153	124.473	11.736	96.376	-281.316	281.316	281.316	0.000
4400	0.153	125.629	11.861	98.886	-281.316	281.316	281.316	0.000
4500	0.153	126.785	11.986	101.396	-281.316	281.316	281.316	0.000
4600	0.153	127.941	12.111	103.906	-281.316	281.316	281.316	0.000
4700	0.153	129.097	12.236	106.416	-281.316	281.316	281.316	0.000
4800	0.153	130.253	12.361	108.926	-281.316	281.316	281.316	0.000
4900	0.153	131.409	12.486	111.436	-281.316	281.316	281.316	0.000
5000	0.153	132.565	12.611	113.946	-281.316	281.316	281.316	0.000
5100	0.153	133.721	12.736	116.456	-281.316	281.316	281.316	0.000
5200	0.153	134.877	12.861	118.966	-281.316	281.316	281.316	0.000
5300	0.153	136.033	12.986	121.476	-281.316	281.316	281.316	0.000
5400	0.153	137.189	13.111	123.986	-281.316	281.316	281.316	0.000
5500	0.153	138.345	13.236	126.496	-281.316	281.316	281.316	0.000
5600	0.153	139.501	13.361	129.006	-281.316	281.316	281.316	0.000
5700	0.153	140.657	13.486	131.516	-281.316	281.316	281.316	0.000
5800	0.153	141.813	13.611	134.026	-281.316	281.316	281.316	0.000
5900	0.153	142.969	13.736	136.536	-281.316	281.316	281.316	0.000
6000	0.153	144.125	13.861	139.046	-281.316	281.316	281.316	0.000

December 31, 1960.

Trifluoromethane (SiHF₃)
(Ideal Gas)

Mol. Wt. = 86.098

ΔH_f° 298.15 = [-283 ± 15] kcal. mole⁻¹S° 298.15 = 66.304 cal. deg.⁻¹ mole⁻¹Point Group C_{3v}

Vibrational Frequencies and Degeneracies

ω cm. ⁻¹	
2315 (1)	999 (2)
859 (1)	644 (2)
425 (1)	305 (2)

Moments of Inertia: I_A = 11.7272 X 10⁻³⁹ g. cm.² I_C = 20.6927 X 10⁻³⁹ g. cm.²
I_B = 11.7272 X 10⁻³⁹ g. cm.² I_C = 20.6927 X 10⁻³⁹ g. cm.²

Heat of Formation. ΔH_f° 298.15 was found estimated in C. B. Henderson and R. S. Scheffer, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were assigned by C. Newman, S. Polo and M. Wilson, Spec. Chim. Acta 15, 793 (1959). Constants used in calculating moment of inertia came from G. Heath, L. Thomas, and J. Sheridan, Trans. Far. Soc. 50, 779 (1954).

Nitrogen Trifluoride (NF₃)

(Ideal Gas) GFW = 71.0019

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log Kp
0	.000	.000	INFINITE	-	30.061	INFINITE
100	8.135	51.551	71.697	-2.832	30.061	60.746
200	10.224	63.387	1.131	-27.995	28.731	27.052
298	12.756	62.299	.000	-31.430	21.515	15.771
300	12.799	62.378	.024	-31.434	21.454	15.629
400	14.765	66.349	1.409	-31.552	16.104	9.692
500	16.169	69.804	2.960	-31.563	16.740	6.443
600	17.072	72.834	4.424	-31.503	11.379	4.105
700	17.706	75.518	5.865	-31.403	2.508	2.508
800	18.157	77.914	6.715	-31.279	4.704	1.285
900	18.458	80.072	6.890	-31.140	1.390	.337
1000	18.728	82.033	70.140	-30.993	1.107	.417
1100	18.914	83.827	71.340	-30.842	5.190	.431
1200	19.059	85.479	72.450	-30.689	6.460	1.521
1300	19.174	87.009	73.512	-30.537	11.717	1.970
1400	19.266	88.434	74.528	-30.386	14.661	2.335
1500	19.342	89.766	75.499	-30.237	18.196	2.651
1600	19.404	91.016	76.431	-30.090	21.419	2.924
1700	19.454	92.186	77.321	-29.945	24.435	3.167
1800	19.500	93.307	78.181	-29.805	27.339	3.340
1900	19.537	94.363	79.005	-29.666	31.039	3.470
2000	19.569	95.366	79.788	-29.530	34.232	3.741
2100	19.597	96.321	80.542	-29.394	37.414	3.894
2200	19.621	97.233	81.260	-29.269	40.593	4.033
2300	19.642	98.106	82.011	-29.143	43.764	4.159
2400	19.660	98.942	82.700	-29.020	46.933	4.274
2500	19.677	99.745	83.365	-28.901	50.095	4.379
2600	19.691	100.517	84.010	-28.787	53.253	4.474
2700	19.716	101.267	84.624	-28.674	56.404	4.566
2800	19.726	102.000	85.212	-28.564	59.555	4.654
2900	19.736	102.669	85.831	-28.454	62.704	4.725
3000	19.744	103.338	86.484	-28.357	65.841	4.786
3100	19.748	103.995	86.941	-28.277	68.970	4.843
3200	19.752	104.642	87.502	-28.162	72.115	4.905
3300	19.759	105.292	88.030	-28.070	75.247	4.963
3400	19.766	105.810	88.544	-27.940	78.374	5.014
3500	19.771	106.383	89.046	-27.895	81.507	5.069
3600	19.777	106.940	89.535	-27.812	84.632	5.138
3700	19.782	107.482	90.013	-27.731	87.753	5.183
3800	19.787	108.010	90.480	-27.658	90.874	5.227
3900	19.791	108.524	90.936	-27.567	93.990	5.267
4000	19.795	109.025	91.382	-27.517	97.108	5.306
4100	19.799	109.514	91.818	-27.452	100.222	5.342
4200	19.802	109.991	92.248	-27.391	103.332	5.377
4300	19.805	110.457	92.663	-27.331	106.451	5.410
4400	19.808	110.912	93.073	-27.277	109.559	5.442
4500	19.811	111.356	93.474	-27.225	112.666	5.472
4600	19.814	111.793	93.864	-27.176	115.774	5.501
4700	19.816	112.219	94.254	-27.131	118.881	5.524
4800	19.818	112.636	94.632	-27.089	121.992	5.554
4900	19.820	113.045	95.004	-27.051	125.094	5.580
5000	19.822	113.446	95.369	-27.017	128.201	5.604
5100	19.824	113.838	95.727	-26.965	131.298	5.627
5200	19.826	114.223	96.079	-26.915	134.395	5.647
5300	19.828	114.601	96.425	-26.832	137.513	5.670
5400	19.829	114.971	96.765	-26.812	140.604	5.691
5500	19.831	115.335	97.099	-26.894	143.715	5.711
5600	19.832	115.693	97.428	-26.880	146.814	5.730
5700	19.835	116.043	97.750	-26.861	150.023	5.746
5800	19.835	116.389	98.070	-26.846	153.023	5.763
5900	19.836	116.728	98.344	-26.834	156.114	5.774
6000	19.837	117.061	98.692	-26.654	159.221	5.800

Dec. 31, 1960; Mar. 31, 1961; Mar. 31, 1964; June 30, 1969

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹
1032 (1)
642 (1)
906 (2)
492 (2)

Bond Distance: N-F = 1.371 Å

Bond Angle: F-N-F = 102.9°

Product of the Moments of Inertia: $I_A I_B I_C = 8.855 \times 10^{-115} \text{ g}^3 \text{ cm}^6$

Heat of Formation

The adopted heat of formation was obtained from a simultaneous adjustment of several interrelated pieces of data relating to the heat of formation of HF (see HF, g table 12-31-68). The data which was considered relating directly to NF₃ was as follows.

A. $8 \text{ NF}_3(\text{g}) + 3 \text{ C}_2\text{H}_2(\text{g}) \rightarrow 6 \text{ CF}_4(\text{g}) + 7 \text{ N}_2(\text{g})$

Walker (1) reported $\Delta H_{298}^\circ = -1308.8 \pm 1.3 \text{ kcal/mol}$.

B. $\text{NF}_3(\text{g}) + 1.5 \text{ H}_2(\text{g}) \rightarrow \text{NH}_3(50 \text{ H}_2\text{O}) + 0.5 \text{ N}_2(\text{g})$

Sinke (2) reported $\Delta H_{298}^\circ = -199.49 \pm 0.22 \text{ kcal/mol}$ for a final state of HF(123 H₂O); the corrected value is $-199.40 \pm 0.22 \text{ kcal/mol}$.

C. $2 \text{ NF}_3(\text{g}) + \text{S}(\text{c, rh}) \rightarrow \text{SF}_6(\text{g}) + \text{N}_2(\text{g})$

Walker (3) reported $\Delta H_{298}^\circ = -228.26 \pm 0.25 \text{ kcal/mol}$.

D. $\text{NF}_3(\text{g}) + 0.5 \text{ N}_2(\text{g}) + 1.5 \text{ F}_2(\text{g})$

Sinke (4) reported $\Delta H_{298}^\circ = 31.44 \pm 0.3 \text{ kcal/mol}$ for the above dissociation from experimental explosion of hydrogen in 10 percent and 100 percent excess NF₃.

E. $\text{NF}_3(\text{g}) + \text{B}(\text{c, p}) \rightarrow \text{BF}_3(\text{g}) + 0.5 \text{ N}_2(\text{g})$

Ludwig and Cooper (5) reported $\Delta H_{298}^\circ = -239.46 \pm 1.2 \text{ kcal/mol}$, 5 percent of the boron remained unreacted and was detected by analysis.

Further details of the simultaneous adjustment are given by Syverud (6).

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Schatz and Levin (7) and are in good agreement with those of Pace and Pierce (8), and Wilson and Polo (9). The adopted values are also in agreement with the Raman studies of Kotov and Tatevskii (10). The bond length and angle were from the microwave studies of Sheridan and Gordy (11), whose values are in substantial agreement with the electron diffraction results of Schomaker and Lu (12).

The individual moments of inertia are $I_A = I_B = 7.854 \times 10^{-39} \text{ g cm}^2$ and $I_C = 14.354 \times 10^{-39} \text{ g cm}^2$.

Pierce and Pace (13) have obtained the entropy of the gas at 144.15°K from solid heat capacity measurements and the heats of melting and vaporization. Their reported value of 54.50 eu is in good agreement with our calculated value of 54.56 eu.

References

1. L. C. Walker, paper presented at 22nd Annual Calorimetry Conference, Thousand Oaks, Calif., June 1967.
2. G. C. Sinke, J. Chem. Eng. Data **10**, 295 (1965).
3. L. C. Walker, J. Phys. Chem. **71**, 361 (1967).
4. G. C. Sinke, J. Phys. Chem. **71**, 359 (1967).
5. J. R. Ludwig and W. J. Cooper, J. Chem. Eng. Data **7**, 76 (1963).
6. A. N. Syverud, AFRPL-TR-69-70, Jan. 1969.
7. F. N. Schatz and I. W. Levin, J. Chem. Phys. **29**, 475 (1958).
8. E. L. Pace and L. Pierce, J. Chem. Phys. **23**, 1248 (1955).
9. M. K. Wilson and S. R. Polo, J. Chem. Phys. **20**, 1716 (1952).
10. Yu. I. Kotov and V. M. Tatevskii, Opt. Spectry. (Eng. Transl.) **14**, 160 (1963), Supplement 2 Molecular Spectroscopy.
11. J. Sheridan and W. Gordy, Phys. Rev. **79**, 513 (1950).
12. V. Schomaker and C. Lu, J. Amer. Chem. Soc. **72**, 1182 (1950).
13. L. Pierce and E. L. Pace, J. Chem. Phys. **23**, 551 (1955).

Trifluoramine Oxide (NOF₃)

(Ideal Gas)

GF_W = 87.0013

(IDEAL GAS)

TRIFLUORAMINE OXIDE (NOF₃)Point Group C_{3v}S₀⁰ = 66.54 ± 0.05 gibbs/mol

Ground State Quantum Weight = 1

GF_W = 87.0013 $\Delta H_f^0 = -37.0 \pm 5.0$ kcal/mol $\Delta H_f^{298.15} = -39.0 \pm 5.0$ kcal/mol

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
1687 (1)	887 (2)
743 (1)	528 (2)
558 (1)	398 (2)

Bond Distance: N-O = [1.151] Å N-F = 1.48 ± 0.1 Å

Bond Angle: ONF = [109° 28'] ONF = [109° 28']

Product of the Moments of Inertia: I_AI_BI_C = [4.0703 × 10⁻¹¹⁴] g³ cm⁶

Heat of Formation

Bougon et al. (1) determined equilibrium constants for the reaction NOF(g) + F₂(g) ⇌ NOF₃(g) as a function of temperature and total pressure. Second and third law analyses of these equilibrium data are given below:

Set I	Set II	No. of Points	Temp. Range, °K	$\Delta H_f^{298.15}$, kcal/mol	Drift, gibbs/mol
7	1	7	533-643	-17.1	-18.7
		1	533.2	-18.2	

Set I contains their equilibrium data as a function of temperature, while Set II is their adopted equilibrium constant, K_p(553.2°K) = 0.015 ± 0.005 atm.⁻¹, corresponding to the lowest pressure (103 atm.) that was studied. Estimated corrections for nonideality are small and neglected. Adopting $\Delta H_f^{298.15}$ = -18.7 ± 1.0 kcal/mol, we derive ΔH_f^0 (NOF₃, g) = -34.4 ± 1.4 kcal/mol with ΔH_f^0 (NOF, g) = -15.7 ± 0.4 kcal/mol (2).

Armstrong and King (3) determined ΔH_f^{304} = -253.7 ± 0.6 kcal/mol for the reaction NOF₃(g) + 5/2 H₂(g) + 122 H₂O(l) + 1/2 N₂(g) + [3HF·123 H₂O(l)] in a constant pressure flame calorimeter. Combining this result with their earlier enthalpy data for reduction reactions involving F₂(g) and O₂(g) with H₂(g), they obtained ΔH_f^{304} (NOF₃, g) = -44.7 ± 1.5 kcal/mol. Very recently, Dbeiler and Walker (4) investigated the photolysis of NOF₃ by mass spectrometry. From their ionization threshold data, they determined ΔH_f^0 (NOF₃, g) = -69.6 ± 1.2 kcal/mol.

The value for the heat of formation of gaseous NOF₃ is tentatively selected as -39.0 ± 5.0 kcal/mol.

Heat Capacity and Entropy

Several recent infrared (5, 6, and 7) and Raman (8) studies of NOF₃ have been reported in the literature. The fundamental vibrational frequencies observed in the infrared spectrum of the molecule by the various investigators are in good agreement, although the assignment of the ν_3 and ν_5 bonding modes has varied. Fox et al. (6) assigned ν_3 = 558 cm⁻¹ and ν_5 = 528 cm⁻¹, while Curtis et al. (7) reversed the assignments. Very recently, Abramowitz and Levin (8) investigated the Raman spectrum of polycrystalline film of NOF₃ at 78°K and assigned ν_3 = 535 cm⁻¹ and ν_5 = 522 cm⁻¹, consistent with the infrared work of Fox et al. (6). The fundamental vibrational frequencies and assignments given by Fox et al. (6) are adopted here.

Fox et al. (6) also investigated the nuclear magnetic resonance spectrum of NOF₃ which indicated that the molecule contained three equivalent fluorine atoms. This result, along with the general appearance of the infrared spectrum, clearly establishes that the molecule has C_{3v} symmetry. The N-O bond distance and bond angles are estimated quantities from the work of Curtis et al. (7). These estimated data have been used in calculating the N-F bond distance from the rotational constants given by Curtis et al. (7). Individual moments of inertia calculated from the structural data given above are: I_A = I_B = 14.86 × 10⁻³⁹ g cm², and I_C = 18.44 × 10⁻³⁹ g cm².

References

1. R. Bougon, J. Chatelet, J. P. Dermoulin, and P. Plurien, *Compt. Rend.*, **276**, 760 (1968).
2. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Mich., June 30, 1961.
3. G. T. Armstrong and R. C. King, *Natl. Bur. Std., AFOSR 69-2154 TR*, July 1, 1969.
4. V. H. Dbeiler and J. A. Walker, *Inorg. Chem.*, **8**, 1728 (1969).
5. N. Bartlett, J. Pasmore, and E. J. Wells, *Chem. Commun.*, **8**, 1728 (1969).
6. W. B. Fox, J. S. Mackenzie, N. Vanderkooi, B. S. Sukornick, C. A. Wamser, J. R. Holmes, R. E. Eibeck, and B. B. Stewart, *J. Am. Chem. Soc.*, **88**, 2604 (1966).
7. E. C. Curtis, D. Filipovich, and M. H. Moberly, *J. Chem. Phys.*, **46**, 2904 (1967).
8. S. Abramowitz and I. W. Levin, *J. Chem. Phys.*, **51**, 463 (1969).
9. W. B. Fox, J. S. Mackenzie, E. R. McCarthy, J. R. Holmes, R. F. Stahl, and R. J. Jaurik, *Inorg. Chem.*, **7**, 2064 (1968).

June 30, 1970

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH_f^0	Log Kp
0	0.000	INFINITE	INFINITE	3.266	-	INFINITE
100	5.000	50.000	50.000	3.027	-37.027	16.891
200	12.535	60.404	60.404	2.821	-38.662	16.891
298	16.219	66.535	66.535	2.421	-39.004	16.891
300	16.277	66.636	66.636	2.404	-39.004	16.715
400	18.824	71.692	71.692	1.794	-39.099	9.400
500	20.535	76.069	76.069	1.329	-39.053	5.329
600	21.721	79.944	79.944	1.083	-38.919	2.488
700	22.569	83.359	83.359	0.907	-38.731	1.466
800	23.191	86.416	86.416	0.800	-38.511	1.040
900	23.658	89.175	89.175	0.733	-38.268	0.803
1000	24.016	91.687	91.687	0.689	-38.012	0.733
1100	24.295	93.990	93.990	0.659	-37.747	0.689
1200	24.517	96.114	96.114	0.636	-37.479	0.659
1300	24.695	98.083	98.083	0.618	-37.204	0.636
1400	24.840	99.919	99.919	0.603	-36.930	0.618
1500	24.959	101.637	101.637	0.590	-36.656	0.603
1600	25.059	103.251	103.251	0.579	-36.384	0.590
1700	25.142	104.773	104.773	0.569	-36.113	0.579
1800	25.213	106.212	106.212	0.560	-35.848	0.569
1900	25.274	107.577	107.577	0.553	-35.583	0.560
2000	25.326	108.875	108.875	0.546	-35.323	0.553
2100	25.372	110.111	110.111	0.540	-35.066	0.546
2200	25.412	111.293	111.293	0.535	-34.815	0.540
2300	25.446	112.423	112.423	0.530	-34.567	0.535
2400	25.477	113.507	113.507	0.525	-34.325	0.530
2500	25.504	114.547	114.547	0.521	-34.089	0.525
2600	25.528	115.548	115.548	0.517	-33.856	0.521
2700	25.550	116.512	116.512	0.513	-33.628	0.517
2800	25.570	117.441	117.441	0.510	-33.405	0.513
2900	25.587	118.339	118.339	0.507	-33.187	0.510
3000	25.603	119.207	119.207	0.504	-32.976	0.507
3100	25.617	120.046	120.046	0.501	-32.767	0.504
3200	25.630	120.860	120.860	0.499	-32.565	0.501
3300	25.642	121.649	121.649	0.497	-32.368	0.499
3400	25.653	122.414	122.414	0.495	-32.175	0.497
3500	25.663	123.158	123.158	0.493	-31.989	0.495
3600	25.672	123.881	123.881	0.492	-31.805	0.493
3700	25.681	124.585	124.585	0.491	-31.628	0.492
3800	25.689	125.270	125.270	0.490	-31.455	0.491
3900	25.696	125.937	125.937	0.489	-31.287	0.490
4000	25.703	126.586	126.586	0.488	-31.123	0.489
4100	25.709	127.223	127.223	0.487	-30.965	0.488
4200	25.715	127.842	127.842	0.486	-30.811	0.487
4300	25.720	128.447	128.447	0.485	-30.659	0.486
4400	25.725	129.039	129.039	0.484	-30.515	0.485
4500	25.730	129.617	129.617	0.483	-30.374	0.484
4600	25.734	130.182	130.182	0.482	-30.236	0.483
4700	25.738	130.736	130.736	0.481	-30.105	0.482
4800	25.742	131.278	131.278	0.480	-29.976	0.481
4900	25.746	131.809	131.809	0.479	-29.852	0.480
5000	25.749	132.329	132.329	0.478	-29.732	0.479
5100	25.753	132.839	132.839	0.477	-29.616	0.478
5200	25.756	133.339	133.339	0.476	-29.504	0.477
5300	25.758	133.829	133.829	0.475	-29.396	0.476
5400	25.761	134.311	134.311	0.474	-29.293	0.475
5500	25.764	134.784	134.784	0.473	-29.192	0.474
5600	25.766	135.248	135.248	0.472	-29.097	0.473
5700	25.769	135.704	135.704	0.471	-28.995	0.472
5800	25.771	136.152	136.152	0.470	-28.916	0.471
5900	25.773	136.595	136.595	0.469	-28.832	0.470
6000	25.775	137.026	137.026	0.468	-28.751	0.469

GF_W = 103.9684

(IDEAL GAS)

PHOSPHORYL FLUORIDE (POF₃) $\Delta H_f^\circ = -293.9 \pm 1.9 \text{ kcal/mol}$ Point Group C_{3v} $\Delta H_f^\circ = -295.6 \pm 1.9 \text{ kcal/mol}$ $S_{298.15}^\circ = 68.10 \pm 0.07 \text{ gibbs/mol}$

Ground State Quantum Weight = 11

Vibrational Frequencies and Degeneracies

$\frac{\omega_e}{\text{cm}^{-1}}$	$\frac{\omega_2}{\text{cm}^{-1}}$
1417.7 (1)	994 (2)
872.8 (1)	483.2 (2)
473.2 (1)	335.6 (2)

Band Distance: P-0 = 1.45 ± 0.03 Å P-F = 1.52 ± 0.02 Å

Band Angle: F-P-F = 102.5° ± 2° F-P-O = 115.8° ± 2°

Product of Moments of Inertia: $I_A I_B I_C = 5.9019 \times 10^{-114} \text{ g cm}^6$

Heat of Formation

Ebel and Bretscher (1) measured the enthalpy change for the following reaction:

They reported a heat of reaction of $-70.6 \pm 1 \text{ kcal/mol}$. Combining this result with the heat of formation of PF₃, $\Delta H_f^\circ = -224.9 \pm 0.9 \text{ kcal/mol}$ (2), we derive, $\Delta H_f^\circ(\text{POF}_3, \text{g}) = -295.6 \pm 1.9 \text{ kcal/mol}$.

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Sellig and Claassen (3) and are in good agreement with the Raman and infrared studies of Gutowsky and Liehr (4). Several microwave studies ($\bar{\nu}$, $\bar{\nu}$, $\bar{\nu}$) of POF₃ have been reported. As pointed out by Williams et al. (2), the rotational constant calculated from their microwave studies leads to a moment of inertia, I_B , which is in disagreement with the moment of inertia calculated from the molecular constants obtained from electron-diffraction studies by Brockway and Beach (5). Since insufficient microwave data were available for an independent determination, Williams et al. (2) sought to find parameters which were consistent with both measurements. Their molecular constants are adopted for this tabulation. Individual moments of inertia are $I_A = I_B = 18.244 \times 10^{-39} \text{ g cm}^2$ and $I_C = 17.731 \times 10^{-39} \text{ g cm}^2$.

References

1. F. Ebel and E. Bretscher, *Helv. Chim. Acta*, **12**, 450 (1929).
2. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, Dec. 31, 1969.
3. H. Sellig and H. H. Claassen, *J. Chem. Phys.*, **44**, 1404 (1966).
4. H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952).
5. S. J. Senatore, *Phys. Rev.*, **78**, 293 (1950).
6. N. J. Hawkins, V. W. Cohen, and W. S. Kaski, *J. Chem. Phys.*, **20**, 528 (1952).
7. C. Williams, J. Sheridan, and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952).
8. C. A. Burrus and W. Gordy, *J. Chem. Phys.*, **26**, 391 (1957).
9. L. O. Brockway and J. Y. Beach, *J. Amer. Chem. Soc.*, **60**, 1836 (1938).

Phosphoryl Fluoride (POF₃)GF_W = 103.9684

(Ideal Gas)

T, K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^c	Log K _p
0	0.000	0.000	INFINITE	-3.385	-293.919	INFINITE
100	8.999	54.770	INFINITE	-2.569	-291.739	437.596
200	13.182	82.276	69.591	-1.661	-290.193	315.413
298	16.447	103.456	88.187	-0.000	-289.400	209.155
300	16.489	103.456	88.188	0.030	-289.404	207.619
400	18.904	121.385	97.866	1.600	-285.873	154.577
500	20.604	137.797	107.221	3.768	-279.237	101.017
600	21.605	151.666	117.612	5.912	-274.666	100.087
700	22.662	165.095	127.470	8.137	-271.080	84.635
800	23.287	176.184	136.436	10.434	-268.497	74.595
900	23.752	185.916	144.724	12.789	-266.370	66.914
1000	24.104	194.456	152.473	15.183	-264.688	57.421
1100	24.377	199.767	159.760	17.608	-263.438	50.949
1200	24.591	204.868	166.684	20.056	-262.571	45.718
1300	24.762	209.673	173.256	22.524	-262.026	41.295
1400	24.901	214.173	179.581	25.008	-261.738	37.507
1500	25.015	218.435	185.699	27.504	-261.659	34.276
1600	25.110	105.053	166.296	30.010	-261.841	31.358
1700	25.189	104.578	165.845	32.525	-262.250	28.659
1800	25.256	104.019	165.348	35.047	-262.864	26.194
1900	25.313	103.386	164.809	37.570	-263.651	24.075
2000	25.362	102.686	164.231	40.100	-264.598	22.270
2100	25.405	113.924	92.616	42.648	-265.704	21.117
2200	25.442	113.107	92.566	45.191	-266.987	19.654
2300	25.474	112.239	92.481	47.736	-268.400	18.301
2400	25.503	111.324	92.371	50.285	-269.914	17.062
2500	25.529	110.365	92.240	52.837	-271.561	15.922
2600	25.551	117.347	96.043	55.391	-273.347	14.872
2700	25.571	118.232	97.670	57.947	-275.254	13.999
2800	25.589	119.016	99.163	60.505	-277.281	13.287
2900	25.604	120.160	100.414	63.065	-279.431	12.717
3000	25.620	121.059	99.153	65.626	-281.697	12.282
3100	25.634	121.669	99.872	68.189	-284.086	11.942
3200	25.646	122.683	100.573	70.753	-286.596	11.686
3300	25.657	123.472	101.255	73.318	-289.226	11.496
3400	25.667	124.238	101.919	75.884	-291.974	11.345
3500	25.676	124.987	102.568	78.451	-294.840	11.215
3600	25.685	125.706	103.200	81.019	-297.821	11.104
3700	25.693	126.410	103.818	83.588	-300.918	11.007
3800	25.700	127.095	104.422	86.158	-304.131	10.924
3900	25.707	127.763	105.012	88.728	-307.459	10.850
4000	25.713	128.414	105.584	91.299	-310.896	10.784
4100	25.718	129.049	106.153	93.871	-314.444	10.724
4200	25.724	129.668	106.706	96.443	-318.100	10.669
4300	25.729	130.274	107.247	99.016	-321.864	10.619
4400	25.733	130.868	107.777	101.589	-325.736	10.574
4500	25.736	131.444	108.296	104.162	-329.714	10.533
4600	25.742	132.009	108.806	106.736	-333.800	10.494
4700	25.746	132.563	109.305	109.311	-338.000	10.456
4800	25.749	133.105	109.796	111.885	-342.313	10.419
4900	25.753	133.636	110.277	114.461	-346.739	10.383
5000	25.756	134.156	110.749	117.034	-351.274	10.347
5100	25.759	134.666	111.213	119.612	-355.918	10.311
5200	25.762	135.167	111.669	122.188	-360.671	10.276
5300	25.764	135.657	112.117	124.764	-365.533	10.241
5400	25.767	136.139	112.557	127.341	-370.504	10.206
5500	25.769	136.612	112.990	129.917	-375.584	10.171
5600	25.771	137.076	113.416	132.494	-380.772	10.136
5700	25.774	137.532	113.836	135.072	-386.069	10.101
5800	25.776	137.981	114.248	137.649	-391.477	10.066
5900	25.778	138.421	114.654	140.227	-396.994	10.031
6000	25.779	138.855	115.054	142.805	-402.621	10.000

Mar. 31, 1963; Dec. 31, 1963; Dec. 31, 1969

Phosphorus Trifluoride (PF₃)
(Ideal Gas)GF_W = 87.969PHOSPHORUS TRIFLUORIDE (PF₃)
(IDEAL GAS)GF_W = 87.969Point Group C_{3v} $\Delta H_f^\circ = -224.0 \pm 0.9 \text{ kcal/mol}$ $\Delta H_f^\circ = -224.9 \pm 0.9 \text{ kcal/mol}$ $S_{298.15}^\circ = 65.23 \pm 0.03 \text{ gibbs/mol}$

Ground State Quantum Weight = [1]

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	kcal/mol	ΔG°	Log Kp
0	8.7700	53.2000	147.141E	-3.092	-223.045	-223.045	147.141E	
100	11.6200	60.1233	46.8433	-1.266	-224.639	-224.639	46.8433	
200	14.0277	65.2333	45.2333	.000	-224.900	-224.900	45.2333	
300	14.0666	65.3200	45.2333	.026	-224.904	-224.904	45.2333	
400	15.7911	65.6199	45.6088	1.5255	-225.093	-225.093	45.6088	
500	16.9920	66.7445	46.8433	3.165	-225.235	-225.235	46.8433	
600	17.678	67.4311	48.269	4.897	-225.351	-225.351	48.269	
700	18.187	67.9177	49.637	6.692	-225.464	-225.464	49.637	
800	18.543	68.1650	50.968	8.530	-225.564	-225.564	50.968	
900	18.799	68.3850	52.297	10.397	-225.659	-225.659	52.297	
1000	18.990	68.5841	53.553	12.267	-225.769	-225.769	53.553	
1100	19.135	68.758	54.758	14.194	-225.842	-225.842	54.758	
1200	19.247	68.912	55.900	16.113	-225.911	-225.911	55.900	
1300	19.336	69.072	57.003	18.043	-225.960	-225.960	57.003	
1400	19.407	69.230	58.068	19.980	-226.000	-226.000	58.068	
1500	19.465	69.369	59.033	21.924	-226.031	-226.031	59.033	
1600	19.513	69.506	59.966	23.873	-226.057	-226.057	59.966	
1700	19.553	69.631	60.869	25.826	-226.079	-226.079	60.869	
1800	19.587	69.749	61.774	27.783	-226.098	-226.098	61.774	
1900	19.615	69.861	62.651	29.743	-226.114	-226.114	62.651	
2000	19.640	69.967	63.523	31.706	-226.128	-226.128	63.523	
2100	19.661	70.023	64.200	33.671	-226.139	-226.139	64.200	
2200	19.680	70.070	64.850	35.638	-226.149	-226.149	64.850	
2300	19.696	70.112	65.474	37.607	-226.156	-226.156	65.474	
2400	19.710	70.150	66.074	39.577	-226.161	-226.161	66.074	
2500	19.723	70.183	66.663	41.549	-226.164	-226.164	66.663	
2600	19.734	70.212	67.200	43.522	-226.166	-226.166	67.200	
2700	19.744	70.238	67.703	45.496	-226.168	-226.168	67.703	
2800	19.753	70.261	68.174	47.470	-226.169	-226.169	68.174	
2900	19.761	70.281	68.611	49.446	-226.169	-226.169	68.611	
3000	19.768	70.298	69.019	51.422	-226.169	-226.169	69.019	
3100	19.774	70.312	69.400	53.399	-226.169	-226.169	69.400	
3200	19.780	70.323	69.754	55.377	-226.169	-226.169	69.754	
3300	19.786	70.333	70.089	57.356	-226.169	-226.169	70.089	
3400	19.791	70.341	70.409	59.334	-226.169	-226.169	70.409	
3500	19.795	70.348	70.714	61.314	-226.169	-226.169	70.714	
3600	19.799	70.354	71.000	63.293	-226.169	-226.169	71.000	
3700	19.803	70.359	71.267	65.273	-226.169	-226.169	71.267	
3800	19.807	70.363	71.514	67.254	-226.169	-226.169	71.514	
3900	19.811	70.367	71.744	69.234	-226.169	-226.169	71.744	
4000	19.815	70.370	71.959	71.216	-226.169	-226.169	71.959	
4100	19.818	70.373	72.161	73.197	-226.169	-226.169	72.161	
4200	19.821	70.376	72.350	75.179	-226.169	-226.169	72.350	
4300	19.824	70.379	72.529	77.161	-226.169	-226.169	72.529	
4400	19.827	70.382	72.699	79.143	-226.169	-226.169	72.699	
4500	19.829	70.385	72.861	81.126	-226.169	-226.169	72.861	
4600	19.832	70.388	73.014	83.108	-226.169	-226.169	73.014	
4700	19.835	70.391	73.159	85.089	-226.169	-226.169	73.159	
4800	19.838	70.394	73.299	87.074	-226.169	-226.169	73.299	
4900	19.841	70.397	73.434	89.057	-226.169	-226.169	73.434	
5000	19.844	70.400	73.564	91.041	-226.169	-226.169	73.564	
5100	19.847	70.403	73.689	93.024	-226.169	-226.169	73.689	
5200	19.850	70.406	73.810	95.008	-226.169	-226.169	73.810	
5300	19.853	70.409	73.926	96.992	-226.169	-226.169	73.926	
5400	19.856	70.412	74.038	98.977	-226.169	-226.169	74.038	
5500	19.859	70.415	74.146	100.959	-226.169	-226.169	74.146	
5600	19.862	70.418	74.250	102.944	-226.169	-226.169	74.250	
5700	19.865	70.421	74.350	104.928	-226.169	-226.169	74.350	
5800	19.868	70.424	74.446	106.912	-226.169	-226.169	74.446	
5900	19.871	70.427	74.539	108.896	-226.169	-226.169	74.539	
6000	19.874	70.430	74.628	110.881	-226.169	-226.169	74.628	

Dec. 31, 1960; June 30, 1962; Dec. 31, 1963; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
892 (1)	860 (2)
487 (1)	344 (2)

Bond Distance: P-F = $1.5700 \pm 0.0012 \text{ \AA}$ F...F = $2.3643 \pm 0.0028 \text{ \AA}$ Bond Angle: F-P-F = $97.8 \pm 0.2^\circ$ Product of Moments of Inertia: $2.0621 \times 10^{-114} \text{ g}^3 \text{ cm}^6$ $\sigma = 3$

Heat of Formation

Berthelot (1) measured the heats of hydrolysis of PF₃(g) and PCl₃(l). These results can be combined to give, $\Delta H_f^\circ =$ 24.5 kcal/mol , for the reaction $\text{PF}_3(\text{g}) + 3\text{HCl} \cdot 157 \text{ H}_2\text{O} + \text{PCl}_3(\text{l}) + 3\text{H}_2\text{O} \cdot 112 \text{ H}_2\text{O}$

Combining this result with the following heat of formation data,

 $\Delta H_f^\circ(\text{PCl}_3, \text{l}) = -72.2 \text{ kcal/mol}$ (2) $\Delta H_f^\circ(\text{PCl}_3, \text{g}) = -100.0 \text{ kcal/mol}$ (3)we derive, $\Delta H_f^\circ(\text{PF}_3, \text{g}) = -212.2 \text{ kcal/mol}$.Duus and Nykytnik (4) reported a heat of reaction of -2.361 kcal/mol (corrected to 25°C) for the following reaction $\text{PCl}_3(\text{g}) + 3/2 \text{ CaF}_2(\text{s}) + \text{PF}_3(\text{g}) + 3/2 \text{ CaCl}_2(\text{s})$

Combining this result with the following heat of formation data,

 $\Delta H_f^\circ(\text{PCl}_3, \text{g}) = -64.4 \text{ kcal/mol}$ (2) $\Delta H_f^\circ(\text{CaF}_2, \text{s}) = -293.0 \pm 1.5 \text{ kcal/mol}$ (5)we derive, $\Delta H_f^\circ(\text{PF}_3, \text{g}) = -221.9 \text{ kcal/mol}$.Recently, Rudzitis et al. (6) measured the heat of combustion of PF₃ in fluorine in a two-chambered bomb calorimeter at 25°C . They reported a heat of combustion of $-152.0 \pm 0.2 \text{ kcal/mol}$ for the reaction $\text{PF}_3(\text{g}) + \text{F}_2(\text{g}) + \text{PF}_5(\text{g})$ Combining this result with the heat of formation of PF₅, $\Delta H_f^\circ(\text{PF}_5, \text{g}) = -376.9 \pm 0.7 \text{ kcal/mol}$ (7), we derive, $\Delta H_f^\circ(\text{PF}_3, \text{g}) = -224.9 \pm 0.9 \text{ kcal/mol}$. This result is adopted for this tabulation.

Heat Capacity and Entropy

The vibrational frequencies are those reported by Wilson and Palo (8). Several different values for the P-F bond length and F-P-F bond angle have been reported in the literature. This problem was recently discussed by Morino et al. (9), who also reported new data obtained from electron-diffraction studies. Their results are adopted for this tabulation.

Individual moments of inertia calculated according to their structure are: $I_A = I_B = 10.814 \times 10^{-39} \text{ g cm}^2$ and $I_C = 17.634 \times 10^{-39} \text{ g cm}^2$.

References

1. M. Berthelot, Compt. Rend. 100, 81 (1885). M. Berthelot and W. Loungine, Ann. Chim. Phys. (5), 6, 305 (1875).
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. U. S. Natl. Bur. Std. Circ. 500, 1952.
4. H. C. Duus and D. P. Nykytnik, J. Chem. Eng. Data, 9, 585 (1964).
5. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, December 31, 1968.
6. E. Rudzitis, private communication, Argonne Natl. Lab., 1969.
7. Ref. 5, December 31, 1969.
8. M. Kent Wilson and S. R. Palo, J. Chem. Phys., 20, 1716 (1952).
9. Y. Morino, K. Kuchitsu, and T. Moritani, Inorg. Chem., 8, 867 (1969).

Point Group C_{3v}

$$\Delta H_f^\circ = (-236 \pm 15) \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = [-237 \pm 15] \text{ kcal/mol}$$

$$S^\circ_{298.15} = 71.23 \pm 0.05 \text{ gibbs/mol}$$

Ground State Quantum Weight = {1}

Thiophosphoryl Fluoride (PSF₃)

(Ideal Gas) GFW = 120.033

T, °K	C _p ^o	$\frac{\text{gibbs/mol}}{S^\circ}$	$\frac{-(C_p^\circ - H^\circ_{298})/T}{-H^\circ - H^\circ_{298}}$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	Log Kp
0	-0.000	INFINITE	-	235.567	INFINITE
100	9.747	56.533	84.656	235.133	513.683
200	14.452	64.793	72.760	236.019	255.724
298	17.818	71.230	60.000	237.000	170.552
300	17.820	71.241	60.033	237.007	169.481
400	20.202	76.823	71.942	237.483	126.275
500	21.744	81.509	73.415	238.499	100.249
600	22.771	85.570	75.110	238.976	92.857
700	23.372	89.136	76.800	239.000	86.553
800	24.324	95.149	80.263	239.072	81.653
900	24.590	97.726	81.901	239.134	77.937
1000	24.793	100.000	83.448	239.181	74.521
1200	25.071	102.247	84.335	239.215	71.424
1400	25.318	104.384	85.184	239.238	68.599
1600	25.535	106.419	85.999	239.252	65.937
1800	25.726	108.356	86.784	239.258	63.424
2000	25.898	110.198	87.544	239.256	61.060
2200	26.052	111.950	88.276	239.246	58.840
2400	26.188	113.623	88.988	239.229	56.756
2600	26.308	115.223	89.680	239.205	54.800
2800	26.413	116.755	90.352	239.174	52.968
3000	26.505	118.223	91.000	239.136	51.256
3200	26.585	119.633	91.624	239.091	49.660
3400	26.653	121.000	92.232	239.039	48.176
3600	26.710	122.333	92.824	238.981	46.796
3800	26.756	123.633	93.400	238.917	45.516
4000	26.792	124.900	93.960	238.848	44.332
4200	26.818	126.133	94.500	238.774	43.248
4400	26.835	127.333	95.024	238.695	42.260
4600	26.843	128.500	95.532	238.611	41.364
4800	26.843	129.633	96.024	238.522	40.556
5000	26.835	130.733	96.500	238.428	39.832
5200	26.818	131.800	96.960	238.329	39.192
5400	26.792	132.833	97.400	238.225	38.636
5600	26.756	133.833	97.824	238.116	38.164
5800	26.710	134.800	98.232	238.002	37.776
6000	26.653	135.733	98.624	237.883	37.472
6200	26.585	136.633	99.000	237.759	37.252
6400	26.505	137.500	99.360	237.631	37.116
6600	26.413	138.333	99.704	237.498	37.064
6800	26.308	139.133	100.032	237.361	37.096
7000	26.188	139.900	100.344	237.219	37.212
7200	26.052	140.633	100.640	237.073	37.416
7400	25.898	141.333	100.920	236.923	37.708
7600	25.726	142.000	101.184	236.769	38.088
7800	25.535	142.633	101.432	236.611	38.556
8000	25.318	143.233	101.664	236.449	39.112
8200	25.071	143.800	101.880	236.283	39.756
8400	24.793	144.333	102.080	236.113	40.488
8600	24.590	144.833	102.264	235.939	41.312
8800	24.324	145.300	102.432	235.761	42.228
9000	24.000	145.733	102.584	235.579	43.236
9200	23.618	146.133	102.720	235.393	44.336
9400	23.178	146.500	102.840	235.203	45.520
9600	22.688	146.833	102.944	235.009	46.788
9800	22.150	147.133	103.032	234.811	48.132
10000	21.568	147.400	103.104	234.609	49.552

Mar. 31, 1963; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}
981 (1)	945 (2)	
442 (1)	275 (2)	
695 (1)	402 (2)	
Bond Distance: P-S = 1.87 ± 0.03 Å P-F = 1.53 ± 0.02 Å		
Bond Angle: F-P-F = 100.3° ± 2° F-P-S = 117.6° ± 2°		
Product of Moments of Inertia: $I_A I_B I_C = 1.7316 \times 10^{-113} \text{ g}^3 \text{ cm}^6$		
$\sigma = 3$		

Heat of Formation

The heat of formation of PSF₃ is calculated from the heat of formation of POF₃ and estimated P-O and P-S bond strengths. Mortimer (1) calculated several P-O and P-S bond dissociation energies from heat of reaction data reported in the literature. Some of these data are given below.

Reaction	D(P=O)	D(P=S)
kcal/mole		
130.3		
ΔH oxidation PF ₃ to POF ₃		
ΔH oxidation P(OEt) ₃ to PS(OEt) ₃		
81.6		
ΔH oxidation PPr ₃ to PSPr ₃		
82.6		

Mole and McCoubrey (2) reported the following heat of reaction:

$$\text{PCl}_3(\text{g}) + \text{S}(\text{c}) + \text{PSCl}_3(\text{g}) \rightarrow \text{PSCl}_3(\text{g}) \quad \Delta H_r = -5.6 \text{ kcal/mol.}$$

Combining this result with heat of vaporization data for PCl₃ (3) and PSCl₃ (4), along with the heat of sublimation of S (5), we derive, D(P=S) = 71 kcal/mol. Averaging this result with the two values given above, we obtain D(P=S) = 78.4 kcal/mol.

We assume that this result represents the enthalpy change for reaction

$$\text{PSF}_3(\text{g}) + \text{PF}_3(\text{g}) + \text{S}(\text{g}).$$

Combining this result with similar data for POF₃, namely D(P=O) = 130.3 kcal/mol and ΔH_f^o(POF₃, g) = -295.6 ± 1.9 kcal/mol (6), we derive, ΔH_f^o(PSF₃, g) = -237 ± 15 kcal/mol, from the relationship

$$\Delta H_{f298}^\circ(\text{PSF}_3, \text{g}) = \Delta H_{f298}^\circ(\text{POF}_3, \text{g}) + \Delta H_{f298}^\circ(\text{S}, \text{g}) - \text{D}(\text{P=O}) + \text{D}(\text{P=S}).$$

Heat Capacity and Entropy

Several recent infrared and Raman studies (7, 8, 9, 10) of PSF₃ have been reported. These data are in good agreement, except for the ν₁ fundamental. Dewaulle and Francois (11) assigned this fundamental to the 469 cm⁻¹ band observed in their spectra. The recent work indicates that this fundamental should be assigned to the 981 cm⁻¹ band. Average values of the vibrational frequencies reported by (8, 9, 10) are adopted for this tabulation. The molecular structure of this molecule was determined by Williams et al. (12) and Hawkins and Cohen (13) from microwave studies. The individual moments of inertia calculated from the constants given by Williams et al. (12) are I_A = I_B = 3.1527 × 10⁻³⁸ g cm² and I_C = 1.7410 × 10⁻³⁸ g cm².

References

1. C. T. Mortimer, Pure Appl. Chem., **2**, 71 (1961).
2. M. F. Mole and J. C. McCoubrey, Nature, **202**, 450 (1964).
3. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, Sept. 30, 1962.
4. D. E. Rogers and G. Nickless in "Inorganic Sulphur Chemistry," G. Nickless, Ed., Elsevier Publishing Co., New York, N. Y., 1968, chapter 9.
5. Ref. 3, Dec. 31, 1965.
6. Ref. 3, Dec. 31, 1965.
7. H. H. Horn, A. Müller, and O. Glemser, Z. Naturforsch., **20a**, 746 (1965).
8. R. G. Cavell, Spectrochimica Acta, **23a**, 249 (1967).
9. A. Müller, B. Krebs, E. Niecke, and A. Rueff, Ber. Bunsenges Phys. Chem., **71** (6), 571 (1967).
10. J. R. Durig and J. W. Clark, J. Chem. Phys., **46**, 3057 (1967).
11. M. L. Dewaulle and F. Francois, Compt. Rend. **226**, 894 (1948).
12. Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys., **20**, 164 (1952).
13. N. J. Hawkins, V. W. Cohen, and W. S. Koski, J. Chem. Phys., **20**, 528 (1952).

Point Group C_{3v} $\Delta H_f^\circ = [-282.3 \pm 5] \text{ kcal/mol}$ $\Delta H_f^\circ = [-263 \pm 5] \text{ kcal/mol}$ $S^\circ_{298.15} = 67.45 \pm 0.5 \text{ gibbs/mol}$

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

 $\omega_e, \text{ cm}^{-1}$ 832 (1)
406 (1)
954 (2)
290 (2)

Bond Distance: Si-F = (1.56) Å

Bond Angle: F-Si-F = (109.47)°

Product of the Moments of Inertia: $I_A I_B I_C = 2.5135 \times 10^{-114} \text{ g}^3 \text{ cm}^6$ $\sigma = 3$

Heat of Formation

The heat of formation is estimated from the assumption of a 0.5 kcal heat for the reaction:

 $\text{SiF}_4(\text{g}) + \text{SiF}_2(\text{g}) + 2\text{SiF}_3(\text{g})$ $\Delta H = 0.5 \text{ kcal}$ $\Delta H_f^\circ(\text{SiF}_3, \text{g}) = -263 \text{ kcal/mol}$ is derived from $\Delta H_f^\circ(\text{SiF}_4, \text{g}) = -385.98 \text{ kcal/mol}$ and $\Delta H_f^\circ(\text{SiF}_2, \text{g}) = -140.5 \text{ kcal/mol}$. The above value is confirmed by the observations of Layne (1), whose total pressure data above the silicon-fluoride system agree with those calculated from these tables.

Heat Capacity and Entropy

The bond length is estimated between those of SiF₄ and SiF₂. The vibrational frequencies are from Milligan et al. (2), and the angle is taken to be tetrahedral, since they also reported an angle of approximately 71° between the Si-F bonds and the threefold axis. The spectra of the radical were obtained in inert gas matrices and all the fundamentals were observed. The individual moments of inertia are $I_A = I_C = 11.081 \times 10^{-39} \text{ g cm}^2$, $I_B = 20.472 \times 10^{-39} \text{ g cm}^2$.

References

1. G. S. Layne, Dow Chemical Co., Midland, Mich., private communication, Aug. 1969.
2. D. E. Milligan, M. E. Jacox and W. A. Guillory, J. Chem. Phys. **49**, 5330 (1969).

Silicon Trifluoride (SiF₃)

(Ideal Gas) GFW = 85.0812

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	0.000	14.15141E	-	3.202	-262.264	-262.264	INFINITE
100	12.145	62.195	66.694	1.300	-262.803	-262.803	832 (1)
200	14.250	67.454	67.454	.000	-263.000	-263.000	406 (1)
300	14.285	67.583	67.583	.026	-263.004	-263.004	954 (2)
400	15.266	71.461	69.035	1.538	-263.154	-263.154	290 (2)
500	16.532	74.547	68.140	3.151	-263.268	-263.268	
600	17.660	76.698	70.510	4.913	-263.350	-263.350	
700	18.142	81.660	71.841	6.705	-263.419	-263.419	
800	18.517	83.910	71.234	8.500	-263.483	-263.483	
900	18.766	85.177	71.545	10.406	-263.543	-263.543	
1000	18.966	86.085	72.002	12.293	-263.607	-263.607	
1100	19.115	86.910	72.003	14.198	-263.676	-263.676	
1200	19.230	87.579	72.149	16.115	-263.749	-263.749	
1300	19.320	88.122	72.262	18.043	-263.830	-263.830	
1400	19.393	88.556	80.285	19.979	-263.920	-263.920	
1500	19.453	88.880	81.282	21.891	-264.019	-264.019	
1600	19.502	89.153	82.235	23.869	-264.129	-264.129	
1700	19.543	89.337	83.148	25.821	-264.242	-264.242	
1800	19.578	89.455	84.023	27.778	-264.314	-264.314	
1900	19.607	89.514	84.863	29.737	-264.395	-264.395	
2000	19.631	89.521	85.671	31.689	-264.484	-264.484	
2100	19.654	89.479	86.449	33.643	-264.554	-264.554	
2200	19.673	89.394	87.199	35.630	-264.637	-264.637	
2300	19.690	89.269	87.922	37.598	-264.722	-264.722	
2400	19.705	89.107	88.614	39.541	-264.809	-264.809	
2500	19.718	88.912	89.267	41.539	-264.899	-264.899	
2600	19.729	88.685	89.950	43.511	-264.991	-264.991	
2700	19.739	88.430	90.584	45.484	-265.086	-265.086	
2800	19.748	88.148	91.194	47.454	-265.182	-265.182	
2900	19.755	87.834	91.785	49.414	-265.281	-265.281	
3000	19.764	87.511	92.374	51.430	-265.385	-265.385	
3100	19.771	87.159	92.938	53.387	-265.494	-265.494	
3200	19.777	86.787	93.486	55.364	-265.597	-265.597	
3300	19.783	86.401	94.019	57.342	-265.704	-265.704	
3400	19.789	86.004	94.544	59.321	-265.814	-265.814	
3500	19.793	85.604	95.068	61.306	-265.921	-265.921	
3600	19.797	85.218	95.584	63.279	-266.031	-266.031	
3700	19.801	84.840	96.093	65.259	-266.144	-266.144	
3800	19.804	84.464	96.594	67.240	-266.260	-266.260	
3900	19.807	84.084	97.093	69.223	-266.378	-266.378	
4000	19.811	83.704	97.590	71.201	-266.496	-266.496	
4100	19.814	83.324	98.084	73.182	-266.616	-266.616	
4200	19.817	82.944	98.575	75.164	-266.738	-266.738	
4300	19.819	82.564	99.064	77.146	-266.862	-266.862	
4400	19.821	82.184	99.554	79.128	-266.988	-266.988	
4500	19.824	81.804	99.514	81.110	-267.116	-267.116	
4600	19.826	81.424	99.474	83.092	-267.246	-267.246	
4700	19.828	81.044	99.434	85.075	-267.378	-267.378	
4800	19.829	80.664	99.394	87.058	-267.512	-267.512	
4900	19.831	80.284	99.354	89.041	-267.648	-267.648	
5000	19.833	79.904	99.314	91.024	-267.786	-267.786	
5100	19.834	79.524	99.274	93.008	-267.926	-267.926	
5200	19.836	79.144	99.234	94.991	-268.068	-268.068	
5300	19.838	78.764	99.194	96.975	-268.212	-268.212	
5400	19.840	78.384	99.154	98.958	-268.358	-268.358	
5500	19.843	78.004	99.114	100.942	-268.506	-268.506	
5600	19.841	77.624	99.074	102.926	-268.656	-268.656	
5700	19.842	77.244	99.034	104.910	-268.808	-268.808	
5800	19.843	76.864	98.994	106.895	-268.962	-268.962	
5900	19.845	76.484	98.954	108.879	-269.118	-269.118	
6000	19.845	76.104	98.914	110.863	-269.276	-269.276	

Titanium Trifluoride (TiF₃)

(Crystal) GFW = 104.8952

TITANIUM TRIFLUORIDE (TiF₃)

(CRYSTAL)

GFW = 104.8952

T, °K	Cp*	$\frac{\text{cal}}{\text{mole}} \times \frac{1}{T}$	$-(C_p^* - H^* - H_{298}^*)/T$	$\frac{\text{kcal}}{\text{mole}}$	ΔH°	ΔG°	Log Kp
100							
200							
298	21.594	21.000	.000	- 343.100	- 325.510	- 325.510	238.606
300	22.000	21.136	.041	- 343.091	- 325.502	- 325.502	237.055
400	22.300	21.499	.253	- 342.655	- 324.406	- 324.406	197.456
500	22.570	21.813	.456	- 342.255	- 323.430	- 323.430	137.184
600	23.536	22.778	.681	- 341.834	- 322.210	- 322.210	112.265
700	24.178	23.414	.922	- 341.414	- 320.638	- 320.638	94.488
800	24.746	23.717	1.168	- 340.979	- 318.159	- 318.159	81.172
900	25.190	23.919	1.417	- 340.523	- 315.674	- 315.674	70.528
1000	25.660	24.374	1.674	- 340.042	- 312.674	- 312.674	62.265
1100	26.756	25.187	1.937	- 339.528	- 309.920	- 309.920	55.814
1200	27.478	25.853	2.209	- 339.014	- 307.578	- 307.578	50.190
1300	28.224	26.482	2.481	- 338.502	- 305.432	- 305.432	45.432
1400	28.600	26.602	2.784	- 338.026	- 303.470	- 303.470	41.364
1500	28.860	26.634	3.060	- 337.593	- 301.751	- 301.751	37.846
1600	30.000	27.563	4.153	- 336.738	- 294.590	- 294.590	34.775
1700	30.200	27.606	4.206	- 335.688	- 289.481	- 289.481	32.073
1800	30.400	27.650	4.258	- 335.046	- 284.426	- 284.426	29.677
1900	30.600	27.694	4.310	- 334.209	- 279.413	- 279.413	27.539
2000	30.800	27.738	4.362	- 333.620	- 274.240	- 274.240	25.602

 $\Delta H^\circ_0 = \text{unknown}$ $S^\circ_{298.15} = [21.0 \pm 3.0]$ $\Delta H^\circ_{298.15} = -343.1 \pm 10.0 \text{ kcal/mol}$ $\Delta H^\circ = 52.97 \text{ kcal/mol}$ $T_s = 1309.7^\circ \text{K}$

Heat of Formation

Blocher and Hall (1) have reported vapor pressure data for the process $1/2\text{Hg}_2\text{F}_2 + \text{TiF}_3(\text{c}) = \text{TiF}_4(\text{g}) + \text{Hg}(\text{l})$. Second and third law analyses of their data give a second law ΔH°_{298} of 23.7 kcal/mol, a third law ΔH°_{298} of 29.86, and a third law drift of 11.9 ± 1.0 eu. The third law value is combined with the JANAF values for the heat of formation of $\text{Hg}_2\text{F}_2(\text{c})$ and $\text{TiF}_4(\text{g})$ to give a ΔH°_{298} of -343.1 ± 10.0 kcal/mol. The large uncertainty on ΔH°_{298} is assigned because Blocher and Hall were not able to identify $\text{TiF}_3(\text{c})$ as the reaction product in the above process. They reported that the X-ray pattern of the products contained lines corresponding to $\text{Hg}_2\text{F}_2(\text{c})$ plus others that did not correspond to $\text{TiF}_3(\text{c})$.

Heat Capacity and Entropy

The heat capacity of $\text{TiF}_3(\text{c})$ is estimated from the heat capacities of ZrF_4 and TiF_4 . The entropy, S°_{298} , is estimated from CrF_3 and from ionic entropy contributions. Both methods give values which are within ± 0.8 eu of the chosen value of 21 ± 3 eu.

Heat of Sublimation

The heat of sublimation is calculated from the vapor pressure data of Zmbov and Margrave (2). See $\text{TiF}_3(\text{g})$ table for details. The sublimation temperature is taken as the point at which $\Delta G = 0$ for the reaction $\text{TiF}_3(\text{c}) = \text{TiF}_3(\text{g})$.

References

1. J. N. Blocher, Jr. and E. N. Hall, J. Phys. Chem. **63**, 127 (1959).
2. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).

Dec. 31, 1960; June 30, 1964; Dec. 31, 1967; June 30, 1968

Titanium Trifluoride (TiF₃)F₃Ti

(Ideal Gas)

GFW = 104.8952

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔG°	Log Kp
0	-0.000	-0.000	∞	∞	-283.104	-283.104	14.71171E
100	6.131	54.491	61.514	2.502	-282.810	-282.810	618.040
200	12.764	63.937	70.971	1.407	-283.874	-281.935	308.138
298	15.675	66.622	72.622	1.000	-284.100	-281.007	205.984
300	15.718	66.719	72.625	1.000	-284.103	-280.988	204.700
400	17.513	74.509	77.263	3.500	-284.204	-279.930	151.400
500	18.567	78.581	79.524	3.500	-284.254	-278.857	121.488
600	19.150	81.586	80.556	5.368	-284.278	-277.775	101.179
700	19.565	84.575	81.493	7.337	-284.301	-276.689	86.386
800	19.846	87.561	82.351	9.307	-284.340	-275.600	75.290
900	19.995	90.540	83.136	11.268	-284.380	-274.500	65.552
1000	20.074	92.557	83.758	13.228	-284.400	-273.400	57.552
1100	20.151	93.974	84.056	15.310	-284.606	-272.285	50.098
1200	20.209	95.730	84.290	17.328	-285.685	-271.150	43.378
1300	20.251	97.827	84.464	19.278	-286.731	-269.992	37.271
1400	20.281	100.152	84.584	21.168	-287.743	-268.807	31.649
1500	20.305	102.652	84.644	23.008	-288.725	-267.460	26.549
1600	20.328	105.363	84.663	25.439	-289.779	-266.229	21.865
1700	20.342	108.296	84.635	27.473	-290.808	-265.051	17.535
1800	20.348	111.459	84.565	29.130	-291.813	-263.924	13.517
1900	20.345	114.859	84.455	30.459	-292.793	-262.849	9.577
2000	20.337	118.504	84.314	31.500	-293.750	-261.828	5.728
2100	20.322	122.428	84.143	32.267	-294.685	-260.861	2.013
2200	20.300	126.584	83.945	32.767	-295.598	-259.956	0.433
2300	20.272	130.998	83.717	33.017	-296.480	-259.109	-0.143
2400	20.240	135.696	83.461	33.140	-297.333	-258.330	-0.717
2500	20.205	140.696	83.180	33.140	-298.155	-257.624	-1.283
2600	20.168	145.996	82.880	33.017	-298.945	-256.996	-1.839
2700	20.130	151.596	82.565	32.767	-299.703	-256.449	-2.383
2800	20.090	157.496	82.237	32.417	-300.430	-255.882	-2.915
2900	20.048	163.696	81.895	31.950	-301.125	-255.295	-3.435
3000	20.005	170.196	81.540	31.375	-301.788	-254.688	-3.943
3100	19.960	176.996	81.175	30.700	-302.417	-254.061	-4.439
3200	19.915	184.096	80.800	29.925	-302.999	-253.424	-4.923
3300	19.870	191.496	80.415	29.050	-303.533	-252.777	-5.395
3400	19.825	199.196	80.020	28.075	-304.020	-252.120	-5.855
3500	19.780	207.196	79.615	27.000	-304.460	-251.453	-6.303
3600	19.735	215.496	79.200	25.825	-304.853	-250.776	-6.739
3700	19.690	224.096	78.775	24.550	-305.200	-250.089	-7.163
3800	19.645	232.896	78.340	23.175	-305.500	-249.392	-7.575
3900	19.600	241.896	77.895	21.700	-305.753	-248.685	-7.975
4000	19.555	251.096	77.440	20.125	-305.960	-247.968	-8.363
4100	19.510	260.496	76.975	18.450	-306.120	-247.241	-8.739
4200	19.465	270.096	76.500	16.675	-306.243	-246.504	-9.103
4300	19.420	279.896	76.015	14.800	-306.320	-245.757	-9.455
4400	19.375	289.896	75.520	12.825	-306.353	-245.000	-9.797
4500	19.330	299.996	75.015	10.750	-306.343	-244.233	-10.129
4600	19.285	310.196	74.500	8.575	-306.290	-243.456	-10.451
4700	19.240	320.596	73.975	6.300	-306.193	-242.669	-10.763
4800	19.195	331.196	73.440	3.925	-306.053	-241.872	-11.065
4900	19.150	341.996	72.895	1.450	-305.868	-241.065	-11.357
5000	19.105	352.896	72.340	-0.925	-305.638	-240.248	-11.639
5100	19.060	363.896	71.775	-3.200	-305.363	-239.421	-11.911
5200	19.015	374.996	71.200	-5.425	-305.043	-238.584	-12.173
5300	18.970	386.196	70.615	-7.600	-304.678	-237.737	-12.425
5400	18.925	397.496	70.020	-9.725	-304.268	-236.880	-12.667
5500	18.880	408.896	69.415	-11.800	-303.813	-235.913	-12.899
5600	18.835	420.396	68.800	-13.825	-303.313	-234.936	-13.121
5700	18.790	431.996	68.175	-15.800	-302.768	-233.949	-13.333
5800	18.745	443.696	67.540	-17.725	-302.178	-232.952	-13.535
5900	18.700	455.396	66.895	-19.600	-301.543	-231.945	-13.727
6000	18.655	467.096	66.240	-21.425	-300.863	-230.928	-13.910

Dec. 31, 1950; June 30, 1964; Dec. 31, 1967; June 30, 1968

TITANIUM TRIFLUORIDE (TiF₃)

(IDEAL GAS)

GFW = 104.8952

Point Group = C_{3v}ΔH°_f = -283.1 ± 10.0S°_{298.15} = [69.6 ± 1.0] gibbs/molΔH°_{f,298.15} = -284.1 ± 10.0 kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i
0	[2]
[600]	[2]
[1500]	[2]
[4000]	[2]
[10000]	[2]

Vibrational Frequencies and Degeneracies

ω _i , cm ⁻¹	l
[800] (1)	
[450] (1)	
[750] (2)	
[300] (2)	

Bond Distance: Ti-F = [1.9] Å

Bond Angle: F-Ti-F = [100°]

Product of the Moments of Inertia: I_AI_BI_C = [7.45 × 10⁻¹¹⁴ g³ cm⁶]

Heat of Formation

The heat of formation of TiF₃(g) is calculated from that of TiF₃(c) and the heat of sublimation determined from the mass spectrometric vapor pressure data of Zmbov and Margrave (1). Their data give nine points over the temperature range 759 - 865°K.

Second and third law analyses of their data give a second law ΔH°_{f,298} of 61.2 ± 0.4 kcal/mol and a third law ΔH°_{f,298} of 59.0 kcal/mol with an entropy drift of -2.7 ± 0.5 units. The third law value is used to calculate ΔH°_{f,298}.

Heat Capacity and Entropy

The interatomic distance is estimated from those of TiF₄(g), and TiCl₄(g), and TiCl₃(g). The pyramidal bond angle is estimated assuming TiF₃(g) similar to the group V trihalides. The principal moments of inertia are I_A = I_B = 1.68 × 10⁻³⁶ g cm² and I_C = 2.66 × 10⁻³⁶ g cm². The vibrational frequencies are estimated from those of PF₃ and AsF₃. The electronic levels are estimated from the levels of Ti³⁺ (2).

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
2. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

F₃Ti

Zirconium Trifluoride (ZrF₃)

GFW = 148.2152

S_{298.15}^o = [21 ± 2] gibbs/molΔHf^o = UnknownΔHf_{298.15}^o = [-335 ± 20] kcal/molΔHs_{298.15}^o = [70.1] kcal/mol

Heat of Formation

The heat of formation at 298°K for ZrF₃(c) was reported as -350 kcal/mol (2) which was estimated by Brewer (2). Based on this ΔHf₂₉₈ value, the crystal lattice energy (U) of ZrF₃(c) is calculated to be 1371 kcal/mol by the Born-Haber cycle method (3). For the evaluation of U from the relation: ΔHf^o(ZrF₃, c) = Σ I_i + L - 3(E - D/2) - U, the following values (kcal/mol) are used: Σ I_i (the sum of the successive three ionization potentials of Zr metal) = 1055 (4), L (the enthalpy of sublimation of Zr metal) = 148.3 (5), E (the electron affinity of fluorine) = 79.5 (6), and D (the enthalpy of dissociation of fluorine) = 37.7 (7). The derived value of U(ZrF₃, c) is of the same order of magnitude of the value, U(TiF₃, c) = 1376 kcal/mol, calculated by Cavell and Clark (3) using the same method.

From ΔHf₂₉₈^o(ZrF₃, c) = -350 kcal/mol, the derived ΔGf^o(ZrF₃, c) values indicate that ZrF₃(c) is thermodynamically more stable than the system ZrF₄(c) + Zr(c). For example, in the temperature range 798-1200°K, the Gibbs energy changes for the reaction 3 ZrF₃(c) + Zr(c) = 4 ZrF₄(c) are about -29 ± 1 kcal/mol. However, this product ZrF₃(c) has never been prepared successfully from this reaction in many laboratories (8). In order to make the ΔGf^o(ZrF₃, c) values consistent with the experimental observations, the heat of formation of ZrF₃(c) is arbitrarily adjusted to be 15 kcal/mol less negative, or ΔHf₂₉₈^o(ZrF₃, c) = -335 kcal/mol with uncertainty as high as ±20 kcal/mol. This value is tentatively adopted.

The Gibbs energy changes for the reaction 3 ZrF₃(g) + Zr(c) = 4 ZrF₄(c) are evaluated to be very favorable at temperatures below 900°K, e.g., ΔGr^o = -93.9 and -6.7 kcal/mol at 298 and 900°K, respectively. But according to Larsen and Leddy (9), this reaction does not occur in the temperature range 473-973°K, and pressure range 5-15 atm. One possible explanation is that these heterogeneous reactants may require very high activation energy to initiate the reaction. In other words, this reaction is unfavorable at these temperatures probably due to kinetic rather than thermodynamic reasons.

Heat Capacity and Entropy

The heat capacities of ZrF₃(c) are not available in the literature. They are estimated from the Cp values of ZrF₄(c) by deduction of one F atom Cp contributions which are calculated as 1/4(Cp_{ZrF₄}(c) - Cp_{ZrF₃}(c)). The S_{298.15}^o is taken to be 1/2(S₂₉₈^o(ZrF₄, c) + S₂₉₈^o(ZrF₂, c)) of which the value S₂₉₈^o(ZrF₂, c) is estimated (see ZrF₂(c) table for details).

Heat of Sublimation

The difference between ΔHf₂₉₈^o for ZrF₃(g) and ZrF₃(c) is ΔHs₂₉₈^o. Actually, ZrF₃(c) is thermodynamically unstable, e.g., the Gibbs energy changes for the reaction 4 ZrF₃(c) = 3 ZrF₄(c) + Zr(c) are about -30 kcal/mol in the temperature range 298-1400°K. In other words, ZrF₃(c) decomposes into ZrF₄(c) + Zr(c) before sublimation occurs.

References

1. U. S. Natl. Bur. Std. Circ. 500, 1952.
2. L. Brewer, private communication, University of California, Berkeley, California; cited in reference 1.
3. R. G. Cavell and H. C. Clark, J. Chem. Soc. 1965, 444 (1965).
4. C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. III, 1958.
5. JANAF Zr(c) table, Dec. 31, 1967.
6. U. S. Natl. Bur. Std. Rept. 8628, January 1965.
7. JANAF F(g) table, Sept. 30, 1965.
8. T. B. Douglas, private communication, Natl. Bur. Std., July 10, 1961.
9. E. M. Larsen and J. J. Leddy, J. Am. Chem. Soc. 78, 5983 (1956).

June 30, 1961; June 30, 1964; June 30, 1969

T, °K	Cp ^o	gibbs/mol S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	kcal/mol ΔHf ^o	ΔGf ^o	Log Kp
0							
100							
200							
298	20,000	21,000	21,000	.000	-335,000	-316,617	232.233
300	20,150	21,124	21,000	.037	-334,995	-316,705	230,710
400	21,950	27,192	21,814	2,187	-334,563	-316,736	230,736
500	23,150	32,215	23,405	4,405	-334,760	-306,690	133,184
600	24,800	36,515	25,241	6,765	-333,833	-296,625	108,687
700	24,600	40,261	27,124	9,195	-333,385	-293,026	91,487
800	25,100	43,560	28,978	11,689	-332,930	-287,292	76,484
900	25,450	46,557	30,769	14,210	-332,464	-281,544	63,484
1000	25,750	49,255	32,484	16,771	-332,000	-275,797	60,317
1100	25,930	51,719	34,123	19,355	-331,604	-270,403	53,724
1200	26,020	53,979	35,684	21,953	-331,268	-264,605	48,228
1300	26,100	56,065	37,173	24,559	-331,490	-259,224	43,509
1400	26,170	58,001	38,592	27,173	-331,405	-254,065	38,769
1500	26,230	59,609	39,947	29,793	-331,405	-248,184	36,140

Point Group C_{3v}ΔH_f⁰ = -263.3 ± 5 kcal/molS_{298.15}⁰ = [73.0 ± 2] gibbs/molΔH_{f,298.15}⁰ = -264.2 ± 5 kcal/mol

Ground State Quantum Weight = [2]

Zirconium Trifluoride (ZrF₃)

(Ideal Gas) GFV = 148.2152

T, °K	C _p ⁰	S ⁰	gibbs/mol -(G ⁰ -H ²⁹⁸)/T	H ⁰ -H ²⁹⁸	ΔH ⁰	ΔG ⁰	Log Kp
0	0	0.000	0.000	3.610	-263.324	-263.324	INFINITE
100	10.621	56.513	85.684	2.737	-263.704	-263.704	575.042
200	14.099	74.407	104.099	1.492	-264.037	-264.037	286.771
298	16.212	73.047	104.212	0.000	-264.260	-264.260	191.710
300	16.244	73.147	104.244	0.030	-264.202	-264.202	190.516
400	17.614	78.023	110.761	1.778	-264.282	-264.282	142.391
500	18.594	82.058	116.982	3.538	-264.134	-264.134	113.509
600	19.165	85.495	122.768	5.328	-264.373	-264.373	94.251
700	19.628	88.486	128.144	7.165	-264.415	-264.415	80.981
800	19.965	91.130	133.066	9.046	-264.464	-264.464	70.173
900	20.210	93.486	137.566	11.355	-264.533	-264.533	62.144
1000	20.390	95.636	141.766	13.886	-264.619	-264.619	55.770
1100	20.523	97.586	145.687	16.532	-264.728	-264.728	50.041
1200	20.620	99.376	149.364	19.289	-264.712	-264.712	44.044
1300	20.692	101.029	152.834	22.155	-265.495	-265.495	39.155
1400	20.743	102.565	156.147	25.127	-265.604	-265.604	34.355
1500	20.779	103.997	159.347	28.203	-265.495	-265.495	30.369
1600	20.803	105.339	162.482	31.487	-265.714	-265.714	27.070
1700	20.817	106.601	165.564	34.982	-265.750	-265.750	24.004
1800	20.824	107.791	168.597	38.673	-265.801	-265.801	21.325
1900	20.825	108.917	171.597	42.554	-265.865	-265.865	19.004
2000	20.822	109.985	174.564	46.585	-265.945	-265.945	16.991
2100	20.816	111.000	177.500	50.769	-266.041	-266.041	15.213
2200	20.798	112.693	180.412	55.100	-266.157	-266.157	13.647
2300	20.764	114.663	183.300	59.584	-266.292	-266.292	12.264
2400	20.717	116.778	186.163	64.223	-266.447	-266.447	11.040
2500	20.676	118.697	189.000	69.023	-266.622	-266.622	10.004
2600	20.765	115.441	181.834	64.588	-266.481	-266.481	9.222
2700	20.753	116.225	182.800	65.666	-266.410	-266.410	8.584
2800	20.742	116.979	183.856	66.939	-266.305	-266.305	8.044
2900	20.731	117.707	184.986	68.406	-266.166	-266.166	7.584
3000	20.720	118.410	186.115	70.065	-266.000	-266.000	7.191
3100	20.710	119.089	187.243	71.812	-265.808	-265.808	6.854
3200	20.691	119.746	188.370	73.647	-265.590	-265.590	6.566
3300	20.673	120.383	189.497	75.566	-265.344	-265.344	6.322
3400	20.656	121.001	190.624	77.566	-265.070	-265.070	6.122
3500	20.643	121.600	191.750	79.647	-264.778	-264.778	5.954
3600	20.635	122.182	192.878	81.812	-264.469	-264.469	5.812
3700	20.627	122.748	193.997	84.065	-264.144	-264.144	5.684
3800	20.620	123.299	195.100	86.406	-263.804	-263.804	5.566
3900	20.613	123.835	196.188	88.834	-263.449	-263.449	5.454
4000	20.606	124.358	197.261	91.354	-263.080	-263.080	5.347
4100	20.629	124.867	198.320	93.965	-262.697	-262.697	5.244
4200	20.623	125.364	199.364	96.665	-262.300	-262.300	5.144
4300	20.617	125.850	200.394	99.454	-261.889	-261.889	5.044
4400	20.611	126.324	201.412	102.337	-261.464	-261.464	4.944
4500	20.605	126.787	202.420	105.300	-261.026	-261.026	4.844
4600	20.599	127.239	203.418	108.354	-260.576	-260.576	4.744
4700	20.594	127.682	204.406	111.497	-260.114	-260.114	4.644
4800	20.589	128.116	205.384	114.722	-259.640	-259.640	4.544
4900	20.584	128.548	206.354	118.037	-259.154	-259.154	4.444
5000	20.579	128.976	207.318	121.444	-258.654	-258.654	4.344
5100	20.574	129.394	208.270	124.944	-258.144	-258.144	4.244
5200	20.569	129.800	209.212	128.534	-257.624	-257.624	4.144
5300	20.564	130.195	210.134	132.212	-257.094	-257.094	4.044
5400	20.560	130.580	211.044	135.977	-256.554	-256.554	3.944
5500	20.556	130.954	211.944	140.834	-256.004	-256.004	3.844
5600	20.551	131.320	212.834	145.784	-255.444	-255.444	3.744
5700	20.547	131.680	213.712	150.824	-254.874	-254.874	3.644
5800	20.543	132.034	214.584	155.954	-254.294	-254.294	3.544
5900	20.540	132.384	215.444	161.174	-253.704	-253.704	3.444
6000	20.536	132.734	216.294	166.584	-253.104	-253.104	3.344

T, °K.	C _p ^o	S ^o - (F ^o -H ₂₉₈)/T	Π ^o -H ₂₉₈	ΔH _f ^o	Log K _p
0	-∞	INFINITE	4.100	-409.478	INFINITE
100	10.361	57.433	3.339	-407.478	800.535
200	17.222	66.733	1.957	-404.983	441.889
298	22.287	74.659	-0.000	-400.602	293.649
300	22.361	74.767	-0.031	-400.532	291.708
400	25.489	81.667	2.447	-390.682	216.737
500	27.376	87.574	7.737	-392.753	171.672
600	28.559	92.678	12.512	-388.782	141.614
700	29.337	97.162	17.797	-384.775	120.132
800	30.021	101.099	23.486	-380.729	103.019
900	30.621	104.638	29.576	-376.680	91.070
1000	30.530	107.841	36.065	-372.222	81.349
1100	30.741	110.761	42.969	-367.635	73.042
1200	30.903	113.463	50.292	-363.014	66.114
1300	31.034	115.956	58.046	-358.269	60.546
1400	31.134	118.276	66.237	-353.411	56.004
1500	31.217	120.376	74.860	-348.361	52.065
1600	31.286	122.393	83.933	-343.155	48.695
1700	31.343	124.252	93.461	-337.811	45.829
1800	31.389	125.978	103.450	-332.340	43.460
1900	31.423	127.583	113.902	-326.763	41.583
2000	31.447	129.096	124.819	-321.093	40.150
2100	31.467	130.532	136.199	-315.346	39.118
2200	31.483	131.898	148.043	-309.531	38.456
2300	31.496	133.193	160.352	-303.659	38.020
2400	31.506	134.424	173.126	-297.739	37.780
2500	31.514	135.598	186.365	-291.782	37.695
2600	31.520	136.724	200.068	-285.798	37.718
2700	31.523	137.800	214.234	-279.688	37.800
2800	31.523	138.826	228.861	-273.456	37.920
2900	31.523	139.800	243.948	-267.106	38.060
3000	31.523	140.724	259.486	-260.642	38.210
3100	31.523	141.600	275.474	-254.068	38.370
3200	31.523	142.424	291.912	-247.388	38.540
3300	31.523	143.198	308.799	-240.606	38.720
3400	31.523	143.922	326.136	-233.728	38.910
3500	31.523	144.596	343.922	-226.758	39.110
3600	31.523	145.220	362.158	-219.698	39.320
3700	31.523	145.794	380.844	-212.552	39.540
3800	31.523	146.318	400.000	-205.324	39.770
3900	31.523	146.792	419.626	-198.018	40.010
4000	31.523	147.216	439.722	-190.638	40.260
4100	31.523	147.590	460.288	-183.188	40.520
4200	31.523	147.914	481.424	-175.664	40.790
4300	31.523	148.188	503.030	-168.070	41.070
4400	31.523	148.412	525.106	-160.412	41.360
4500	31.523	148.586	547.642	-152.688	41.660
4600	31.523	148.710	570.638	-144.902	41.970
4700	31.523	148.784	594.094	-137.058	42.290
4800	31.523	148.808	618.010	-129.160	42.620
4900	31.523	148.782	642.376	-121.212	42.960
5000	31.523	148.706	667.192	-113.218	43.310
5100	31.523	148.580	692.458	-105.174	43.670
5200	31.523	148.404	718.174	-97.086	44.040
5300	31.523	148.178	744.340	-88.950	44.420
5400	31.523	147.902	770.956	-80.762	44.810
5500	31.523	147.576	798.022	-72.518	45.210
5600	31.523	147.200	825.538	-64.224	45.620
5700	31.523	146.774	853.504	-55.884	46.040
5800	31.523	146.300	881.920	-47.502	46.470
5900	31.523	145.774	910.786	-39.074	46.910
6000	31.523	145.200	940.102	-30.606	47.360

Point Group [D_{2h}]
ΔH_f^o 0 = -409.5 ± 3.4 kcal. mole⁻¹
ΔH_f^o 298.15 = -411.9 ± 3.4 kcal. mole⁻¹
S_{298.15} = [74.63] cal. deg.⁻¹ mole⁻¹
Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω _v , cm. ⁻¹	ω _v , cm. ⁻¹
[450] (1)	[390] (1)
[260] (1)	[660] (1)
[330] (1)	[930] (1)
[250] (1)	[700] (1)
[720] (1)	[500] (1)
[700] (1)	[500] (1)

Bond Distance: Mg-F = [1.77] Å
Bond Angle: F-Mg-F = [135]°
Product of the Moments of Inertia: I_AI_BI_C = [5.571 X 10⁻¹¹³] g.³ cm.⁶

Heat of Formation.

The enthalpy change, ΔH_f^o = 30 kcal. mole⁻¹, for the reaction MgF₂(c) + MgF₂(g) = (MgF₂)₂(g) was determined by J. Berkowitz and J. R. Marquart, J. Chem. Phys. 3, 1853 (1962). Hence the heat of formation for (MgF₂)₂(g) was calculated.

Heat Capacity and Entropy.

The molecular structure was assumed to be planar. The two Mg atoms are at the two opposite corners of a square. The other two corners of the square are occupied by two F atoms. The two remaining F atoms are situated outside the square on a straight line joining the two Mg atoms. The bond distance between Mg and F atom was estimated to be the same as that in the MgF₂(g) molecule. Vibrational frequencies were estimated by comparison with those for MgF(g) and (NaF)₂. The vibrational frequencies for (NaF)₂ were calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960). The three principal moments are 9.8896 X 10⁻³⁹, 7.0235 X 10⁻³⁸, and 8.0163 X 10⁻³⁸ g. cm.²

GFW = 187.933

(IDEAL GAS)

MOLYBDENUM OXYTETRAFLUORIDE (MoOF₄)Molybdenum Oxytetrafluoride (MoOF₄)
(Ideal Gas) GFW = 187.933 $\Delta H_f^\circ = [-298 \pm 30] \text{ kcal/mol}$ Point Group $[C_{4v}]$ $\Delta H_f^\circ_{298.15} = [-300 \pm 30] \text{ kcal/mol}$ $S^\circ_{298.15} = [78.99 \pm 2.00] \text{ gibbs/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies			
ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}	
1045 (1)	[600] (1)	720 (2)	
[300] (1)	[300] (1)	530 (2)	
680 (1)	[200] (1)	[150] (2)	

Bond Distance: Mo-O = $(1.64) \text{ \AA}$ Mo-F = $(1.82) \text{ \AA}$ Bond Angle: O-Mo-F = (90°) F-Mo-F = (90°) Product of Moments of Inertia: $I_A I_B I_C = [3.1468 \times 10^{-113}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

Zimov et al. (1) investigated the stabilities of some molybdenum and tungsten oxyfluorides by means of mass spectrometry. These studies led to heats of formation for $\text{MoO}_2\text{F}_2(\text{g})$, $\text{WO}_2\text{F}_2(\text{g})$, and $\text{MoF}_4(\text{g})$ which were used by the authors to develop a correlation among the heats of formation of the oxides, oxyfluorides, and fluorides of Mo and W. ΔH_f° varies almost linearly with the number of oxygen atoms (1) for the series VF_6 , VOF_4 , and VO_2F_2 . Assuming a similar variation for MoF_6 , MoOF_4 , and MoO_2F_2 , we estimate $\Delta H_f^\circ(\text{MoOF}_4, \text{g}) = -320 \text{ kcal/mol}$.

Heat of formation data (2) for $\text{MoF}_6(\text{g})$, $\text{MoOF}_4(\text{g})$, $\text{MoO}_2(\text{g})$, and $\text{MoO}_3(\text{g})$ have been used to derive the following average bond dissociation energies:

$$\bar{D}(\text{Mo-F}) = 107 \text{ kcal/mol}$$

$$\bar{D}(\text{Mo-O}) = 135 \text{ kcal/mol}$$

From these data we derive $\Delta H_f^\circ(\text{MoOF}_4, \text{g}) = -271 \text{ kcal/mol}$.

The heat of formation for MoOF_4 is tentatively selected as $300 \pm 30 \text{ kcal/mol}$.

Heat Capacity and Entropy

Blanchard (3) suggested that $\text{MoOF}_4(\text{g})$ possessed C_{4v} symmetry by reason of the similarity of its infrared spectra with that of $\text{XeOF}_4(\text{g})$. X-ray diffraction studies of crystalline MoOF_4 by Edwards et al. (4, 5) support this view. The structure of the molecule is assumed to be square-pyramidal. The bond lengths are from the crystallographic studies of MoOF_4 by Edwards et al. (4, 5). Individual moments of inertia are $I_A = I_B = 27.437 \times 10^{-39}$, $I_C = 41.801 \times 10^{-39} \text{ g cm}^2$.

Blanchard (3) reported the following vibrational frequencies and assignments:

$$\nu_1 = 1045, \nu_2 = 720, \nu_3 = 680, \text{ and } \nu_6 = 530 \text{ cm}^{-1}$$

Similar frequencies have been reported by Edwards et al. (4) from their study of the infrared spectra of gaseous MoOF_4 .

The rest of the frequencies and assignments are estimated by comparison with data for XeOF_4 (5).

References

1. K. F. Zimov, O. M. Uy, and J. L. Margrave, *J. Phys. Chem.*, **23**, 3008 (1969).
2. JANAF Data.
3. S. Blanchard, Commissariat a l'Energie Atomique report CEA-R 3194, 1967.
4. A. J. Edwards, G. R. Jones, and B. R. Steventon, *Chem. Commun.*, 462 (1967).
5. A. J. Edwards and B. R. Steventon, *J. Chem. Soc.*, 2503 (1968).
6. G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log Kp
0	-0.000	INFINITE	-	4.638	-298.295	INFINITE
100	12.901	59.771	66.982	-3.672	-298.173	644.226
200	23.121	76.992	78.992	-2.000	-298.319	209.144
300	23.185	79.135	78.993	.043	-300.000	207.769
400	25.959	86.213	79.939	2.510	-300.021	153.146
500	27.631	92.196	81.608	5.194	-299.932	120.366
600	28.720	97.337	83.978	6.015	-299.784	98.520
700	29.445	101.624	86.214	10.926	-299.607	82.925
800	29.948	105.769	88.417	13.697	-299.419	71.236
900	30.304	109.338	90.548	16.911	-299.222	62.150
1000	30.575	112.546	92.592	19.956	-299.027	54.687
1100	30.776	115.470	94.539	23.024	-298.836	48.947
1200	30.932	118.155	96.397	26.109	-298.655	44.001
1300	31.055	120.636	98.167	29.209	-298.490	39.618
1400	31.154	122.941	99.855	32.320	-298.344	35.234
1500	31.234	125.093	101.467	35.439	-298.219	31.130
1600	31.301	127.111	103.007	38.566	-298.110	27.267
1700	31.356	129.011	104.482	41.699	-298.041	23.620
1800	31.402	130.804	105.895	44.837	-297.995	20.197
1900	31.442	132.503	107.251	47.979	-297.973	16.942
2000	31.476	134.117	108.554	51.125	-297.962	13.822
2100	31.505	135.653	109.808	54.274	-297.922	10.723
2200	31.530	137.119	111.017	57.426	-297.896	7.641
2300	31.553	138.521	112.182	60.580	-297.890	4.581
2400	31.572	139.865	113.306	63.736	-297.906	1.525
2500	31.589	141.154	114.396	66.895	-297.956	0.461
2600	31.605	142.393	115.449	70.054	-298.032	-0.606
2700	31.618	143.586	116.469	73.215	-298.174	-1.679
2800	31.631	144.736	117.458	76.378	-298.390	-2.757
2900	31.642	145.846	118.418	79.542	-306.738	-3.840
3000	31.652	146.919	119.351	82.706	-306.956	-4.928
3100	31.661	147.957	120.257	85.872	-307.177	-6.021
3200	31.669	148.963	121.138	89.038	-307.405	-7.116
3300	31.676	149.937	121.996	92.206	-307.639	-8.213
3400	31.683	150.883	122.832	95.374	-307.878	-9.312
3500	31.689	151.802	123.647	98.542	-308.125	-10.413
3600	31.695	152.694	124.441	101.712	-308.374	-11.516
3700	31.700	153.563	125.216	104.881	-308.632	-12.622
3800	31.705	154.408	125.974	108.052	-308.894	-13.736
3900	31.710	155.232	126.713	111.222	-309.163	-14.856
4000	31.714	156.035	127.436	114.394	-309.436	-15.981
4100	31.718	156.810	128.143	117.565	-309.716	-17.111
4200	31.721	157.562	128.835	120.737	-310.000	-18.246
4300	31.725	158.329	129.513	123.909	-310.288	-19.386
4400	31.728	159.056	130.176	127.082	-310.585	-20.531
4500	31.731	159.771	130.828	130.255	-310.884	-21.681
4600	31.734	160.469	131.462	133.428	-311.189	-22.836
4700	31.736	161.151	132.087	136.601	-311.500	-24.000
4800	31.739	161.819	132.699	139.775	-311.814	-25.171
4900	31.741	162.474	133.300	142.949	-312.135	-26.348
5000	31.743	163.115	133.890	146.124	-312.461	-27.531
5100	31.745	163.744	134.469	149.298	-312.797	-28.721
5200	31.747	164.360	135.038	152.473	-313.143	-29.916
5300	31.749	164.965	135.597	155.647	-313.497	-31.116
5400	31.750	165.556	136.147	158.822	-313.856	-32.321
5500	31.752	166.141	136.687	161.997	-314.219	-33.531
5600	31.753	166.713	137.218	165.173	-314.587	-34.746
5700	31.755	167.275	137.740	168.348	-314.959	-35.966
5800	31.756	167.827	138.254	171.524	-315.334	-37.191
5900	31.758	168.370	138.760	174.699	-315.714	-38.421
6000	31.759	168.904	139.256	177.875	-316.099	-39.656

(Ideal Gas) Mol. Wt. = 104.016

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INF INFINITE	3.710	0.582	INF INFINITE	0.582	INF INFINITE	
100	9.981	57.235	85.581	2.635	12.256	5.609	12.256	
200	14.303	65.365	73.440	1.637	13.352	12.219	13.352	
298	18.922	71.962	71.962	0.000	13.985	16.080	13.985	
300	19.000	72.079	71.962	0.035	13.984	16.080	13.984	
400	22.584	78.066	72.754	2.125	14.373	26.313	14.373	
500	25.047	83.388	74.359	4.514	14.609	33.423	14.609	
600	26.717	88.112	76.266	7.108	14.754	40.507	14.754	
700	27.624	91.848	78.148	9.746	14.844	47.556	14.844	
800	28.684	95.110	80.252	12.570	14.888	54.568	14.888	
900	29.277	98.514	82.214	15.570	14.929	61.481	14.929	
1000	29.719	102.623	84.102	18.421	14.944	68.380	14.944	
1100	30.057	105.472	85.917	21.510	14.948	75.239	14.948	
1200	30.320	108.025	87.582	24.872	14.945	82.061	14.945	
1300	30.528	110.534	89.325	27.572	14.937	88.861	14.937	
1400	30.696	112.803	90.922	30.634	14.923	95.598	14.923	
1500	30.833	114.893	92.459	33.710	14.907	102.321	14.907	
1600	30.946	116.919	93.919	36.800	14.890	109.014	14.890	
1700	31.042	118.882	95.325	39.894	14.871	115.663	14.871	
1800	31.120	120.795	96.682	42.994	14.851	122.284	14.851	
1900	31.188	122.529	97.984	46.123	14.831	128.844	14.831	
2000	31.246	123.860	99.238	49.244	14.811	135.344	14.811	
2100	31.296	125.386	100.447	52.372	14.790	142.117	14.790	
2200	31.337	126.237	101.742	55.500	14.769	148.516	14.769	
2300	31.378	127.227	102.942	58.628	14.748	154.816	14.748	
2400	31.412	129.571	104.832	61.779	14.727	161.740	14.727	
2500	31.441	130.856	106.887	64.922	14.706	168.245	14.706	
2600	31.468	132.090	108.910	68.067	14.687	174.737	14.687	
2700	31.493	133.225	110.907	71.215	14.668	181.217	14.668	
2800	31.515	134.253	112.879	74.371	14.649	187.684	14.649	
2900	31.532	135.530	114.769	77.517	14.630	194.131	14.630	
3000	31.549	136.599	116.908	80.672	14.610	200.561	14.610	
3100	31.564	137.634	118.592	83.827	14.592	206.985	14.592	
3200	31.579	138.636	119.453	86.984	14.574	213.400	14.574	
3300	31.593	139.609	120.276	90.143	14.556	219.802	14.556	
3400	31.603	140.591	121.276	93.303	14.538	226.204	14.538	
3500	31.614	141.467	113.606	96.463	14.522	232.578	14.522	
3600	31.624	142.358	114.684	99.625	14.506	238.952	14.506	
3700	31.633	143.225	115.444	102.788	14.489	245.313	14.489	
3800	31.641	144.080	116.117	105.949	14.474	251.669	14.474	
3900	31.649	144.880	116.912	109.117	14.458	258.016	14.458	
4000	31.657	145.692	117.621	112.282	14.443	264.348	14.443	
4100	31.663	146.474	118.316	115.448	14.428	270.675	14.428	
4200	31.669	147.237	118.995	118.614	14.413	276.997	14.413	
4300	31.674	147.980	119.661	121.782	14.399	283.315	14.399	
4400	31.681	148.710	120.305	124.945	14.385	289.616	14.385	
4500	31.686	149.422	120.932	128.118	14.371	295.916	14.371	
4600	31.690	150.119	121.578	131.287	14.358	302.213	14.358	
4700	31.695	150.800	122.193	134.456	14.345	308.499	14.345	
4800	31.699	151.465	122.796	137.626	14.332	314.785	14.332	
4900	31.703	152.121	123.386	140.796	14.319	321.055	14.319	
5000	31.707	152.762	123.968	143.966	14.307	327.329	14.307	
5100	31.710	153.390	124.539	147.137	14.294	333.583	14.294	
5200	31.713	154.005	125.100	150.308	14.283	339.854	14.283	
5300	31.716	154.605	125.651	153.480	14.271	346.108	14.271	
5400	31.719	155.200	126.201	156.651	14.260	352.352	14.260	
5500	31.722	155.784	126.726	159.824	14.249	358.601	14.249	
5600	31.725	156.356	127.250	162.996	14.238	364.841	14.238	
5700	31.727	156.918	127.765	166.168	14.227	371.081	14.227	
5800	31.729	157.470	128.273	169.341	14.217	377.313	14.217	
5900	31.732	158.012	128.773	172.514	14.206	383.533	14.206	
6000	31.734	158.545	129.244	175.688	14.196	389.758	14.196	

Mar. 31, 1964

TETRAFLUOROHYDRAZINE (N₂F₄)Point Group = C₂S_{298.15} = 71.96 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

(IDEAL GAS)

MOL. WT. = 104.016

ΔH_f⁰ = 0.6 ± 2.5 kcal. mole⁻¹ΔH_f⁰ 298.15 = -2.0 ± 2.5 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
1010 (1)	549 (1)	946 (1)	
998 (1)	330 (1)	737 (1)	
933 (1)	122 (1)	519 (1)	
591 (1)	959 (1)	467 (1)	

Bond Distances: N-N = [1.47 Å] N-F = [1.37 Å]

Bond Angles: F-N-F = [108°] N-N-F = [104°] Dihedral Angle = [65°]

Product of the Moments of Inertia: I_AI_BI_C = [1.1817 X 10⁻¹¹³] gm.³ cm.⁶

Heat of Formation.

O. T. Armstrong, S. Marantz, and C. F. Coyle, National Bureau of Standards Report No. 5584, October, 1959, studied the reaction



From this reaction, they calculate the heat of formation of N₂F₄ to be -2.0 ± 2.5 kcal. mole⁻¹. The recalculated heat of formation of NH₄F(s) (see NF₂ table) differs from the value quoted in Circular 500 by 0.06 kcal. mole⁻¹. This correction would make the heat of formation of tetrafluorohydrazine more negative by 0.24 kcal. mole⁻¹. In view of the large uncertainty in the heat of formation, however, this correction was not applied.

Heat Capacity and Entropy.

The fundamental frequencies were taken from the vapor phase infrared work of J. R. Durig and R. C. Lord, Spectrochim. Acta 19, 1877 (1963). The principal moments of inertia were calculated from the rotational constants reported by D. R. Lide, Jr. and D. E. Mann, J. Chem. Phys. 31, 1129 (1959). Lide and Mann calculated the bond angles for assumed values of the NN and NF distances.

The principal moments of inertia are: I_A = 1.5051 X 10⁻³⁸ gm. cm.², I_B = 2.6315 X 10⁻³⁹ gm. cm.², I_C = 2.9836 X 10⁻³⁸ gm. cm.².

continued from the table nitrogen difluoride (NF₂) (ideal gas).

Heat Capacity and Entropy.

M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys. 35, 1129 (1961), investigated the infrared spectrum of NF₂. They were able to assign the band center at 1074 cm.⁻¹ to the symmetric stretching mode ω₁. The absorption in the 930-940 cm.⁻¹ region was assigned to ω₃.

M. D. Harmony and R. J. Myers, J. Chem. Phys. 37, 636 (1962), performed matrix isolation experiments on NF₂. They arrived at the assignment ω₁ = 1070 cm.⁻¹, ω₂ = 573 cm.⁻¹, and ω₃ = 931 cm.⁻¹. The stretching frequencies for similar molecules in an N₂ matrix are about 5 cm.⁻¹ below the gas phase values. A comparison of the gas phase and matrix values of ω₁ show excellent agreement.

F. A. Johnson and C. B. Colburn, Inorg. Chem. 1, 431 (1962), report infrared studies on NF₂ but they draw no definite conclusions.

The gas phase value for ω₁ and the matrix values for ω₂ and ω₃ were taken to represent the fundamental vibrational frequencies of NF₂.

Harmony, Myers, Schoen, Lide, and Mann estimated the N-F distance as 1.37 Å and used this with their data to calculate an F-N-F angle of 104.2°. Using these data the moments of inertia are: I_A = 7.3728 X 10⁻³⁹ gm. cm.², I_B = 1.2035 X 10⁻³⁹ gm. cm.², I_C = 8.5763 X 10⁻³⁹ gm. cm.².

Tungsten Oxytetrafluoride (WOF₄)
(Crystal) GFW = 275.843

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ^o ₂₉₈)/T	— kcal/mol H ^o - H ^o ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	31.926	42.000	42.000	.000	- 355.370	- 329.371
300	32.000	42.198	42.001	.000	- 355.356	- 329.356
400	36.000	47.851	55.850	.850	- 355.356	- 329.356
500	39.800	50.410	55.896	7.257	- 353.224	- 312.304
600	42.700	57.937	48.954	11.390	- 351.743	- 304.256
700	48.500	74.670	52.156	15.760	- 350.085	- 296.470
800	50.715	80.175	52.156	20.629	- 348.321	- 288.931
900	46.900	81.117	52.156	29.629	- 346.463	- 281.510
1000	47.300	91.137	51.502	29.635	- 346.413	- 274.311

TUNGSTEN OXYTETRAFLUORIDE (WOF₄) (CRYSTAL)

OPW = 275.843 F₄OW

ΔH_f^o = Unknown

ΔH_f^o_{298.15} = [-355.37 ± 6] kcal/mol

ΔH_m^o = 1.219 ± 2 kcal/mol

S^o_{298.15} = [42.0 ± 4] gibbs/mol

T_m = 379°K

Heat of Formation.

The heat of formation, ΔH_f^o₂₉₈(WOF₄, c) = -355.37 kcal/mol, is calculated from that of the gas less the heat of sublimation, ΔH_{sub}^o₂₉₈ = 16.97 kcal/mol. The latter is calculated by the third law method from the vapor pressure equation determined by G. H. Cady and G. B. Hargreaves, J. Chem. Soc., 1563 (1961). The second law ΔH_f^o₂₉₈ is 17.01 kcal/mol.

Heat Capacity and Entropy.

The heat capacities are estimated from those of WOCl₄(c), WO₃(c), WO₂(c), WOCl₂(c) and WF₆(c,l).

The entropy, S₂₉₈^o = 42.0 eu, is calculated from ΔS₃₄₈^o = 37.0 eu for WOF₄(c) → WOF₄(g), obtained from the second law analysis of the vapor pressure equation given by Cady and Hargreaves, loc. cit.

It is surprising that this entropy is larger than the corresponding value for WOCl₄(c) (JANAF WOF₄(c) table dated Mar. 31, 1967). In both cases the entropies of the condensed phases are derived from the gas phase values using second law analysis of sublimation and vaporization data. The resulting entropy of melting for WOF₄, 3.2 eu, is much smaller than the value 22.4 eu for WOCl₄. This extreme difference may be a reflection of the uncertainty inherent in derivation of ΔS_m^o as the difference between the values for sublimation and vaporization. If the values of ΔS_m^o are correct, they suggest the possibility of an undiagnosed solid state transition for WOF₄ similar to that observed for WF₆.

Melting Data.

T_m is calculated as the temperature at which the Gibbs energy of reaction WOF₄(c) → WOF₄(l) approaches zero. The difference between the heats of formation for crystal and liquid at the melting point is ΔH_m^o.

O. Ruff, P. Eianer, and W. Heller, Z. Anorg. Chem. 52, 256 (1907), reported the melting point as 393°K. Cady and Hargreaves, loc. cit., derived the melting point as 378°K, and the heat of fusion as 2.26 kcal/mol from vapor pressure equations for crystal and liquid. This second law value of ΔH_m^o, when corrected for ΔC_p of vaporization and sublimation, is in good agreement with the value adopted in the tabulation.

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^c	ΔG _f ^c	Log K _p
0							
100							
200							
298	43.500	42.800	42.800	.000	-354.955	-329.194	241.306
300	43.500	43.049	42.801	.080	-354.920	-329.035	239.702
400	43.500	51.583	44.537	4.330	-351.055	-326.560	175.217
500	43.500	55.280	47.729	8.780	-351.285	-312.807	136.728
600	43.500	73.221	51.337	13.130	-349.588	-305.271	111.195
700	43.500	89.254	54.534	17.530	-347.530	-295.043	91.605
800	43.500	97.755	57.487	21.830	-346.130	-290.095	79.095
900	43.500	99.859	61.769	26.180	-344.815	-284.163	69.004
1000	43.500	95.442	64.911	30.530	-343.302	-277.505	60.649

June 30, 1962; Mar. 31, 1967

TUNGSTEN OXYTETRAFLUORIDE (WOF₄)

(LIQUID)

OFW = 275.843

$$\Delta H_{f, 298.15}^{\circ} = [-354.955] \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 1.219 \pm 2 \text{ kcal/mol}$$

$$\Delta H_v^{\circ} = 13.4 \text{ kcal/mol}$$

$$S_{298.15}^{\circ} = [42.8 \pm 4] \text{ gibbs/mol}$$

$$T_m = 379^{\circ}\text{K}$$

$$T_b = 460^{\circ}\text{K}$$

Heat of Formation.

The heat of formation, $\Delta H_{f, 298}^{\circ}$ (WOF₄, l) = -354.955 kcal/mol, is calculated from that of the gas less the heat of vaporization, $\Delta H_{v, 298}^{\circ} = 16.555$ kcal/mol. The latter is calculated by the third law method from the vapor pressure equation determined by O. H. Cady and O. B. Hargreaves, J. Chem. Soc., 1563 (1961). The second law $\Delta H_{v, 298}^{\circ}$ is 16.60 kcal/mol.

Heat Capacity and Entropy.

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom as suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1959.

The entropy, $S_{298}^{\circ} = 42.8$ eu, is calculated from $\Delta S_{415}^{\circ} = 31.2$ eu for WOF₄(l) → WOF₄(g), obtained from the second law analysis of the vapor pressure equation given by Cady and Hargreaves, loc. cit.

Melting Data.

See WOF₄(c) table (Mar. 31, 1967).

Vaporization Data.

T_b is calculated as the temperature at which the Gibbs energy of reaction WOF₄(l) → WOF₄(g) approaches zero. The difference between the heats of formation for liquid and gas at the boiling point is ΔH_v° .

O. Ruff, P. Elsner and W. Heller, Z. Anorg. Chem. 52, 256 (1907), reported the boiling point as 459°K. Cady and Hargreaves, loc. cit., derived the boiling point as 459°K, and the heat of vaporization as 14.23 kcal/mol from the vapor pressure equation for the liquid. This second law value of ΔH_v° , when corrected for ΔC_p of vaporization, is in good agreement with the value adopted in the tabulation.

Tungsten Oxytetrafluoride (WOF₄)
(Ideal Gas) $\Delta H_f^\circ = 275.843$

T, °K	Cp°	gibbs/mol S°	(G°-H° ₂₉₈)/T	— kcal/mol — H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	-0.000	-0.000	INFINITE	- 4.467	- 336.420	- 336.420	INFINITE
100	12.552	61.838	97.238	- 3.540	- 337.387	- 333.132	728.059
200	18.170	72.462	82.338	- 1.975	- 338.050	- 328.500	359.067
298	21.914	80.448	80.448	- 0.000	- 338.400	- 323.464	237.399
300	21.975	80.583	80.448	- 0.041	- 338.405	- 323.774	235.849
400	24.749	85.309	81.346	2.385	- 336.505	- 318.451	177.223
500	26.341	89.049	83.127	6.361	- 336.550	- 315.951	137.228
600	27.919	92.026	85.205	7.693	- 338.470	- 309.037	112.566
700	29.400	102.400	87.355	10.531	- 338.344	- 304.139	94.956
800	30.872	106.289	97.493	13.484	- 338.195	- 299.266	81.756
900	32.357	110.178	107.625	16.437	- 338.024	- 294.411	71.141
1000	33.842	112.948	117.757	19.419	- 337.862	- 289.571	63.286
1100	35.327	115.840	127.889	22.450	- 337.695	- 284.751	56.575
1200	36.812	118.500	137.924	25.507	- 337.531	- 279.943	50.965
1300	38.297	121.251	147.969	28.581	- 337.369	- 275.149	46.257
1400	39.782	124.002	158.014	31.673	- 337.209	- 270.366	42.557
1500	41.267	126.753	168.059	34.771	- 337.054	- 265.596	38.697
1600	42.752	129.504	178.104	37.884	- 336.971	- 260.835	35.629
1700	44.237	132.255	188.149	41.002	- 336.860	- 256.079	32.921
1800	45.722	135.006	198.194	44.128	- 336.765	- 251.333	30.516
1900	47.207	137.757	208.239	47.254	- 336.671	- 246.595	28.428
2000	48.692	140.508	218.284	50.380	- 336.587	- 241.861	26.575
2100	50.177	143.259	228.329	53.506	- 336.503	- 237.111	24.941
2200	51.662	146.010	238.374	56.632	- 336.433	- 232.378	23.085
2300	53.147	148.761	248.419	59.758	- 336.367	- 227.653	21.031
2400	54.632	151.512	258.464	62.884	- 336.306	- 222.938	18.973
2500	56.117	154.263	268.509	66.010	- 336.248	- 218.224	16.915
2600	57.602	157.014	278.554	69.136	- 336.193	- 213.510	14.857
2700	59.087	159.765	288.599	72.262	- 336.141	- 208.797	12.800
2800	60.572	162.516	298.644	75.388	- 336.091	- 204.084	10.743
2900	62.057	165.267	308.689	78.514	- 336.042	- 199.371	8.686
3000	63.542	168.018	318.734	81.640	- 336.000	- 194.658	6.629
3100	65.027	170.769	328.779	84.766	- 335.961	- 189.945	4.572
3200	66.512	173.520	338.824	87.892	- 335.926	- 185.232	2.515
3300	68.000	176.271	348.869	91.018	- 335.894	- 180.519	0.458
3400	69.485	179.022	358.914	94.144	- 335.865	- 175.806	- 1.599
3500	70.970	181.773	368.959	97.270	- 335.839	- 171.093	- 3.646
3600	72.455	184.524	379.004	100.396	- 335.816	- 166.380	- 5.693
3700	73.940	187.275	389.049	103.522	- 335.796	- 161.667	- 7.740
3800	75.425	190.026	399.094	106.648	- 335.779	- 156.954	- 9.787
3900	76.910	192.777	409.139	109.774	- 335.764	- 152.241	- 11.834
4000	78.395	195.528	419.184	112.900	- 335.752	- 147.528	- 13.881
4100	79.880	198.279	429.229	116.026	- 335.742	- 142.815	- 15.928
4200	81.365	201.030	439.274	119.152	- 335.734	- 138.102	- 17.975
4300	82.850	203.781	449.319	122.278	- 335.728	- 133.389	- 19.999
4400	84.335	206.532	459.364	125.404	- 335.724	- 128.676	- 21.999
4500	85.820	209.283	469.409	128.530	- 335.722	- 123.963	- 23.999
4600	87.305	212.034	479.454	131.656	- 335.722	- 119.250	- 25.999
4700	88.790	214.785	489.499	134.782	- 335.724	- 114.537	- 27.999
4800	90.275	217.536	499.544	137.908	- 335.728	- 109.824	- 29.999
4900	91.760	220.287	509.589	141.034	- 335.734	- 105.111	- 31.999
5000	93.245	223.038	519.634	144.160	- 335.742	- 100.398	- 33.999
5100	94.730	225.789	529.679	147.286	- 335.752	- 95.685	- 35.999
5200	96.215	228.540	539.724	150.412	- 335.764	- 90.972	- 37.999
5300	97.700	231.291	549.769	153.538	- 335.778	- 86.259	- 39.999
5400	99.185	234.042	559.814	156.664	- 335.794	- 81.546	- 41.999
5500	100.670	236.793	569.859	159.790	- 335.812	- 76.833	- 43.999
5600	102.155	239.544	579.904	162.916	- 335.832	- 72.120	- 45.999
5700	103.640	242.295	589.949	166.042	- 335.854	- 67.407	- 47.999
5800	105.125	245.046	599.994	169.168	- 335.878	- 62.694	- 49.999
5900	106.610	247.797	609.039	172.294	- 335.904	- 57.981	- 51.999
6000	108.095	250.548	619.084	175.420	- 335.932	- 53.268	- 53.999

June 30, 1962; Mar. 31, 1967

TUNGSTEN OXYTETRAFLUORIDE (WOF₄)
(IDEAL GAS)

Point Group [C_{2v}]
S_{298.15} = [80.4] gibbs/mol
Ground State Quantum Weight = 1

ΔH_{f,0}⁰ = -336.4 ± 6 kcal/mol
ΔH_{f,298.15}⁰ = -338.4 ± 6 kcal/mol

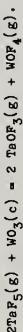
OPW = 275.843

Vibrational Frequencies and Degeneracies	w, cm ⁻¹	w, cm ⁻¹	w, cm ⁻¹
[1000] (1)	[700] (1)	[250] (1)	
[1000] (1)	[700] (1)	[250] (1)	
[900] (1)	[300] (1)	[200] (1)	
[900] (1)	[300] (1)	[200] (1)	

Bond Distance: W-F = [1.85] Å W-O = [1.81] Å
Bond Angle: F-W-O = F-W-F = [120°]
F-W-F = F-W-O = [90°]
F-W-F = [180°]
*Equatorial **Axial
Product of the Moments of Inertia: I_AI_BI_C = [3.868] × 10⁻¹¹³ g³ cm⁶
σ = [2]

Heat of Formation.

The heat of formation, ΔH_{f,298}⁰(WOF₄, g) = -338.4 kcal/mol, is the value determined mass spectrometrically by K. P. Zmbov and J. L. Margrave, Rice Univ., private communication, Mar. 1967, from equilibrium studies of



Heat Capacity and Entropy.

The molecular configuration is assumed to be a trigonal bipyramid similar to that of SOF₄(g), reported by P. L. Oggins, H. L. Roberts and L. A. Woodward.¹ The bond distances W-O and W-F are estimated to be the same as those in WO₃(g) and WF₆(g), respectively. The three principal moments of inertia are I_A = 3.509 × 10⁻³⁸, I_B = 3.698 × 10⁻³⁸ and I_C = 2.981 × 10⁻³⁸ g cm².

All vibrational frequencies are estimated by comparison with those observed in the infrared and Raman spectra for SOF₄(g),¹ MoOCl₄(g),² WO₂Cl₂(g),³ CrO₂Cl₂(g),^{4,5} WO₃(g),⁶ and WF₆(g).⁶ These frequencies are not in point group order.

References.

1. P. L. Oggins, H. L. Roberts and L. A. Woodward, Trans. Faraday Soc. **57**, 1877 (1961).
2. T. V. Iorns and P. E. Stafford, J. Am. Chem. Soc. **88**, 4819 (1966).
3. C. O. Barracough and J. Stala, Aust. J. Chem. **19**, 741 (1966).
4. F. A. Miller, G. L. Carlson and W. B. White, Spectrochim. Acta, **1959**, 709 (1953).
5. H. Stammreich, K. Kawai and Y. Tsvares, Spectrochim. Acta, **1959**, 438 (1959).
6. JANAF WO₃(g) table (Sept. 30, 1966), WF₆(g) table (Mar. 31, 1967).

F₄OW

Lead Tetrafluoride (PbF₄) (Ideal Gas) Mol. Wt. = 283.21

INTERIM TABLE

T, °K.	C _p	S°	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	-0.000	-0.000	INF. INITE	-4.723	-184.859	-184.859	INF. INITE
100	14.2233	60.071	97.046	-3.4013	-185.645	-185.645	309.118
200	19.019	71.555	81.621	-2.0013	-185.965	-179.466	196.100
298	21.735	79.709	79.709	-0.000	-186.000	-176.260	129.196
300	21.772	79.844	79.709	+0.040	-186.000	-176.200	129.355
400	24.070	87.844	82.278	4.669	-185.850	-169.456	74.456
500	24.476	91.616	82.278	4.669	-185.850	-169.404	74.114
600	24.571	96.053	84.214	7.103	-185.770	-166.481	60.638
700	24.686	99.866	86.184	9.577	-186.868	-163.081	50.914
800	25.009	103.204	88.108	12.077	-186.821	-159.087	43.622
900	25.255	106.553	89.793	14.525	-186.769	-155.298	37.953
1000	25.535	109.855	91.713	17.125	-186.715	-151.816	33.418
1100	25.846	112.256	93.379	19.665	-186.658	-148.539	29.709
1200	25.949	113.472	94.962	22.121	-186.596	-145.166	26.619
1300	25.547	115.515	96.465	24.764	-186.536	-142.798	24.005
1400	25.588	117.409	97.895	27.321	-186.478	-139.437	21.766
1500	25.618	119.116	99.255	29.881	-186.424	-136.076	19.825
1600	25.644	120.830	100.552	32.444	-186.378	-132.723	18.128
1700	25.665	122.385	101.791	35.010	-186.337	-129.369	16.631
1800	25.683	123.853	102.977	37.577	-186.308	-126.024	15.301
1900	25.699	125.242	104.112	40.146	-186.285	-122.674	14.110
2000	25.712	126.560	105.202	42.717	-186.271	-119.324	13.038
2100	25.723	127.815	106.249	45.289	-186.261	-115.971	12.087
2200	25.732	129.012	107.257	47.862	-186.260	-112.618	11.252
2300	25.742	130.156	108.228	50.435	-186.268	-109.268	10.539
2400	25.753	131.252	109.164	53.010	-186.281	-105.915	9.934
2500	25.756	132.303	110.069	55.585	-186.293	-102.563	9.434
2600	25.762	133.313	110.944	58.161	-186.309	-99.210	8.934
2700	25.767	134.286	111.790	60.737	-186.330	-95.857	8.434
2800	25.772	135.223	112.614	63.314	-186.354	-92.504	7.934
2900	25.778	136.127	113.406	65.892	-186.382	-89.151	7.434
3000	25.780	137.001	114.178	68.470	-186.414	-85.798	6.934
3100	25.783	137.847	114.928	71.048	-186.450	-82.445	6.434
3200	25.786	138.665	115.657	73.626	-186.490	-79.092	5.934
3300	25.789	139.459	116.366	76.205	-186.534	-75.739	5.434
3400	25.792	140.229	117.057	78.784	-186.582	-72.386	4.934
3500	25.794	140.976	117.730	81.363	-186.634	-69.033	4.434
3600	25.796	141.703	118.386	83.943	-186.690	-65.680	3.934
3700	25.798	142.410	119.025	86.523	-186.750	-62.327	3.434
3800	25.800	143.098	119.650	89.103	-186.814	-58.974	2.934
3900	25.802	143.768	120.260	91.683	-186.882	-55.621	2.434
4000	25.804	144.421	120.856	94.263	-186.954	-52.268	1.934
4100	25.805	145.059	121.438	96.843	-187.030	-48.915	1.434
4200	25.807	145.680	122.008	99.424	-187.110	-45.562	0.934
4300	25.808	146.288	122.566	102.005	-187.194	-42.209	0.434
4400	25.809	146.881	123.112	104.586	-187.282	-38.856	-0.066
4500	25.810	147.461	123.646	107.167	-187.374	-35.503	-0.566
4600	25.811	148.028	124.170	109.748	-187.470	-32.150	-1.066
4700	25.812	148.584	124.684	112.329	-187.570	-28.797	-1.566
4800	25.813	149.127	125.187	114.910	-187.674	-25.444	-2.066
4900	25.814	149.659	125.681	117.491	-187.782	-22.091	-2.566
5000	25.815	150.181	126.166	120.073	-187.894	-18.738	-3.066
5100	25.816	150.692	126.642	122.654	-188.010	-15.385	-3.566
5200	25.816	151.193	127.109	125.236	-188.130	-12.032	-4.066
5300	25.817	151.685	127.568	127.817	-188.254	-8.679	-4.566
5400	25.818	152.168	128.050	130.399	-188.382	-5.326	-5.066
5500	25.818	152.651	128.603	132.981	-188.514	-1.973	-5.566
5600	25.819	153.106	128.899	135.563	-188.650	1.380	-6.066
5700	25.819	153.563	129.328	138.145	-188.790	4.727	-6.566
5800	25.820	154.012	129.749	140.727	-188.934	8.074	-7.066
5900	25.821	154.454	130.164	143.309	-189.082	11.421	-7.566
6000	25.821	154.888	130.573	145.891	-189.234	14.768	-8.066

June 30, 1962

Lead Tetrafluoride (PbF₄) (Ideal Gas)

Mol. Wt. = 283.21

 $\Delta H_f^{298.15} = [-186] \text{ kcal. mole}^{-1}$ $S_g^{298.15} = 79.7 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ Point group T_d

Vibrational Levels and Multiplicities

 $\omega_e, \text{ cm.}^{-1}$

564 (1)

158 (2)

570 (3)

180 (3)

Pb-F distance = 2.08 Å F-Pb-F angle = 109° 28'

 $I_{\text{A}} I_{\text{B}} I_{\text{C}} = 4.8233 \times 10^{-113} \text{ g. cm.}^6$ $\sigma = 12$ Heat of Formation. $\Delta H_f^{298.15}$ was estimated by comparison with the value of $\Delta H_f^{298.15}$ for PbF₂(g).

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagarsajan, Bull. Soc. Chim. Belg., 71, 119 (1962).

GFW = 108.058

(IDEAL GAS)

SULFUR TETRAFLUORIDE (SF₄)Sulfur Tetrafluoride (SF₄)

(Ideal Gas) GFW = 108.058

Point Group C_{2v} $\Delta H_f^\circ = -185.1 \pm 6$ kcal/molS_{298.15} = 71.83 ± 0.10 gibbs/mol $\Delta H_f^\circ = -185.1 \pm 6$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
891.5 (1)	171 (1)	532.2 (1)
1047.7 (1)	558.4 (1)	728 (1)
1247.0 (1)	353 (1)	867 (1)
1296.636		226 (1)

Bond Distance: (S-F)_{eq.} = 1.545 ± 0.003 Å(S-F)_{ax.} = 1.646 ± 0.003 ÅBond Angle: (F-S-F)_{eq.} = 101°33' ± 30'(F-S-F)_{ax.} = 186°56' ± 30'Product of Moments of Inertia: I_AI_BI_C = 6.721 × 10⁻¹¹⁴ g³ cm⁶

Heat of Formation

Vaughn and Muettterties (1) reported calorimetric data for the hydrogenation of SF₄. Their experiments produced HF in amounts ranging from 5.8 to 7.5g. Roughly 1.3g should have been present as saturated, real vapor in the bomb volume of 360 ml at the final temperature of the experiment. Although the authors made allowance for this mixture of HF(g) and HF(real vapor), their values appear to be quite unrealistic. More reliable corrections are readily obtained from the recent report by Vanderzee (2) of PVT and calorimetric data for HF liquid and real vapor.

We choose to reduce the data to a standard state of HF(l), starting from the authors' values of the calorimeter heat capacity and the observed temperature rise. Calculated values for the heat evolved are corrected by a) an increase of ~120 cal for conversion of real vapor to liquid, b) a decrease of 113 to 175 cal for oxidation of H₂S(g) to S(c) in the last three experiments, and c) an increase of 22 to 75 cal for adjustment of the reaction to 25°C from the final temperature of the experiment. At 298.15 K we obtain

SF₄(g) + 2H₂(g) + 4HF(l) + S(c), $\Delta H^\circ = -102.9 \pm 4$ kcal/mol,

where the uncertainty is increased by 1.5 kcal/mol for other possible corrections which are neglected due to insufficient information.

The adopted ΔH_f° , -185.6 ± 6 kcal/mol, is derived from ΔH° using ΔH_f° = -72.38 ± [0.5] kcal/mol (2, 3) for HF(l). Smith (4) quoted a value of ΔH_f° = -176 kcal/mol for SF₄ as determined by Nicholls (5) from hydrolysis studies. We do not have details of the hydrolysis studies, but the result presumably should be adjusted for changes in ΔH_f° of aqueous HF.

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Levin and Berner (6) and are in good agreement with the frequencies reported by Dodd et al. (2) except for the 353 and 171 cm⁻¹ bands. The structural data are from the microwave studies of Tolles and Gwinn (8) and are in good agreement within experimental error with electron-diffraction data reported by Kimura and Bauer (9) and Ewing and Sutton (10). Individual moments of inertia calculated from the rotational constants reported by Tolles and Gwinn (8) are I_A = 1.2552 × 10⁻³⁸ g cm², I_B = 2.0540 × 10⁻³⁸ g cm², and I_C = 2.6069 × 10⁻³⁸ g cm².

References

1. J. D. Vaughn and E. L. Muettterties, J. Phys. Chem., **51**, 1787 (1960).
2. C. E. Vanderzee, submitted for publication in J. Chem. Thermodynamics.
3. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Mich., Dec. 31, 1968.
4. W. C. Smith, Angew. Chem., Intern. Ed., **1**, 467 (1962).
5. Nicholls, Ph.D. Thesis, Durham University, 1958.
6. I. W. Levin and C. W. Berner, J. Chem. Phys., **44**, 2557 (1966).
7. R. E. Dodd, L. A. Woodward, and H. L. Roberts, Trans. Faraday Soc., **52**, 1052 (1956).
8. W. M. Tolles and W. D. Gwinn, J. Chem. Phys., **36**, 1119 (1962).
9. K. Kimura and S. H. Bauer, J. Chem. Phys., **39**, 3172 (1963).
10. V. C. Ewing and L. E. Sutton, Trans. Faraday Soc., **59**, 1241 (1963).

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	Log Kp
0	10.000	INF	INF	3.768	185.095	INF
100	25.400	56.000	11.116	3.768	185.095	1.967
200	25.475	56.000	11.116	3.768	185.095	1.967
298	25.475	56.000	11.116	3.768	185.095	1.967
300	25.475	56.000	11.116	3.768	185.095	1.967
400	25.475	56.000	11.116	3.768	185.095	1.967
500	25.475	56.000	11.116	3.768	185.095	1.967
600	25.475	56.000	11.116	3.768	185.095	1.967
700	25.475	56.000	11.116	3.768	185.095	1.967
800	25.475	56.000	11.116	3.768	185.095	1.967
900	25.475	56.000	11.116	3.768	185.095	1.967
1000	25.475	56.000	11.116	3.768	185.095	1.967
1100	25.475	56.000	11.116	3.768	185.095	1.967
1200	25.475	56.000	11.116	3.768	185.095	1.967
1300	25.475	56.000	11.116	3.768	185.095	1.967
1400	25.475	56.000	11.116	3.768	185.095	1.967
1500	25.475	56.000	11.116	3.768	185.095	1.967
1600	25.475	56.000	11.116	3.768	185.095	1.967
1700	25.475	56.000	11.116	3.768	185.095	1.967
1800	25.475	56.000	11.116	3.768	185.095	1.967
1900	25.475	56.000	11.116	3.768	185.095	1.967
2000	25.475	56.000	11.116	3.768	185.095	1.967
2100	25.475	56.000	11.116	3.768	185.095	1.967
2200	25.475	56.000	11.116	3.768	185.095	1.967
2300	25.475	56.000	11.116	3.768	185.095	1.967
2400	25.475	56.000	11.116	3.768	185.095	1.967
2500	25.475	56.000	11.116	3.768	185.095	1.967
2600	25.475	56.000	11.116	3.768	185.095	1.967
2700	25.475	56.000	11.116	3.768	185.095	1.967
2800	25.475	56.000	11.116	3.768	185.095	1.967
2900	25.475	56.000	11.116	3.768	185.095	1.967
3000	25.475	56.000	11.116	3.768	185.095	1.967
3100	25.475	56.000	11.116	3.768	185.095	1.967
3200	25.475	56.000	11.116	3.768	185.095	1.967
3300	25.475	56.000	11.116	3.768	185.095	1.967
3400	25.475	56.000	11.116	3.768	185.095	1.967
3500	25.475	56.000	11.116	3.768	185.095	1.967
3600	25.475	56.000	11.116	3.768	185.095	1.967
3700	25.475	56.000	11.116	3.768	185.095	1.967
3800	25.475	56.000	11.116	3.768	185.095	1.967
3900	25.475	56.000	11.116	3.768	185.095	1.967
4000	25.475	56.000	11.116	3.768	185.095	1.967
4100	25.475	56.000	11.116	3.768	185.095	1.967
4200	25.475	56.000	11.116	3.768	185.095	1.967
4300	25.475	56.000	11.116	3.768	185.095	1.967
4400	25.475	56.000	11.116	3.768	185.095	1.967
4500	25.475	56.000	11.116	3.768	185.095	1.967
4600	25.475	56.000	11.116	3.768	185.095	1.967
4700	25.475	56.000	11.116	3.768	185.095	1.967
4800	25.475	56.000	11.116	3.768	185.095	1.967
4900	25.475	56.000	11.116	3.768	185.095	1.967
5000	25.475	56.000	11.116	3.768	185.095	1.967

(Ideal Gas) Mol. Wt. = 104.09

SILICON TETRAFLUORIDE (SiF₄)

(IDEAL GAS)

MOL. WT. = 104.09

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(H ^o -H ₂₉₈ ^o)/T	11°-H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-	-	-	-	-	-	-	19.1475
100	2.909	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
200	7.378	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
300	11.563	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
400	15.453	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
500	19.050	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
600	22.477	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
700	25.776	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
800	28.978	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
900	32.104	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
1000	35.154	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
1100	38.129	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
1200	41.024	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
1300	43.835	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
1400	46.559	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
1500	49.191	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
1600	51.734	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
1700	54.191	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
1800	56.559	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
1900	58.835	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
2000	61.024	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
2100	63.129	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
2200	65.154	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
2300	67.104	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
2400	68.978	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
2500	70.776	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
2600	72.504	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
2700	74.159	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
2800	75.734	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
2900	77.224	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
3000	78.635	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
3100	79.978	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
3200	81.254	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
3300	82.469	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
3400	83.624	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
3500	84.724	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
3600	85.774	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
3700	86.774	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
3800	87.724	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
3900	88.624	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
4000	89.474	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
4100	90.274	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
4200	91.024	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
4300	91.724	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
4400	92.374	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
4500	92.974	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
4600	93.524	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
4700	94.024	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
4800	94.474	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
4900	94.874	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
5000	95.224	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
5100	95.524	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
5200	95.774	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
5300	95.974	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
5400	96.124	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
5500	96.224	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
5600	96.274	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
5700	96.274	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
5800	96.224	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
5900	96.124	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475
6000	95.974	52.000	19.1475	3.4559	-385.450	-385.450	-385.450	19.1475

Dec. 31, 1960; Sept. 30, 1963

Point Group T_d

S_{298.15} = 67.433 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹ ω, cm.⁻¹

800 (1) 1031 (3)

268 (2) 391 (3)

Bond Distance: Si-F = 1.54 ± 0.02 Å

Bond Angle: F-Si-F = 109° 28'

Product of the Moments of Inertia: I_AI_BI_C = 7.93269 × 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation.

The heat of formation of SiF₄(g) was measured by direct combination of the elements in a bomb calorimeter by S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, *J. Phys. Chem.* **67**, 815 (1963). ΔH_f^o 298.15 was found to be -385.98 ± 0.19 kcal. mole⁻¹. Heats of the reaction between SiF₄(g) and Ne(g), 1% HF solution, 0.4% HF solution, a solution of NaF saturated with Ne₂SiF₆, and water have been measured by A. P. Vorob'ev, V. P. Kolesov, and S. M. Skuratov, *Zh. Neorg. Khim.* **5**, 1402 (1960). The value of ΔH_f^o 298.15 for SiF₄(g) was reported to be -372.4 ± 0.4 kcal. mole⁻¹ which was not used.

Heat Capacity and Entropy.

The vibrational frequencies used were reported by E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz, and A. H. Nielsen, *J. Chem. Phys.* **19**, 242 (1951). The values of vibrational frequencies were given as 800(1), 285(2), 1000(3), and 431(3) cm.⁻¹ for SiF₄(g) by D. M. Yost, E. M. Leasette, and S. T. Cross, *J. Chem. Phys.* **4**, 325 (1936). The molecular data were obtained from L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.* **57**, 2684 (1935). The three principal moments of inertia are: I_A = I_B = I_C = 1.99437 × 10⁻³⁸ g. cm.²

Titanium Tetrafluoride (TiF₄)
(Crystal) GFW = 123.8936

T, °K	Cp	$\frac{\text{gibbs/mol}}{S}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0	13.000	10.000	INFINITE	0.000	0.000	0.000	INFINITE
100	21.680	22.173	32.167	2.639	383.669	383.669	615.083
200	27.310	32.016	32.016	0.000	379.632	379.632	615.083
298	27.310	32.016	32.016	0.000	372.673	372.673	615.083
300	27.390	32.185	32.017	0.051	372.540	372.540	615.083
400	30.270	40.483	33.128	2.982	365.427	365.427	615.083
500	35.160	47.431	35.315	7.068	352.589	352.589	615.083
600	33.480	53.437	37.848	9.353	351.634	351.634	615.083
700	34.450	58.673	40.457	12.751	345.234	345.234	615.083
800	35.190	63.324	43.030	16.285	338.822	338.822	615.083
900	35.770	67.503	45.521	19.784	332.538	332.538	615.083
1000	36.250	71.297	47.912	23.385	326.378	326.378	615.083
1100	36.640	74.771	50.198	27.030	320.321	320.321	615.083
1200	36.960	77.873	52.381	30.711	314.324	314.324	615.083
1300	37.240	80.943	54.465	34.421	308.379	308.379	615.083
1400	37.480	83.712	56.456	38.157	302.526	302.526	615.083
1500	37.690	86.305	58.361	41.916	296.756	296.756	615.083

TITANIUM TETRAFLUORIDE (TiF₄)

(CRYSTAL)

GFW = 123.8936

$\Delta H^\circ_{298} = -393.57 \pm 0.9 \text{ kcal/mol}$

$\Delta H^\circ_{298,15} = -394.2 \pm 0.9 \text{ kcal/mol}$

$\Delta H^\circ_{298,15} = 21.37 \pm 0.1 \text{ kcal/mol}$

$S^\circ_{298,15} = 32.02 \text{ gibbs/mol}$

$T_s = 558.6^\circ\text{K}$

Heat of Formation

The heat of formation ($\Delta H^\circ_{298,15}$) of TiF₄(c) was measured using a fluorine bomb calorimeter by Greenberg et al. (1). Gross et al. (2) reported a value of -393.4 kcal/mol for ΔH°_{298} . The latter measurements were not corrected for impurities in the titanium sample, thus the value reported by Greenberg et al. is adopted.

Heat Capacity and Entropy

The heat capacity of TiF₄(c) has been measured over the temperature range 6° to 304°K by Euler and Westrum (3). They obtained the value of S°_{298} based on $S^\circ_{10} = 0.11 \text{ eu}$. Heat capacities above 300°K are estimated from those of ZrF₄(c) (4).

Heat of Sublimation

The sublimation point is calculated as the temperature at which $\Delta G^\circ = 0$ for TiF₄(c) = TiF₄(g). The heat of sublimation is obtained from the data of Hall et al. (5).

References

1. E. Greenberg, J. L. Settle, and W. N. Hubbard, J. Phys. Chem. **66**, 1345 (1962).
2. P. Gross, C. Hayman, and D. L. Levi, XVIIIth Internat. Congr. Pure Appl. Chem. Abstr. **1**, 90 (1959).
3. R. D. Euler and E. F. Westrum, Jr., J. Phys. Chem. **65**, 132 (1961).
4. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data **7**, 83 (1962).
5. E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, J. Electrochem. Soc. **105**, 275 (1958).

Titanium Tetrafluoride (TiF₄)
(Ideal Gas)

GFW = 123.8936

T, °K	C _p ^a	S ^b	gibbs/mol -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal/mol	ΔH _f ^c	Log Kp
0	∞.000	∞.000	INFINIT	- 3.498	- 369.936	INFINITE
100	14.013	56.606	91.520	- 370.003	- 367.768	603.746
200	17.607	67.630	77.026	- 370.690	- 364.964	368.636
298	20.357	75.243	75.243	- 370.600	- 362.161	263.471
300	20.397	75.369	75.243	.038	- 370.601	263.795
400	22.124	81.492	76.066	2.170	- 370.627	194.259
500	23.211	86.556	77.672	4.442	- 370.815	155.738
600	24.505	90.853	79.520	6.800	- 370.780	120.795
700	24.364	94.575	81.411	9.215	- 370.760	109.431
800	24.682	97.850	83.245	11.668	- 370.749	94.943
900	24.905	100.771	85.051	14.148	- 370.757	81.709
1000	25.075	103.405	86.807	16.648	- 370.791	74.705
1100	25.201	105.801	88.381	19.162	- 370.850	67.338
1200	25.284	107.998	89.895	21.687	- 370.971	60.190
1300	25.375	110.026	91.395	24.221	- 371.057	55.040
1400	25.436	111.909	92.793	26.761	- 371.160	51.515
1500	25.466	113.685	94.127	29.300	- 371.280	47.645
1600	25.477	115.312	95.400	31.858	- 371.423	44.268
1700	25.472	116.840	96.613	34.413	- 371.587	41.269
1800	25.451	118.322	97.743	36.970	- 372.079	38.613
1900	25.415	119.766	98.901	39.531	- 372.193	36.235
2000	25.636	121.021	100.074	42.093	- 372.783	34.077
2100	25.458	122.272	101.004	44.658	- 376.928	32.116
2200	25.670	123.466	102.000	47.224	- 377.078	30.338
2300	25.684	124.607	102.959	49.792	- 377.230	28.703
2400	25.696	125.701	103.884	52.361	- 377.387	27.209
2500	25.706	126.750	104.777	54.931	- 377.549	25.835
2600	25.716	127.758	105.642	57.502	- 377.718	24.565
2700	25.726	128.739	106.496	60.074	- 377.882	23.366
2800	25.732	129.665	107.291	62.647	- 378.053	22.226
2900	25.739	130.568	108.078	65.220	- 378.230	21.148
3000	25.745	131.440	108.842	67.795	- 378.411	20.328
3100	25.750	132.285	109.585	70.369	- 378.595	19.488
3200	25.756	133.102	110.307	72.945	- 378.783	18.638
3300	25.760	133.895	111.010	75.520	- 378.974	17.820
3400	25.764	134.664	111.694	78.097	- 379.171	17.082
3500	25.768	135.411	112.361	80.673	- 379.373	16.385
3600	25.772	136.137	113.012	83.250	- 381.002	15.711
3700	25.775	136.843	113.646	85.828	- 381.582	15.061
3800	25.778	137.530	114.266	88.405	- 381.580	14.471
3900	25.781	138.200	114.871	90.983	- 381.796	13.943
4000	25.783	138.853	115.462	93.561	- 382.027	13.477
4100	25.786	139.489	116.041	96.140	- 382.274	12.185
4200	25.788	140.111	116.606	98.719	- 382.540	12.133
4300	25.790	140.718	117.160	101.297	- 382.921	10.948
4400	25.792	141.311	117.702	103.877	- 383.118	10.391
4500	25.794	141.890	118.233	106.456	- 383.429	9.857
4600	25.795	142.457	118.758	109.035	- 383.754	9.386
4700	25.797	143.012	119.284	111.615	- 384.094	8.967
4800	25.799	143.555	119.764	114.195	- 384.446	8.588
4900	25.800	144.087	120.255	116.775	- 384.813	8.248
5000	25.801	144.608	120.737	119.355	- 385.192	7.950
5100	25.802	145.119	121.210	121.935	- 385.583	7.699
5200	25.803	145.620	121.676	124.516	- 385.986	7.483
5300	25.805	146.112	122.131	127.096	- 386.399	7.303
5400	25.806	146.594	122.580	129.676	- 386.826	7.156
5500	25.807	147.068	123.021	132.257	- 387.259	7.043
5600	25.808	147.533	123.455	134.838	- 387.705	6.960
5700	25.809	147.989	123.880	137.419	- 388.161	6.900
5800	25.809	148.438	124.300	139.999	- 388.622	6.850
5900	25.810	148.880	124.713	142.580	- 389.094	6.810
6000	25.811	149.313	125.120	145.161	- 389.574	6.780

Sept. 30, 1961; June 30, 1964; Sept. 30, 1967

TITANIUM TETRAFLUORIDE (TiF₄)

(IDEAL GAS)

GFW = 123.8936

Point Group [T_d]

S_{298.15} = 75.24 ± 0.5 gibbs/mol

Ground State Quantum Weight = [1]

ΔH_f⁰ = -369.9 ± 1 kcal/mol

ΔH_f⁰_{298.15} = -370.6 ± 1 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[701] (1)	[750] (3)
[188] (2)	[178] (3)

Bond Distance: Ti-F = [1.40] Å

Bond Angle: F-Ti-F = [109°28']

Product of the Moments of Inertia: I_AI_BI_C = [2.02 × 10⁻¹¹³] g³ cm⁶ σ = [12]

Heat of Formation

The heat of formation of TiF₄(g) is calculated from that of the crystal and the heat of sublimation, ΔH_{sub}²⁹⁸, obtained from vapor pressure measurements. E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, J. Electrochem. Soc. 105, 275 (1958), have reported extensive vapor pressure data for the reaction TiF₄(c) = TiF₄(g). Second and third law analyses of their data yielded the following results.

Method	No. Pts.	Range, °K	ΔH _f ²⁹⁸ , kcal/mol 2nd Law	ΔH _f ²⁹⁸ , kcal/mol 3rd Law	Drift, eu	ΔH _f ²⁹⁸ *
1. Spoon Gauge	26**	441-552	23.5 ± 0.1	23.37	-0.3 ± 0.1	-370.8
2. Ruff-Fischer	6	435-498	23.0 ± 0.4	23.40	+0.9 ± 0.9	-370.8
3. Transpiration	3	425-512	25.8 ± 2.0	23.72	-4.5 ± 4.3	-370.5
4. Rodabush	6	473-537	23.7 ± 0.6	23.39	-0.5 ± 1.2	-370.8
5. 1, 2, and 4	36***	435-552	23.4 ± 0.1	23.37	-0.1 ± 0.1	-370.8

*Calculation based on third law ΔH_f²⁹⁸.

**Four points rejected due to failure of a statistical test.

***Eight points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The interatomic distance is obtained from a correlation of the measured values for TiCl₄(g), TiBr₄(g), TiCl₃⁻², and TiF₆⁻². The principal moments of inertia are I_A = I_B = I_C = 2.724 × 10⁻³⁸ g cm².

The vibrational frequencies are estimated by a valence force field treatment of estimated force constants. The force constants are estimated from a correlation with the constants of CF₄, SiF₄, COCl₂, CBr₄, SiBr₄, TiCl₄ and TiBr₄. The resulting frequencies are adjusted so that calculations of ΔH_f²⁹⁸ by both second and third law methods are in agreement.

Zirconium Tetrafluoride (ZrF₄)

(Crystal)

GFW = 167.2136

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log K ^p
0	0.000	0.000	INFINITE	4.182	455.441	455.441	INFINITE
100	10.060	5.481	43.591	3.811	456.672	446.744	980.733
200	20.210	15.091	27.166	2.235	457.022	440.614	661.480
298	24.760	23.024	23.024	0.000	456.800	432.595	317.101
300	24.810	25.177	25.024	0.046	456.793	432.445	315.036
400	27.120	32.663	26.029	2.653	456.349	424.391	231.676
500	28.610	38.883	27.996	5.444	455.823	416.443	162.036
600	29.430	44.195	30.244	8.359	455.250	408.484	108.808
700	30.350	48.820	32.591	11.360	454.657	400.922	72.721
800	30.930	52.911	34.881	14.424	454.058	393.288	50.441
900	31.510	56.587	37.092	17.546	453.450	385.728	31.668
1000	32.050	59.936	39.211	20.725	452.830	378.237	12.644
1100	32.560	63.018	41.237	23.955	452.201	370.800	7.673
1200	33.050	65.868	43.172	27.233	451.561	363.416	4.541
1300	33.550	68.533	45.021	30.565	451.581	355.999	59.649
1400	34.060	71.039	46.791	33.946	450.719	348.679	54.431

S_{298,15} = 25.024 ± 0.05 gibbs/mol
Tt(α + β) = 723°K
Tm = 1205 ± 2°K
Ts = 1179°K

ΔH_F⁰ = -455.44 ± 0.25 kcal/mol

ΔH_F⁰ = -456.80 ± 0.25 kcal/mol

ΔH_F⁰ = Unavailable

ΔH_m⁰ = 15.35 ± 0.10 kcal/mol

ΔH_s⁰ = 51.64 kcal/mol

ΔH_F⁰ = 56.80 kcal/mol

Heat of Formation

The heat of formation of zirconium tetrafluoride was measured by direct combination of the elements in a bomb calorimeter by Greenberg, Settle, Feder, and Hubbard (1). The reported value ΔH_F⁰(ZrF₄, c) = -456.80 ± 0.25 kcal/mol is adopted.

Heat Capacity and Entropy

The low temperature heat capacities in the temperature range 5 to 307°K were determined by adiabatic calorimetry by Westrum (2). Using these low temperature Cp data the value of S₂₉₈ is derived as 25.024 ± 0.05 eu, based on S₁₀ = 0.0074 eu.

McDonald, Sinke, and Stull (3) measured the high temperature enthalpies of ZrF₄(c) at temperatures 283.9 - 1275.8°K in a copper block drop calorimeter. Smith, Miller, and Taylor (4) used a Bunsen ice calorimeter for the heat-content measurements in the temperature range 273 - 1150°K. These two sets of enthalpy data are not in good agreement. It is possible that the discrepancies are due to the difference in crystal structure of the samples used (see "Transition Data" for more information). In order to join smoothly with the low temperature heat capacities at 298°K, the high temperature heat capacities derived from the enthalpy data of McDonald, Sinke, and Stull (3) are adopted. The Cp values above 1200°K are obtained by smooth extrapolation.

Transition Data

Zirconium tetrafluoride has three crystal structures (α, β and γ) and one amorphous form (δ). From a differential thermal analysis of (NH₄)₃ZrF₇ sample, Chretien and Gaudreau (5) found that ZrF₄(c) has an α and β form with a transition temperature above 678°K. They also determined the densities of α(tetragonal) and β(monoclinic) as 4.25 ± 0.05 and 4.61 ± 0.03 gm/cc, and a transition temperature as Tt(α + β) = 723°K (7). It was observed that the α phase is unstable at all temperatures above 298°K. In reference (5), Gaudreau mentioned the methods of preparation of the four varieties of ZrF₄ and indicated that α-, γ-, and amorphous ZrF₄ transform irreversibly to β-ZrF₄ at 773 - 773°K.

The ZrF₄ sample employed by McDonald, Sinke, and Stull (3) for enthalpy measurement was prepared by dissolving hafnium-free zirconium metal in 48% aqueous HF, and the resulting solution was evaporated to dryness. The crystalline product was heated slowly to 773°K in a platinum boat in a slow current of anhydrous HF. X-ray diffraction showed only crystalline ZrF₄. Wet analysis indicated 54.61 Zr (theory 54.55) and 44.91 F (theory 45.45). Due to the above facts we are uncertain whether the sample prepared is a mixture of α and β forms or a pure ZrF₄(β). Smith, Miller, and Taylor (4) obtained their ZrF₄ sample from the Oak Ridge National Laboratories, Oak Ridge, Tenn. Since the method of preparation of the compound is unavailable from the report, we do not know what kind of sample they used for measurement.

Because of the above complicated situation, we emphasize that this ZrF₄(c) table is not strictly a α, β-combined phase table. However, the differences in the calculated functions are probably not significant.

Melting Data

Tm and ΔH_m⁰ are taken from McDonald, Sinke, and Stull (3). The values were obtained under conditions greater than one atmosphere.

Sublimation Data

The sublimation temperature (Ts) is calculated as the temperature at which the Gibbs energy change of the process ZrF₄(c) = ZrF₄(g) approaches zero. The difference between ΔH_F⁰(g) and ZrF₄(c) at 1179 and 298°K is ΔH_s⁰ and ΔH_F⁰, respectively.

Since the sublimation temperature is lower than the melting point, the ZrF₄ sublimates before it melts.

References

1. E. Greenberg, J. L. Settle, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. **65**, 1168 (1961).
2. E. F. Westrum, Jr., J. Chem. Eng. Data **10**, 140 (1965).
3. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data **7**, 83 (1962).
4. D. F. Smith, W. C. Miller, and A. R. Taylor, Jr., U. S. Bur. Mines RI 5964, 1962.
5. B. Gaudreau, Rev. Chim. Minerale **2** (1), 1 (1965); Chem. Abstr. **63**:17245d.
6. A. Chretien and B. Gaudreau, Compt. Rend. **246**, 2266 (1958).
7. A. Chretien and B. Gaudreau, Compt. Rend. **248**, 2878 (1959).

Zirconium Tetrafluoride (ZrF₄)

(Ideal Gas) GFN = 167.2136

Point Group Td

 $\Delta H_F^\circ = -399.0 \pm 1.0$ kcal/mol $S_{298.15}^\circ = [76.3 \pm 1]$ gibbs/mol $\Delta H_F^\circ = -400.0 \pm 1.0$ kcal/mol

Ground State Quantum Weight = 1

T, °K	C _p ^o	S ^o	-(C _p ^o - H _{298.15})/T	H ^o - H _{298.15}	kcal/mol	ΔH ^o	ΔG ^o	Log Kp
0	.0000	INFINITE		-4.527	-399.986			INFINITE
100	13.653	92.910		-3.535	-396.678			867.375
200	18.119	86.546		-1.925	-399.912			300.559
298	20.887	76.339		-1.000	-400.000			206.660
300	20.927	76.468		-0.919	-400.000			204.872
400	22.603	82.740		-2.223	-399.979			212.022
500	23.593	87.899		-4.537	-399.930			168.316
600	24.205	92.959		-6.929	-399.860			130.187
700	24.573	97.026		-9.326	-399.763			102.773
800	24.873	100.326		-11.865	-399.637			80.636
900	25.065	102.267		-14.343	-399.483			60.626
1000	25.205	103.916		-16.856	-399.309			43.321
1100	25.310	105.293		-19.392	-399.116			29.989
1200	25.385	106.458		-21.949	-398.906			19.811
1300	25.435	107.454		-24.529	-398.681			12.631
1400	25.504	108.316		-27.008	-398.447			7.591
1500	25.588	109.066		-29.561	-398.208			4.745
1600	25.662	109.744		-32.111	-397.963			2.895
1700	25.717	110.366		-34.649	-397.713			1.615
1800	25.758	110.940		-37.179	-397.458			0.845
1900	25.789	111.474		-39.698	-397.200			0.445
2000	25.812	111.974		-42.210	-396.938			0.245
2100	25.828	123.636		-44.717	-396.673			0.135
2200	25.838	125.174		-47.217	-396.404			0.075
2300	25.710	126.174		-49.708	-396.132			0.045
2400	25.720	127.264		-52.191	-395.857			0.028
2500	25.729	128.318		-54.669	-395.579			0.017
2600	25.717	129.327		-57.139	-395.298			0.009
2700	25.686	130.295		-59.600	-395.014			0.005
2800	25.750	131.215		-62.054	-394.727			0.003
2900	25.756	132.139		-64.509	-394.437			0.002
3000	25.761	133.012		-66.965	-394.143			0.001
3100	25.765	133.857		-69.417	-393.845			0.000
3200	25.773	134.668		-71.865	-393.543			0.000
3300	25.777	135.443		-74.309	-393.237			0.000
3400	25.777	136.237		-76.749	-392.927			0.000
3500	25.780	136.985		-79.187	-392.613			0.000
3600	25.783	137.711		-81.622	-392.295			0.000
3700	25.788	138.405		-84.054	-391.973			0.000
3800	25.790	139.075		-86.483	-391.647			0.000
3900	25.790	139.775		-88.910	-391.317			0.000
4000	25.792	140.428		-91.336	-390.982			0.000
4100	25.794	141.065		-93.761	-390.643			0.000
4200	25.798	141.688		-96.187	-390.299			0.000
4300	25.798	142.294		-98.610	-389.951			0.000
4400	25.799	142.887		-101.030	-389.599			0.000
4500	25.801	143.466		-103.447	-389.243			0.000
4600	25.802	144.034		-105.861	-388.883			0.000
4700	25.803	144.593		-108.272	-388.519			0.000
4800	25.805	145.132		-110.680	-388.151			0.000
4900	25.806	145.664		-113.084	-387.779			0.000
5000	25.807	146.185		-115.487	-387.403			0.000
5100	25.808	146.696		-117.889	-387.023			0.000
5200	25.810	147.199		-120.289	-386.639			0.000
5300	25.811	147.699		-122.688	-386.251			0.000
5400	25.811	148.171		-125.084	-385.859			0.000
5500	25.812	148.645		-127.479	-385.463			0.000
5600	25.812	149.110		-129.874	-385.063			0.000
5700	25.812	149.566		-132.268	-384.659			0.000
5800	25.814	150.016		-134.661	-384.251			0.000
5900	25.814	150.457		-137.051	-383.839			0.000
6000	25.815	150.891		-139.443	-383.423			0.000

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; June 30, 1969

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[630] (1)	668 (3)
[180] (2)	190 (3)

Bond Distance: Zr-F = 1.94 ± 0.02 Å

Bond Angle: F-Zr-F = 109.47°

Product of the Moments of Inertia: $I_A I_B I_C = 3.17347 \times 10^{-113} \text{ g cm}^6$

Heat of Formation

The vapor pressures of ZrF₄(c) in the temperature range 617-1150°K were determined by many investigators using various methods. Based on the reported vapor pressure data, the corresponding heats of sublimation are evaluated by the second and third law methods. Using the third law ΔH_{298}° and $\Delta H_{298}^\circ(\text{ZrF}_4, \text{c}) = -456.8$ kcal/mol, the heats of formation at 298°K for ZrF₄(g) are evaluated. The results are presented in the table below. The values of $\Delta H_{298}^\circ(\text{ZrF}_4, \text{g})$ listed in the last column of this table are in excellent agreement which indicate that the estimated missing vibrational frequencies ν_1 and ν_2 are reasonable. The heat of formation at 298°K for ZrF₄(g) is adopted as -400.0 kcal/mol.

Investigator	Method	Temperature, °K	No. of Points	ΔH_{298}° , kcal/mol	Drift, kcal/mol
1. Lauter (1948)	unavailable	950-1150	Equn.	56.49±0.12	56.83
2. Sense et al. (1954)	transpiration	617-881	14	60.67±0.09	57.13
3. Sense et al. (1957)	transpiration	900-1150	6	60.64±0.13	57.24
4. Cantor (1958)	quasistatic	710-808	29	56.11±0.62	56.65
5. Hildenbrand-Theard (1961)	torsion-effusion	748-849	15	55.81±1.44	57.05
6. Hildenbrand-Theard (1961)	torsion-effusion	735-825	10	52.59±0.39	57.09
7. Galkin et al. (1963)	Knudsen-effusion	720-850	5	51.53±0.06	54.79
8. Akishin et al. (1963)	mass spectrometry	700-900	5	59.25±2.34	57.30
9. Fischer et al. (1964)	"bell method"	1000-1150	Equn.	57.38±0.12	56.89
10. Sidorov et al. (1965)	mass spectrometry	769	1	—	57.58

Heat Capacity and Entropy

The molecular structure of ZrF₄(g) has been studied by electron diffraction by Spiridonov (11). The configuration was found to be a regular tetrahedron with interatomic distance Zr-F = 1.94 ± 0.02 Å and F-Zr-F bond angle = 109.47° which are adopted. Employing the estimated interaction coefficients and interatomic distance Zr-F = 1.85 Å, Godnev, Aleksandrovskaia, and Rigina (12) calculated three vibrational frequencies for ZrF₄(g) as $\nu_1 = 600$, $\nu_2 = 150$, and $\nu_3 = 180 \pm 230 \text{ cm}^{-1}$. Buchler, Berkowitz, and Dugre (13) observed the infrared spectra of some group IV halides and assigned $\nu_3 = 668$ and $\nu_4 = 190 \pm 20 \text{ cm}^{-1}$ for ZrF₄(g). The frequency ν_3 has also been reported as 670 cm^{-1} (14). The values of ν_3 and ν_4 adopted here are those reported by Buchler, Berkowitz, and Dugre (13). The adopted ν_1 is obtained by correlating the corresponding frequencies of the tetrafluorides of C, Pb, Si, Ti and Ge with their respective interatomic distances. ν_2 is calculated from ν_1 , ν_3 and ν_4 using the relationship $(12) \nu_1 \nu_2 = \sqrt{2(1-\frac{1}{4})}$, where F and Zr are gram atomic weights of fluorine and zirconium, respectively. The three principal moments of inertia are $I_A = I_B = I_C = 3.166 \times 10^{-38} \text{ g cm}^2$.

References

1. S. Lauter, Dissertation Technische Hochschule Hannover, 1948. (Cited in reference 9)
2. K. A. Sense, M. Snyder, and R. B. Filbert, Jr., J. Phys. Chem. **58**, 995 (1954).
3. K. A. Sense, C. A. Alexander, R. E. Bowman, and R. B. Filbert, Jr., J. Phys. Chem. **61**, 337 (1957).
4. S. Cantor, R. F. Newton, W. R. Glines, and F. Blankenship, J. Phys. Chem. **62**, 96 (1958).
5. D. L. Hildenbrand and L. P. Theard, Aeronautics, U-1187, Ford Motor Company, 15 Mar. 1961.
6. D. L. Hildenbrand and L. P. Theard, Aeronautics, U-1274, Ford Motor Company, 15 June 1961.
7. N. P. Galkin, Y. N. Tumanov, V. I. Tarasov, and Y. D. Shishov, Russ. J. Inorg. Chem. (English Transl.) **8**, 1054 (1963).
8. P. A. Akishin, V. I. Belousov, and L. N. Sidorov, Russ. J. Inorg. Chem. (English Transl.) **8**, 1520 (1963).
9. W. Fischer, T. Petzel, and S. Lauter, Z. Anorg. Allgem. Chem. **333**, 226 (1964).
10. L. N. Sidorov, P. A. Akishin, V. B. Shol'ts, and Y. M. Kornev, Russ. J. Phys. Chem. (English Transl.) **35**, 1146 (1965).
11. V. P. Spiridonov, Vestn. Mosk. Univ. Ser. II, Khim. **23**, No. 1, 113 (1968).
12. I. N. Godnev, A. M. Aleksandrovskaia, and I. V. Rigina, Opt. Spectry, USSR (English Transl.) **7**, 172 (1959).
13. A. Buchler, J. B. Berkowitz-Matuck, and D. H. Dugre, J. Chem. Phys. **34**, 2202 (1961).
14. M. Blander and H. W. Morgan, presented at the 138th Meeting, American Chemical Society, New York, September 1960.
15. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945, p. 182.

IODINE PENTAFLUORIDE (IF₅)

(IDEAL GAS)

GFN = 221.8964

Iodine Pentafluoride (IF₅)(Ideal Gas) GF₅ = 221.8964Point Group C_{4v}S_{298.15} = 79.96 ± 0.5 gibbs/mol

Ground State Quantum Weight = 11

ΔHf° = -136.6 ± 0.4 kcal/mol

ΔHf°_{298.15} = -200.84 ± 0.35 kcal/mol

Bond Distance: I-F(axial) = (1.86) Å

Bond Angle: F-I-F = (90°)

Product of the Moments of Inertia: I_AI_BI_C = (4.10383 × 10⁻¹¹³) g³ cm⁶

Heat of Formation

The adopted value is derived from calorimetric data of Settle et al. (2) for the combustion of iodine in fluorine. Although

the combustions gave various mixtures of IF₃ and IF₅, the proportions ranged up to almost pure pentafluoride. Reduction of thedata gave ΔHf° = -210.80 ± 0.32 kcal/mol for IF₅(g) at 298.15 K. The result is essentially independent of the heptafluoride.

Comparison values of -208.9 ± [21] and -208.6 ± [21.7] kcal/mol may be obtained from calorimetric data of Woolf (2) for

hydrolysis in water and in aqueous KOH. Uncertainties for these values include large contributions due to auxiliary data (3).

In particular, we estimate lower limits of ±0.8 kcal/mol for ΔHf° of HIO₃(1250 H₂O) and KIO₃(1250 H₂O) by comparison with recent

data (4).

ΔHf° for the ideal gas is derived from that of the liquid by use of ΔHv° = 9.96 kcal/mol at 298.15 K. ΔHv° was derived by

Osborne et al. (5) from measurements of vapor pressure and the second virial coefficient.

Heat Capacity and Entropy

There is no published structural determination for gaseous IF₅, but spectral data are consistent with C_{4v} symmetry and

a configuration which is approximately a square pyramid. It is uncertain whether the iodine is located above, in, or

below the base of the pyramid and whether or not the axial and equatorial I-F distances are equal. We adopt the structure

used by Begun et al. (2) in correlation of infrared and Raman spectra of BrF₅, IF₅, ClF₅, and XeOF₄ by normal coordinate

analysis. In this structure the axial bond length is shorter than the equatorial length and the values are close to those

observed experimentally for IF₇. The iodine is presumed to be in the base of the pyramid. Simplified Hückel-molecular-orbital calculations (6) predict that C_{4v} is the most stable symmetry, that the axial bond is shorter, and that the

equatorial fluorines are distorted toward the axial fluorine. It is not clear to what extent these predictions depend on the

simplified HMO model used in the calculations. Begun et al. (2) note that the normal coordinate calculations are insensitive

to changes in the bond angles. Principal moments are I_A = I_B = 10.66 × 10⁻³⁹ and I_C = 43.65 × 10⁻³⁹ g cm².

Vibrational frequencies are based on the assignments of Begun et al. (2) as modified by the vapor-phase Raman spectra

observed by Salig (8). Location of the band center of ν₃ (>200 cm⁻¹) is difficult, so we substitute the liquid value of190 cm⁻¹. The Raman-active fundamental ν₃ is not observed for IF₅, or any of the similar molecules, so its value is taken

from the calculations (2).

Osborne et al. (5) used calorimetric data at low temperatures to derive S° = 57.86 ± 0.06 gibbs/mol for the liquid at

330 K. Combining this with ΔS° based on their vapor pressure equation, the authors obtained S° = 83.06 ± 0.70 gibbs/mol for

the ideal gas at 330 K. The corresponding value from this table (82.50) is lower by 0.56 gibbs/mol. Part of this difference

arises from uncertainties in ν₃, ν₉, and the product of the moments of inertia. We estimate this uncertainty at about

0.5 gibbs/mol. Another source of minor uncertainty is the neglect of anharmonicity in the calculations.

References

1. J. L. Settle, J. H. E. Jeffes, P. A. G. O'Hare and W. N. Hubbard, presented at the 23rd Annual Calorimetry Conference,

Midland, Mich., August, 1968.

2. A. A. Woolf, J. Chem. Soc. 1951, 231 (1951).

3. ΔHf° values for H₂O(l), HIO₃(1250 H₂O) and KIO₃(1250 H₂O) are derived from U. S. Natl. Bur. Std. Tech. Note 270-3, 1968,

in combination with V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965.

4. P. B. Howard and H. A. Skinner, J. Chem. Soc. A1967, 269 (1967); C. Wu, M. M. Birky and L. G. Hepler, J. Phys. Chem. 67,

1202 (1963).

5. D. W. Osborne, F. Schreiner, H. Selig, to be published.

6. H. Selig and H. Holzman, Israel J. Chem. 2, 417 (1968).

7. G. H. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42, 2236 (1965).

8. R. M. Gavin, J. Chem. Educ. 46, 413 (1969).

T, °K	C _p ^o	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔHf°	ΔGf°	Log Kp
0	-0.000	-0.000	INF INITE	-	198.780	198.780	198.780	INF INITE
100	12.552	59.852	98.521	3.867	198.957	195.039	426.258	207.400
200	20.063	71.020	92.081	2.212	200.641	189.804	135.191	135.191
298	24.156	79.959	94.959	0.066	200.841	184.329	134.284	134.284
300	24.651	80.111	95.061	2.650	202.748	178.755	97.667	97.667
400	27.188	87.586	82.928	5.447	207.730	172.290	75.308	75.308
500	28.635	93.822	80.961	8.358	207.367	165.037	60.188	60.188
600	29.512	98.127	85.197	11.339	206.943	158.250	49.408	49.408
700	30.076	103.721	87.522	14.367	206.531	151.323	41.340	41.340
800	30.457	107.764	89.805	17.427	206.113	144.447	35.077	35.077
900	30.726	111.367	92.004	20.510	205.695	137.618	30.076	30.076
1000	30.922	114.615	94.105	23.610	205.279	130.832	25.904	25.904
1100	31.049	117.570	96.106	26.723	204.863	124.080	22.598	22.598
1200	31.182	120.278	98.009	29.845	204.452	117.364	19.731	19.731
1300	31.271	122.778	99.820	32.976	204.045	110.681	17.278	17.278
1400	31.342	125.068	101.543	36.113	203.642	104.025	15.156	15.156
1500	31.399	127.162	103.187	39.254	203.248	97.398	13.304	13.304
1600	31.446	129.000	104.755	42.402	202.850	90.793	11.672	11.672
1700	31.486	130.518	106.255	45.553	202.463	84.217	10.228	10.228
1800	31.519	132.099	107.691	48.706	202.080	77.656	8.932	8.932
1900	31.547	134.703	109.069	51.862	201.701	71.115	7.771	7.771
2000	31.571	136.322	110.391	55.020	201.329	64.599	6.723	6.723
2100	31.591	137.943	111.643	58.180	200.963	58.097	5.774	5.774
2200	31.609	139.333	112.888	61.342	200.600	51.609	4.904	4.904
2300	31.625	140.739	114.068	64.505	200.245	45.139	4.110	4.110
2400	31.639	142.085	115.208	67.669	199.896	38.685	3.382	3.382
2500	31.651	143.377	116.300	70.835	199.552	32.242	2.710	2.710
2600	31.662	144.618	117.374	74.002	199.213	26.481	2.099	2.099
2700	31.671	145.813	118.405	77.169	198.878	21.197	1.514	1.514
2800	31.678	146.957	119.405	80.338	198.551	16.289	0.979	0.979
2900	31.684	148.077	120.374	83.507	198.231	11.804	0.481	0.481
3000	31.695	149.151	121.316	86.674	197.914	7.820	0.016	0.016
3100	31.701	150.191	122.231	89.847	197.604	4.153	-	-
3200	31.707	151.197	123.120	93.018	197.300	12.516	-	-
3300	31.712	152.173	123.986	96.189	197.000	18.870	-	-
3400	31.717	153.120	124.829	99.361	196.708	25.220	-	-
3500	31.721	154.039	125.650	102.533	196.420	31.584	-	-
3600	31.725	154.933	126.451	105.706	196.138	37.984	-	-
3700	31.729	155.802	127.233	108.879	195.862	44.209	-	-
3800	31.732	156.648	127.996	112.053	195.594	50.516	-	-
3900	31.735	157.473	128.741	115.226	195.329	56.826	-	-
4000	31.738	158.276	129.470	118.400	195.072	63.126	-	-
4100	31.741	159.060	130.182	121.574	194.820	69.421	-	-
4200	31.744	159.825	130.879	124.749	194.571	75.713	-	-
4300	31.746	160.572	131.560	127.924	194.333	81.993	-	-
4400	31.748	161.302	132.228	131.098	194.098	88.268	-	-
4500	31.750	162.015	132.862	134.274	193.867	94.541	-	-
4600	31.752	162.713	133.523	137.449	193.645	100.808	-	-
4700	31.754	163.396	134.151	140.624	193.426	107.076	-	-
4800	31.755	164.064	134.768	143.800	193.213	113.335	-	-
4900	31.757	164.719	135.372	146.976	193.010	119.586	-	-
5000	31.759	165.361	135.966	150.152	192.807	125.827	-	-
5100	31.760	165.990	136.548	153.328	192.615	132.083	-	-
5200	31.761	166.607	137.120	156.504	192.426	138.329	-	-
5300	31.762	167.212	137.682	159.680	192.245	144.557	-	-
5400	31.763	167.805	138.235	162.857	192.067	150.797	-	-
5500	31.765	168.388	138.778	166.033	191.898	157.030	-	-
5600	31.766	168.954	139.312	169.210	191.734	163.261	-	-
5700	31.767	169.523	139.837	172.387	191.572	169.486	-	-
5800	31.768	170.075	140.353	175.563	191.419	175.704	-	-
5900	31.769	170.618	140.862	178.740	191.272	181.927	-	-
6000	31.770	171.152	141.362	181.927	191.127	188.150	-	-

Mar. 31, 1962; Dec. 31, 1963; Mar. 31, 1965; Dec. 31, 1969

Point Group D_{3h} $\Delta H_f^\circ = -374.7 \pm 0.7$ kcal/mol $\Delta H_f^\circ = -376.9 \pm 0.7$ kcal/mol $S_{298.15}^\circ = 71.87 \pm 0.5$ gibbs/mol

Ground State Quantum Weight = 11

Phosphorus Pentafluoride (PF₅)(Ideal Gas) GF_W = 125.966

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K ^e
0	0.000	INFINITE	-	374.713	- 374.713	- 374.713	INFINITE
100	10.539	55.939	46.608	3.067	- 375.658	- 370.920	510.665
200	21.476	71.066	71.066	1.000	- 376.000	- 360.591	264.321
298	22.278	71.866	71.866	1.000	- 376.000	- 360.591	264.321
300	20.352	71.094	71.094	1.038	- 376.906	- 360.491	262.617
400	23.718	78.342	72.711	2.252	- 377.150	- 354.975	193.949
500	25.941	83.891	78.405	4.743	- 377.256	- 349.450	152.731
600	27.416	86.760	76.400	7.416	- 377.256	- 343.052	125.240
700	28.421	93.066	78.479	10.211	- 377.221	- 336.287	105.610
800	29.128	96.910	80.547	13.000	- 377.590	- 330.081	92.388
900	29.640	100.372	82.561	16.030	- 377.276	- 330.614	80.284
1000	30.021	103.515	84.562	19.014	- 376.944	- 323.227	70.841
1100	30.310	106.391	86.363	22.031	- 376.598	- 315.072	62.750
1200	30.536	109.038	88.143	25.074	- 376.240	- 306.568	56.194
1300	30.714	111.490	89.846	28.137	- 375.879	- 297.924	50.645
1400	30.857	113.771	91.475	31.215	- 375.513	- 289.099	45.894
1500	30.974	115.904	93.033	34.307	- 375.144	- 280.747	41.779
1600	31.071	117.907	94.526	37.410	- 374.774	- 272.536	38.183
1700	31.151	119.793	95.957	40.521	- 374.404	- 264.342	35.012
1800	31.219	121.575	97.331	43.639	- 374.043	- 256.177	32.197
1900	31.277	123.265	98.652	46.764	- 373.677	- 248.095	29.600
2000	31.327	124.870	99.923	49.895	- 373.314	- 240.894	27.416
2100	31.369	126.400	101.148	53.029	- 372.954	- 233.785	25.371
2200	31.407	127.860	102.329	56.168	- 372.599	- 226.689	23.513
2300	31.439	129.257	103.470	59.311	- 372.245	- 219.609	21.810
2400	31.468	130.596	104.572	62.456	- 371.897	- 212.548	20.264
2500	31.493	131.881	105.639	65.604	- 371.552	- 205.497	18.839
2600	31.516	133.116	106.672	68.754	- 371.212	- 198.443	17.523
2700	31.536	134.306	107.674	71.907	- 370.875	- 191.438	16.305
2800	31.554	135.453	108.646	75.061	- 370.541	- 184.430	15.176
2900	31.570	136.561	109.589	78.218	- 370.213	- 177.427	14.125
3000	31.584	137.631	110.509	81.375	- 369.892	- 170.448	13.146
3100	31.598	138.667	111.398	84.534	- 369.572	- 163.469	12.230
3200	31.610	139.671	112.246	87.695	- 369.259	- 156.504	11.372
3300	31.621	140.643	113.111	90.856	- 368.949	- 149.547	10.566
3400	31.631	141.588	113.935	94.019	- 368.645	- 142.600	9.809
3500	31.640	142.505	114.738	97.183	- 368.344	- 135.656	9.095
3600	31.648	143.396	115.522	100.347	- 368.050	- 128.727	8.422
3700	31.656	144.263	116.287	103.512	- 367.761	- 121.807	7.785
3800	31.663	145.108	117.034	106.678	- 367.476	- 114.888	7.183
3900	31.670	145.930	117.765	109.845	- 367.199	- 107.984	6.612
4000	31.676	146.732	118.479	113.012	- 366.923	- 101.087	6.070
4100	31.682	147.518	119.178	116.180	- 366.655	- 94.197	5.554
4200	31.687	148.278	119.861	119.344	- 366.392	- 87.307	5.063
4300	31.692	149.023	120.511	122.517	- 366.131	- 80.426	4.596
4400	31.696	149.752	121.147	125.687	- 365.880	- 73.552	4.150
4500	31.701	150.464	121.830	128.857	- 365.631	- 66.687	3.724
4600	31.705	151.161	122.460	132.027	- 365.387	- 59.827	3.318
4700	31.709	151.843	123.078	135.198	- 365.150	- 52.968	2.928
4800	31.712	152.511	123.684	138.369	- 364.916	- 46.110	2.555
4900	31.715	153.165	124.279	141.540	- 364.689	- 39.240	2.197
5000	31.719	153.805	124.863	144.712	- 364.467	- 32.419	1.854
5100	31.722	154.434	125.437	147.884	- 364.251	- 25.590	1.525
5200	31.724	155.058	126.000	151.056	- 364.039	- 18.747	1.208
5300	31.727	155.654	126.554	154.229	- 363.832	- 11.913	0.904
5400	31.729	156.247	127.098	157.401	- 363.633	- 5.099	0.611
5500	31.732	156.829	127.634	160.574	- 363.434	- 1.268	0.329
5600	31.734	157.401	128.160	163.748	- 363.247	- 1.487	0.056
5700	31.736	157.963	128.678	166.921	- 363.061	- 5.371	- 0.204
5800	31.738	158.515	129.146	170.095	- 362.882	- 12.142	- 0.459
5900	31.740	159.057	129.600	173.269	- 362.707	- 18.985	- 0.703
6000	31.742	159.591	130.143	176.443	- 362.539	- 25.794	- 0.940

June 30, 1963; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
817 (1)	1025 (2)	
840 (1)	532.5 (2)	
946.6 (1)	179 (2)	
575.1 (1)	514 (2)	

Bond Distance: (P-F)_{eq} = 1.534 ± 0.004 Å (P-F)_{ax} = 1.577 ± 0.005 Å

Bond Angle: F_{eq}-P-F_{eq} = 120° ± 0.4° F_{eq}-P-F_{ax} = 74.3° ± 0.4°

Product of Moments of Inertia: I_AI_BI_C = 1.614 × 10⁻¹¹³ g³ cm⁶

Heat of Formation

Gross, Hayman, and Stuart (1) measured the heat of combustion of α-white phosphorus in fluorine at 25°C. They reported a heat of formation of -381.4 ± 0.8 kcal/mol (based on α-white phosphorus standard state) calculated from their combustion studies. Similar combustion studies were performed by O'Hare and Hubbard (2). They reported a heat of formation of -380.8 ± 0.3 kcal/mol (α-white phosphorus standard state), which is in excellent agreement with the work of Gross et al. (1). An average value of -381.1 ± 0.5 kcal/mol is adopted for this tabulation. Converting to the P(red, V) standard state with a ΔH trans = 4.2 ± 0.2 kcal/mol (3), we derive, ΔH_f²⁹⁸(PF₅, g) = -376.9 ± 0.7 kcal/mol.

Heat Capacity and Entropy

The molecular structure and bond lengths given above for PF₅ were recently determined by Hansen and Bartell (4) from electron-diffraction studies. These results indicate that PF₅ has a trigonal bipyramidal structure with nonequivalent axial and equatorial bonds. Wyatt et al. (5) determined rotational constants for PF₅ from a study of the infrared vibration-rotation band contour of the ν₄ (575 cm⁻¹) fundamental. Their analysis led to the following P-F bond lengths which are in excellent agreement with the electron-diffraction results: r_{ax} = 1.534 ± 0.024 Å and r_{eq} = 1.581 ± 0.025 Å. Individual moments of inertia, calculated from the rotational constants given by Wyatt et al. (5) and adopted for this table, are I_A = 2.230 × 10⁻³⁸ g cm² and I_B = I_C = 2.690 × 10⁻³⁸ g cm². The electron diffraction data lead to a product of moments of inertia of 1.604 × 10⁻¹¹³ g³ cm⁶.

Several recent infrared and Raman studies (6, 7, and 8) have been reported for PF₅. These data are in good agreement except for the ν₇ fundamental. Griffiths et al. (6) originally assigned this fundamental to the 126 cm⁻¹ band observed in their infrared spectra. Hoskins (7) later attributed this band to one of the pure rotational lines of hydrogen fluoride, which he felt was present in the sample as an impurity. Further work by Griffiths (10) on the pressure dependence of the infrared spectra of PF₅ indicated that the missing fundamental should be assigned to the weak band at 301 cm⁻¹. Deiters and Holmes (11) recently showed that this band is not a fundamental of PF₅ but a difference band (ν₃-ν₂). Very recently, Levin (8) investigated the Raman spectra of solid phosphorus pentafluoride and assigned the ν₇ fundamental to the 179 cm⁻¹ band. Also, Beattie et al. (12) investigated the Raman spectra of PF₅ in the gas phase at 25°C and 125°C and assigned the ν₇ fundamental to 175 cm⁻¹ band which is in excellent agreement with Levin's assignment (8). The fundamental vibrational frequencies of Holmes and Lord (7) are adopted along with Levin's assignment (8) of the ν₇ fundamental (179 cm⁻¹).

References

1. P. Gross, C. Hayman, and M. C. Stuart, *Trans. Faraday Soc.*, **52**, 2715 (1956).
2. P. A. G. O'Hare and W. N. Hubbard, *Trans. Faraday Soc.*, **52**, 2709 (1956).
3. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Mich., June 30, 1961.
4. K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **5**, 1775 (1965).
5. R. Wyatt, J. T. Roberts, R. E. Wentz, and R. M. Wilt, *J. Chem. Phys.*, **50**, 2552 (1969).
6. J. E. Griffiths, R. P. Carter, and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964).
7. L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, **46**, 2402 (1967).
8. I. W. Levin, *J. Chem. Phys.*, **50**, 1031 (1969).
9. L. C. Hoskins, *J. Chem. Phys.*, **42**, 2631 (1965).
10. J. E. Griffiths, *J. Chem. Phys.*, **42**, 2632 (1965).
11. R. M. Deiters and R. R. Holmes, *J. Chem. Phys.*, **48**, 4796 (1968).
12. I. R. Beattie, K. M. S. Livingston, and D. J. Reynolds, *J. Chem. Phys.*, **51**, 4269 (1969).

Molybdenum Hexafluoride (MoF₆)

(Liquid)

GFW = 209.930

T, °K	C _p ^a	S ^b	-(G° - H° ₂₉₈)/T	kcal/mol ΔH ^c	ΔG ^d	Log K _p
0						
100	36.502	66.733	62.648	-378.180	-361.269	394.776
200	40.582	62.068	62.068	-379.060	-352.214	256.160
298						
300	40.659	62.318	62.069	-379.056	-352.048	256.487
400	44.744	60.186	60.186	-379.032	-334.816	167.349
500	48.974	60.033	60.033	-376.032	-334.816	146.749
600	53.131	94.329	70.756	-374.053	-326.755	119.021
700	57.289	102.632	74.739	-371.728	-319.050	99.612
800	61.446	110.753	78.751	-369.042	-311.707	85.154
900	65.603	118.750	82.763	-365.945	-304.160	73.476
1000	69.761	125.358	86.775	-362.528	-296.095	65.149

MOLYBDENUM HEXAFLUORIDE (MoF₆)

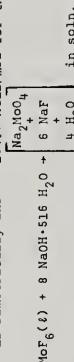
(LIQUID)

GFW = 209.930

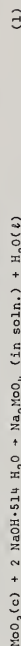
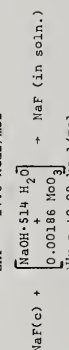
S°_{298.15} = 62.07 ± 0.06 gibbs/molΔH_f^o_{298.15} = -379.080 ± 0.3 kcal/molT_m = 290.76°KΔH_m^o = 1.034 ± 0.001 kcal/molT_b = 307.04°K (l + real gas, P = 1 atm, f = 0.966 atm)ΔH_v^o = 6.512 ± 0.04 kcal/molT_b = 308.0°K (l + ideal gas, P = f = 1 atm)ΔH_v^o = 6.562 kcal/mol

Heat of Formation

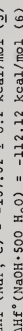
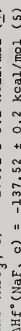
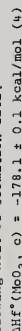
The adopted heat of formation, ΔH_f^o(MoF₆, l) = -379.080 ± 0.3 kcal/mol, is calculated from the heat of formation of the gas, ΔH_f^o(MoF₆, g) = -372.4 ± 0.2 kcal/mol (1), and the heat of vaporization, ΔH_v^o = 6.680 ± 0.03 kcal/mol at 298.15°K. The value for the heat of vaporization is obtained from a third law analysis of the vapor pressure data reported by Osborne et al. (2). Myers and Brady (3) determined calorimetrically ΔH_r = -154.7 kcal/mol for the hydrolysis reaction:



Heats of formation of Na₂MoO₄ and NaF in the final solution were determined from the following two auxiliary heat of reaction measurements:

ΔH_r = -17.6 kcal/molΔH_r = +0.09 Kcal/mol

Combining these results with the following heat of formation data:



we derive ΔH_f(Na₂MoO₄, in soln.) = -351.6 kcal/mol and ΔH_f(NaF, in soln.) = -137.4 kcal/mol. These data, when combined with the results for the hydrolysis of MoF₆, lead to ΔH_f^o(MoF₆, l) = -379.6 kcal/mol. This result is not in agreement with the adopted value.

Heat Capacity and Entropy

The heat capacity measurements for liquid MoF₆ by Osborne et al. (2) are adopted. Outside the observed range C_p was extrapolated linearly with temperature. S°_{298.15} is evaluated from the thermal data of Osborne et al. (2) and the third law of thermodynamics. They reported heat capacity data in the range 5°-350°K with S°₀K = 0.024 gibbs/mol.

Melting Data

Melting point and heat of melting data for MoF₆ have been reported by several investigators. These results are summarized below.

Investigator	Method	Melting Point, °K	ΔH _m ^o , kcal/mol
Osborne et al. (2)	Calorimetric	290.76 ± 0.02	1.034 ± 0.001
Brady et al. (2)	Calorimetric	290.7	1.059 ± 0.010
Cady and Hargreaves (8)	Vapor Pressure	290.55	1.00 ± 0.03*
Ruff and Ascher (9)	Vapor Pressure	290.65	1.31 ± 0.2*

* This value is the difference between the 2nd law heat of sublimation corrected for ΔC_p of the process and the adopted heat of vaporization calculated at 290.76°K with (H°_{290.76}H°_{298.15}) for the vapor and liquid.

The value ΔH_m^o_{290.76} = 1.034 ± 0.001 kcal/mol from Osborne et al. (2) is adopted.

Vaporization Data

Second and third law analyses of various sets of vapor pressure data (2, 8, 9) are summarized below. Corrections for nonideality of the vapor have been calculated from the second virial coefficient equation reported by Osborne et al. (2).

Investigator	Temp. Range, °K	No. of Points	Boiling Point, °K	ΔH _v ^o ₂₉₈ , kcal/mol
Osborne et al. (2)	291.15 - 320.15	21	307.04	6.690
Cady and Hargreaves (8)	290.55 - 307.15	Equation	307.15	6.74
Ruff and Ascher (9)	290.65 - 294.85	4	308.15	5.99

* With ΔC_p = -11.77 gibbs/mol

The value ΔH_v^o₂₉₈ = 6.680 ± 0.03 (ΔH_v^o_{307.04} = 6.512 ± 0.04) kcal/mol, determined from the vapor pressure data of Osborne et al. (2), is adopted in the tabulation. The temperature at which ΔG_v^o = 0 is 308.0°K and the corresponding ΔH_v^o = 6.562 kcal/mol.

References

1. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, June 30, 1970.
2. D. W. Osborne, F. Schreiner, J. G. Malm, H. Sellig, and L. Rochester, J. Chem. Phys., **44**, 2802 (1966).
3. O. E. Myers and A. P. Brady, J. Phys. Chem., **55**, 591 (1960).
4. Ref. 1, December 31, 1968.
5. U. S. Natl. Bur. Std. Circ. 500, 1952.
6. A. P. Brady, O. E. Myers, and J. K. Claus, J. Phys. Chem., **64**, 586 (1960).
7. G. H. Cady and G. B. Hargreaves, J. Chem. Soc., 1563 (1961).
8. O. Ruff and E. Ascher, Z. Anorg. Allgem. Chem., **195**, 413 (1931).

June 30, 1970

Point Group O_h

$$\Delta H_f^\circ = -370.7 \pm 0.2 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -372.4 \pm 0.2 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 83.76 \pm 0.50 \text{ gibbs/mol}$$

Ground State Quantum Weight = 1

Molybdenum Hexafluoride (MoF₆)

(Ideal Gas) GFW = 209.930

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log K _p
0	-0.000	INF,INITE	-	5.740	-370.718	-370.718	INF,INITE
100	16.070	59.431	105.853	-4.642	-365.365	-365.365	798.548
200	23.949	73.216	86.257	-2.608	-372.325	-372.325	391.961
298	28.816	83.762	83.761	-0.000	-372.400	-372.400	250.024
300	29.087	83.840	83.762	-0.053	-372.400	-372.400	250.381
400	32.657	92.684	87.249	-6.386	-372.400	-372.400	147.863
500	33.439	100.011	87.239	-6.386	-372.004	-372.004	147.863
600	34.751	106.250	89.901	-9.809	-371.708	-371.562	120.771
700	35.478	111.665	92.632	-13.323	-371.390	-370.895	101.437
800	35.976	116.437	95.315	-16.897	-371.066	-370.286	86.950
900	36.316	120.786	97.956	-20.516	-370.736	-369.556	73.486
1000	36.568	124.537	100.377	-24.140	-370.410	-368.157	60.692
1100	36.763	128.034	102.735	-27.829	-370.091	-366.647	59.336
1200	36.934	131.241	104.979	-31.515	-369.782	-365.215	53.211
1300	37.052	134.203	107.114	-35.215	-369.482	-363.768	48.032
1400	37.141	136.948	109.158	-38.924	-369.191	-362.324	43.725
1500	37.224	139.516	111.089	-42.643	-368.913	-360.893	39.755
1600	37.287	141.922	112.941	-46.369	-368.650	-359.457	36.396
1700	37.340	144.164	114.713	-50.100	-368.400	-358.026	33.434
1800	37.384	146.320	116.410	-53.837	-368.164	-356.607	30.803
1900	37.422	148.392	117.938	-57.577	-367.941	-355.207	28.449
2000	37.454	150.282	119.402	-61.321	-367.729	-353.824	26.331
2100	37.482	152.090	121.106	-65.068	-367.528	-352.456	24.416
2200	37.507	153.835	122.554	-68.817	-367.336	-351.103	22.675
2300	37.527	155.502	123.951	-72.569	-367.152	-349.766	21.086
2400	37.543	157.100	125.298	-76.323	-366.975	-348.443	19.529
2500	37.556	158.633	126.592	-80.077	-366.805	-347.132	18.000
2600	37.577	160.106	127.862	-83.835	-366.650	-345.840	16.503
2700	37.597	161.525	129.083	-87.593	-366.500	-344.565	15.030
2800	37.601	162.892	130.266	-91.353	-366.356	-343.313	13.583
2900	37.612	164.214	131.414	-95.113	-366.219	-342.081	12.159
3000	37.621	165.487	132.529	-98.873	-366.086	-340.870	10.766
3100	37.630	166.721	133.612	-102.638	-365.956	-339.678	9.400
3200	37.637	167.916	134.665	-106.401	-365.831	-338.503	8.051
3300	37.644	169.074	135.690	-110.165	-365.710	-337.344	6.726
3400	37.651	170.198	136.689	-113.930	-365.593	-336.199	5.424
3500	37.657	171.289	137.662	-117.695	-365.481	-335.066	4.143
3600	37.662	172.350	138.611	-121.461	-365.373	-333.943	2.881
3700	37.667	173.382	139.537	-125.228	-365.269	-332.831	1.636
3800	37.672	174.387	140.441	-128.994	-365.169	-331.730	0.406
3900	37.676	175.365	141.324	-132.762	-365.073	-330.643	-0.811
4000	37.680	176.319	142.187	-136.530	-364.981	-329.566	-2.043
4100	37.684	177.250	143.031	-140.298	-364.892	-328.506	-3.281
4200	37.687	178.158	143.856	-144.066	-364.806	-327.461	-4.524
4300	37.690	179.045	144.664	-147.835	-364.724	-326.430	-5.771
4400	37.693	179.911	145.455	-151.604	-364.645	-325.413	-7.021
4500	37.696	180.756	146.231	-155.374	-364.569	-324.409	-8.271
4600	37.698	181.587	146.990	-159.144	-364.496	-323.416	-9.521
4700	37.701	182.398	147.735	-162.914	-364.426	-322.433	-10.771
4800	37.703	183.191	148.465	-166.684	-364.358	-321.460	-12.021
4900	37.705	183.969	149.182	-170.454	-364.292	-320.496	-13.271
5000	37.707	184.730	149.885	-174.225	-364.228	-319.541	-14.521
5100	37.709	185.477	150.576	-177.996	-364.166	-318.596	-15.771
5200	37.711	186.209	151.254	-181.767	-364.106	-317.661	-17.021
5300	37.713	186.928	151.921	-185.538	-364.048	-316.735	-18.271
5400	37.714	187.633	152.579	-189.309	-363.992	-315.818	-19.521
5500	37.716	188.325	153.219	-193.081	-363.937	-314.909	-20.771
5600	37.717	189.004	153.852	-196.852	-363.884	-314.006	-22.021
5700	37.719	189.672	154.475	-200.624	-363.832	-313.109	-23.271
5800	37.720	190.328	155.087	-204.396	-363.781	-312.218	-24.521
5900	37.721	190.973	155.690	-208.168	-363.731	-311.331	-25.771
6000	37.722	191.607	156.283	-211.940	-363.681	-310.448	-27.021

June 30, 1970

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	g_i , cm ⁻¹
741 (1)	262 (3)
643 (2)	312 (3)
741 (3)	122 (3)

Bond Distance: Mo-F = 1.84 ± 0.02 Å

Bond Angle: F-Mo-F = 90°

Product of Moments of Inertia: I_AI_BI_C = 7.771 × 10⁻¹¹³ g cm⁶

σ = 24

Heat of Formation

Settle et al. (1) measured the heat of formation of gaseous MoF₆ by direct combination of its elements in a nickel bomb calorimeter. Their result was $\Delta H_f^\circ(\text{MoF}_6, g) = -372.4 \pm 0.2 \text{ kcal/mol}$. This value is adopted in the tabulation.

Heat Capacity and Entropy

Tanner and Duncan (2) investigated the Raman spectra of liquid MoF₆, and their results indicated that the structure of the molecule was a regular octahedron with O_h symmetry rather than an unsymmetrical structure as reported by Braune and Pinnow (3) from electron diffraction studies. The Mo-F bond length is from the electron diffraction studies of Nazarian (4). Individual moments of inertia are I_A = I_B = I_C = 4.268 × 10⁻³⁸ g cm².

Several infrared (5, 6, 7) and Raman (5, 7) studies of MoF₆ have been reported. The vibrational frequencies reported for MoF₆ from these studies are in good agreement except for the infrared and Raman inactive ν_6 vibration. Burke et al. (5) and Hellberg et al. (6) derived $\nu_6 = 234 \text{ cm}^{-1}$, while Claassen et al. (7) assigned $\nu_6 = 130 \text{ cm}^{-1}$ and Gaunt (6) assigned $\nu_6 = 240 \text{ cm}^{-1}$. Weinstock and Goodman (8) recently analyzed the infrared and Raman data for MoF₆ and assigned $\nu_6 = 122 \text{ cm}^{-1}$.

Osborne et al. (10) calculated $S^\circ = 62.06 \pm 0.06 \text{ gibbs/mol}$ for liquid MoF₆ at 298.15°K from their low temperature thermal data. Combining this with ΔS° , they obtained $S^\circ = 83.75 \pm 0.10 \text{ gibbs/mol}$ for the ideal gas at 298.15°K. Accepting the assignments of Weinstock and Goodman (8), we calculate $S_{298.15}^\circ = 83.76 \text{ gibbs/mol}$, which is in excellent agreement with the thermal results. The other assignments given above for ν_6 all lead to ideal gas entropies that are lower than the thermal results. Therefore, the assignments given by Weinstock and Goodman (8) are adopted here.

References

1. J. L. Settle, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., **65**, 1337 (1961).
2. K. M. Tanner and A. B. F. Duncan, J. Amer. Chem. Soc., **73**, 1164 (1951).
3. H. Braune and P. Pinnow, Z. Physik, **35**, 239 (1937).
4. G. M. Nazarian, Ph.D. Thesis, California Institute of Technology, 1957.
5. T. G. Burke, D. F. Smith, and A. H. Nielsen, J. Chem. Phys., **20**, 447 (1952).
6. J. Gaunt, Trans. Faraday Soc., **49**, 1122 (1953).
7. H. H. Claassen, H. Selig, and J. G. Malm, J. Chem. Phys., **36**, 2088 (1962).
8. K. H. Hellberg, A. Müller, and O. Glemser, Z. Naturforsch., **21b**, 118 (1966).
9. B. Weinstock and G. L. Goodman, Advan. Chem. Phys., **9**, 169 (1965).
10. D. W. Osborne, F. Schreiner, J. G. Malm, H. Selig, and L. Rochester, J. Chem. Phys., **44**, 2802 (1966).

Sulfur Hexafluoride (SF₆)

(Ideal Gas) Mol. wt. = 146.0544

T, °K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f	Log K _p
0	0.000	0.000	INFINITE	-288.460	-288.460	INFINITE
100	9.280	53.312	85.652	-289.890	-282.716	617.846
200	16.505	61.798	71.637	-291.117	-275.020	300.520
298	23.224	68.713	58.713	-291.780	-266.986	195.682
300	23.329	69.857	69.713	-291.799	-266.813	194.364
400	27.852	77.237	70.689	-292.632	-258.408	141.181
500	30.705	83.783	72.657	-293.052	-249.802	109.183
600	32.544	89.555	75.011	-293.236	-241.130	87.827
700	33.772	92.279	76.003	-293.270	-232.467	71.693
800	34.624	94.239	76.903	-293.270	-224.067	61.693
900	35.235	103.354	82.384	-305.842	-214.862	52.173
1000	35.687	107.091	84.580	-305.390	-204.778	44.752
1100	36.029	110.509	86.784	-304.923	-194.741	38.490
1200	36.294	113.656	88.894	-304.441	-184.744	33.645
1300	36.503	116.569	90.913	-303.955	-174.786	29.383
1400	36.670	119.281	92.843	-303.464	-164.870	25.736
1500	36.807	121.816	94.691	-302.971	-154.987	22.580
1600	36.913	124.195	96.461	-302.477	-145.138	19.924
1700	37.013	126.436	98.159	-301.984	-135.317	17.595
1800	37.092	128.554	99.790	-301.494	-125.534	15.241
1900	37.159	130.561	101.357	-300.904	-115.767	13.316
2000	37.217	132.469	102.865	-300.517	-106.029	11.586
2100	37.266	134.286	104.318	-300.036	-96.332	10.024
2200	37.309	136.020	105.720	-299.557	-86.630	8.605
2300	37.347	137.680	107.074	-299.082	-76.962	7.313
2400	37.380	139.270	108.383	-298.612	-67.315	6.130
2500	37.410	140.797	109.649	-298.149	-57.689	5.043
2600	37.436	142.264	110.875	-297.690	-48.077	4.041
2700	37.459	143.678	112.064	-297.234	-38.485	3.115
2800	37.480	145.040	113.218	-296.783	-28.913	2.257
2900	37.498	146.356	114.338	-296.339	-19.348	1.458
3000	37.515	147.627	115.426	-295.903	-9.811	0.715
3100	37.531	148.858	116.485	-295.468	-	0.20
3200	37.545	150.049	117.515	-295.032	-	-
3300	37.557	151.205	118.519	-294.620	-	-
3400	37.569	152.326	119.497	-294.204	-	-
3500	37.579	153.416	120.450	-293.796	-	-
3600	37.588	154.474	121.381	-293.390	-	-
3700	37.598	155.504	122.289	-292.994	-	-
3800	37.606	156.507	123.177	-292.601	-	-
3900	37.614	157.484	124.044	-292.218	-	-
4000	37.621	158.436	124.892	-291.838	-	-
4100	37.628	159.365	125.721	-291.465	-	-
4200	37.634	160.272	126.533	-291.099	-	-
4300	37.639	161.158	127.328	-290.735	-	-
4400	37.645	162.023	128.107	-290.384	-	-
4500	37.650	162.869	128.870	-290.035	-	-
4600	37.654	163.697	129.618	-289.692	-	-
4700	37.659	164.507	130.352	-289.358	-	-
4800	37.663	165.300	131.072	-289.027	-	-
4900	37.667	166.076	131.778	-288.704	-	-
5000	37.670	166.837	132.472	-288.388	-	-
5100	37.674	167.583	133.153	-288.074	-	-
5200	37.677	168.315	133.822	-287.774	-	-
5300	37.680	169.033	134.480	-287.475	-	-
5400	37.683	169.737	135.126	-287.186	-	-
5500	37.685	170.428	135.762	-286.899	-	-
5600	37.688	171.107	136.387	-286.622	-	-
5700	37.690	171.774	137.002	-286.352	-	-
5800	37.693	172.430	137.607	-286.083	-	-
5900	37.695	173.074	138.203	-285.824	-	-
6000	37.697	173.708	138.789	-285.571	-	-

Dec. 31, 1960 Sept. 30, 1965

SULFUR HEXAFLUORIDE (SF₆) (IDEAL GAS)

Point Group O_h

S°_{298.15} = 69.713 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH_f° 0 = -288.46 ± 0.24 kcal. mole⁻¹

ΔH_f° 298.15 = -291.79 ± 0.24 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
770 (1)	345 (3)	
640 (2)	615 (3)	
522 (3)	947 (3)	

Bond Length = 1.564 Å

Bond Angle: F-S-F = 90°

Product of the Moments of Inertia: I_AI_BI_C = 29,400 X 10⁻¹¹⁷ g.³ cm.⁶

σ = 24

Heat of Formation.

P. A. O. O'Hare, J. L. Settle, and W. N. Hubbard, Preprint of Paper XIV on Fluorine Bomb Calorimetry, July, 1965, measured the enthalpy of combustion of rhombic sulfur in fluorine. Their result yields ΔH_f° 298 = -291.79 ± 0.24 kcal. mole⁻¹. P. Gross, C. Hayman, and L. L. Levi, XVIII Intern. Congr. Pure and Appl. Chem., Abstr., 1, 30 (1959), reported -289.5 kcal. mole⁻¹ also based on direct combination of the elements. O'Hare, Settle, and Hubbard mentioned a private communication from Dr. Gross indicating -289.5 kcal. mole⁻¹ may be in error due to oxygen in the fluorine used and preliminary results of a redetermination are in better agreement with -291.79 kcal. mole⁻¹. D. M. Yost and W. H. Clausen, J. Am. Chem. Soc. 55, 887 (1933) determined -262 kcal. mole⁻¹, again by direct reaction of the elements, which now appears too low. The work of O'Hare et al., loc. cit., is adopted.

Heat Capacity and Entropy.

V. C. Ewing and L. E. Sutton, Trans. Faraday Soc. 59, 124 (1963) measured the bond length adopted here by the electron diffraction technique. Earlier less accurate work by the same method by H. Braune and S. Knoke, Z. physik. Chem. B21, 297 (1933) and L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci. USA 19, 68 (1933) is in agreement within experimental error. T. E. Norys, Ber. Bunsenges Physik. Chem. 68, 277 (1964) reviewed the literature on Raman and infrared spectra. Frequencies given here differ slightly from his selection because more weight was given to the Raman frequencies of C. W. Oullikaon, J. R. Nielsen, and A. T. Stair, Jr., J. Mol. Spectroscopy 1, 151 (1957). Calculated functions by Morry loc. cit. are in reasonable agreement with the present work.

A. Eucken and E. Schröder, Z. physik. Chem. 41B, 307 (1938) measured low temperature thermal data from which K. K. Kelley and E. O. King, U. S. Bur. Mines Bull. 592 (1961) calculated s°₂₉₈ = 70.3 ± 0.7 cal. mole⁻¹ deg.⁻¹ which agrees within experimental error with the spectroscopic result.

The three principal moments of inertia are I_A = I_B = I_C = 3.0863 X 10⁻³⁸ g. cm.²

TUNGSTEN HEXAFLUORIDE (WF₆) (LIQUID)

OPW = 297.8404

T, °K	Cp°	gibbs/mol S°	-(C°-H°)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	log Kp
100							
200	40.300	41.393	53.269	-3.873	-419.187	-392.187	0.25-0.10
298	40.300	56.566	56.566	0.000	-417.876	-389.876	0.65-0.54
300	40.300	59.815	59.815	0.075	-417.849	-389.794	0.63-0.66
400	40.300	71.466	61.153	4.125	-416.697	-390.621	2.07-0.82
500	40.300	80.303	68.153	8.175	-415.669	-371.726	1.62-0.81
600	40.300	87.687	67.512	12.225	-414.726	-363.025	1.32-0.32
700	40.300	94.130	70.890	16.275	-413.850	-354.477	1.10-0.73
800	40.300	99.538	74.132	20.325	-413.031	-346.055	0.84-0.36
900	40.300	104.308	77.225	24.375	-412.251	-337.725	0.62-0.12
1000	40.300	108.375	80.150	29.425	-411.510	-329.449	0.72-0.10

ΔH°_{298.15} = -417.87 ± 0.5 kcal/mol
ΔH° = 0.980 kcal/mol
ΔH° = 6.485 ± 0.08 kcal/mol

Heat of Formation.

The adopted heat of formation, -417.87 kcal/mol, is calculated from the chosen ΔH°_{298.3} = 6.485 ± 0.08 kcal/mol with ΔH°₂₉₈(WF₆,g) = -411.5 ± 0.4 kcal/mol using all JANAF functions. The value of ΔH°_{298.3} is obtained by corrected 2nd law analysis of vapor pressure data^{6,7,8} which are given in the vaporization section of this table.

O. E. Myer and A. P. Brady¹ measured calorimetrically ΔH°₂₉₈ = -150.1 kcal/mol for the reaction
WF₆(l) + 8 NaOH(500H₂O) → Na₂WO₄(4900H₂O) + 8NaF(500H₂O) + 8NaF(500H₂O)²
metrically ΔH°₂₉₈ = -13.8 kcal/mol for the reaction WO₃(c) + 2 NaOH(500H₂O) → Na₂WO₄(4200H₂O) + H₂O(l). Based on these data and auxiliary data for NaOH(aq)^{3,9}, NaF(aq)^{3,10} and Na₂WO₄(aq)⁴, we obtain ΔH°₂₉₈ = -138.2 kcal/mol for WF₆(l) + 8 NaOH(500H₂O) → WO₃(c) + 3 H₂O(l) + 8 NaF(500H₂O). This leads to ΔH°₂₉₈(WF₆,l) = -418.9 ± 1 kcal/mol which is in good agreement with the value adopted.

Heat Capacity and Entropy.

The heat capacity, 40.5 gibbs/mol, is obtained from a graph of the Cp versus temperature curve determined calorimetrically by E. F. Westrum, Jr.⁵

The entropy, S°₂₉₈ = 59.584 eu, is calculated from the chosen ΔH°_{298.3} = 6.485 kcal/mol with S°₂₉₈(WF₆,g) = 81.504 eu using all JANAF functions.

Melting Data.

Melting point and heat of melting have been reported by the following investigators, and their results are summarized below. Ruff and Acher's value, 2.40 kcal/mol, is too high because they did not know of the existence of a solid-solid transition⁵ at 264.7°K with ΔH° = 2.087 kcal/mol. Westrum's data are adopted in the tabulation.

Investigator ⁵	Method	Melting Point (°K)	ΔH° (kcal/mol)
Westrum ⁵	Calorimetric	275.2	0.940
Ruff and Acher ⁷	Vapor pressure	275.4	2.400*
Barber & Cady ⁸	Warming curve	275.1	0.500
Cady & Hargreaves ⁶	Vapor pressure	275.2	0.420*

*This value is the difference between the 2nd law heats of sublimation and vaporization without correction for ΔCp° for both processes.

Vaporization Data.

Second law analyses of the data^{6,7,8}, neglecting corrections for nonideality of the vapor, are summarized below. The value of ΔH°₂₉₈ = 6.37 kcal/mol (ΔH°_{298.3} = 6.485 kcal/mol) is selected in the tabulation.

Investigator ⁷	Temp. Range (°K)	No. of Points	Boiling Point (°K)	ΔH° ₂₉₈ (kcal/mol)	ΔS° ₂₉₈ (eu)
Ruff and Acher ⁷	275 - 287.5	5	290.7 ± 0.2	6.30 ± 0.12	21.70
Barber and Cady ⁸	285 - 324.5	16	290.2 ± 0.05	6.37 ± 0.01	21.94
Cady and Hargreaves ⁶	275 - 290	Equation	290.3 ± 0.05	8.12	21.09

*From second law analysis using ΔCp° = -12.4 gibbs/mol

References.

- O. E. Myer and A. P. Brady, J. Phys. Chem. **64**, 591 (1960).
- V. I. Spitzayn and N. N. Patsukova, Russ. J. Inorg. Chem. (English Transl.) **10**, 1304 (1965).
- "Thermal Properties of Aqueous Uni-univalent Electrolytes," V. B. Parker, NBS-NS2 Natl. Bur. Std., Washington, D.C., Apr. 1965.
- We have assumed ΔH°₂₉₈ = 0 for Na₂WO₄(4900H₂O) → Na₂WO₄(4900H₂O) based on the dilution data of R. L. Orban and L. O. Hepler, J. Am. Chem. Soc. **80**, 3538 (1958).
- E. F. Westrum, Jr., Pure & Appl. Chem. **37**, 187 (1964); J. Chem. Ed. **39**, 443 (1962).
- O. H. Cady and O. B. Hargreaves, J. Chem. Soc., 1563 (1961).
- O. Ruff and E. Acher, Z. Anorg. Allgem. Chem. **196**, 413 (1931).
- E. J. Barber and O. H. Cady, J. Phys. Chem. **60**, 505 (1956).
- JANAF NaOH(c) table dated Mar. 31, 1966.
- U.S. Natl. Bur. Std. Tech. Note 270-1, 1965.

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1967

Tungsten Hexafluoride (WF₆)

(Ideal Gas) GFW = 297.8404

T, °K	Cp ^a	gibbs/mol S ^b - (C ^a - H ²⁹⁸)/T	H ²⁹⁸ - H ²⁹⁸ /T	ΔH ²⁹⁸ /T	ΔG ²⁹⁸	Log Kp
0	0.00	INFINITE	0.00	0.00	0.00	INFINITE
100	18.220	58.370	5.435	-409.416	-409.416	INFINITE
200	23.197	71.775	2.586	-411.358	-397.154	433.990
300	28.448	81.404	1.504	-411.500	-390.140	265.760
400	31.452	81.450	0.53	-411.500	-390.004	264.121
500	33.508	81.452	0.341	-411.500	-389.956	264.242
600	34.560	81.453	0.254	-411.500	-389.908	264.301
700	35.412	81.454	0.183	-411.500	-389.860	264.331
800	36.125	81.455	0.125	-411.500	-389.812	264.351
900	36.720	81.456	0.075	-411.500	-389.764	264.361
1000	37.220	81.457	0.030	-411.500	-389.716	264.361
1100	37.675	81.458	0.000	-411.500	-389.668	264.351
1200	38.092	81.459	0.000	-411.500	-389.620	264.331
1300	38.475	81.460	0.000	-411.500	-389.572	264.301
1400	38.828	81.461	0.000	-411.500	-389.524	264.261
1500	39.155	81.462	0.000	-411.500	-389.476	264.211
1600	39.462	81.463	0.000	-411.500	-389.428	264.161
1700	39.745	81.464	0.000	-411.500	-389.380	264.111
1800	40.008	81.465	0.000	-411.500	-389.332	264.061
1900	40.255	81.466	0.000	-411.500	-389.284	264.011
2000	40.490	81.467	0.000	-411.500	-389.236	263.961
2100	40.708	81.468	0.000	-411.500	-389.188	263.911
2200	40.912	81.469	0.000	-411.500	-389.140	263.861
2300	41.098	81.470	0.000	-411.500	-389.092	263.811
2400	41.268	81.471	0.000	-411.500	-389.044	263.761
2500	41.425	81.472	0.000	-411.500	-388.996	263.711
2600	41.572	81.473	0.000	-411.500	-388.948	263.661
2700	41.708	81.474	0.000	-411.500	-388.900	263.611
2800	41.835	81.475	0.000	-411.500	-388.852	263.561
2900	41.955	81.476	0.000	-411.500	-388.804	263.511
3000	42.068	81.477	0.000	-411.500	-388.756	263.461
3100	42.175	81.478	0.000	-411.500	-388.708	263.411
3200	42.278	81.479	0.000	-411.500	-388.660	263.361
3300	42.375	81.480	0.000	-411.500	-388.612	263.311
3400	42.468	81.481	0.000	-411.500	-388.564	263.261
3500	42.558	81.482	0.000	-411.500	-388.516	263.211
3600	42.645	81.483	0.000	-411.500	-388.468	263.161
3700	42.728	81.484	0.000	-411.500	-388.420	263.111
3800	42.808	81.485	0.000	-411.500	-388.372	263.061
3900	42.885	81.486	0.000	-411.500	-388.324	263.011
4000	42.958	81.487	0.000	-411.500	-388.276	262.961
4100	43.028	81.488	0.000	-411.500	-388.228	262.911
4200	43.095	81.489	0.000	-411.500	-388.180	262.861
4300	43.158	81.490	0.000	-411.500	-388.132	262.811
4400	43.218	81.491	0.000	-411.500	-388.084	262.761
4500	43.275	81.492	0.000	-411.500	-388.036	262.711
4600	43.330	81.493	0.000	-411.500	-387.988	262.661
4700	43.382	81.494	0.000	-411.500	-387.940	262.611
4800	43.432	81.495	0.000	-411.500	-387.892	262.561
4900	43.480	81.496	0.000	-411.500	-387.844	262.511
5000	43.525	81.497	0.000	-411.500	-387.796	262.461
5100	43.568	81.498	0.000	-411.500	-387.748	262.411
5200	43.608	81.499	0.000	-411.500	-387.700	262.361
5300	43.645	81.500	0.000	-411.500	-387.652	262.311
5400	43.680	81.501	0.000	-411.500	-387.604	262.261
5500	43.712	81.502	0.000	-411.500	-387.556	262.211
5600	43.742	81.503	0.000	-411.500	-387.508	262.161
5700	43.770	81.504	0.000	-411.500	-387.460	262.111
5800	43.798	81.505	0.000	-411.500	-387.412	262.061
5900	43.825	81.506	0.000	-411.500	-387.364	262.011
6000	43.852	81.507	0.000	-411.500	-387.316	261.961

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1967

TUNGSTEN HEXAFLUORIDE (WF₆)

(IDEAL GAS)

OFW = 297.8404 F₆^W

Point Group O_h

ΔH_f^{298.15} = -409.4 ± 0.4 kcal/mol

S_{298.15} = 81.504 gibbs/mol

ΔH_f^{298.15} = -411.5 ± 0.4 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

W, cm ⁻¹	W, cm ⁻¹
769 (1)	256 (3)
670 (2)	322 (3)
712 (3)	216 (3)

Bond Distance: W-F = 1.83 Å

Bond Angle: F-W-F = 90°

Product of the Moments of Inertia: I_AI_BI_C = 7.54576 x 10⁻¹¹³ g³ cm⁶

σ = 24

Heat of Formation

P. A. O. O'Hare and W. N. Hubbard, J. Phys. Chem. **70**, 3353 (1966), determined the heat of formation, ΔH_f²⁹⁸(WF₆) = -411.5 ± 0.4 kcal/mol, by combustion of tungsten in fluorine in a bomb calorimeter. This value is adopted in the tabulation.

Heat Capacity and Entropy.

The molecular configuration and vibrational frequencies were obtained from the infrared and Raman spectroscopic studies by J. Gaunt¹, T. O. Burke, D. P. Smith and A. H. Nielsen², K. N. Tanner and A. B. P. Duncan³, K. N. Tanner and A. B. P. Duncan⁴, based on the preliminary result of V. Schomaker, M. Kimura and B. Weinstein⁵ who determined the bond distance by electron diffraction. J. Gaunt⁶ derived W-F = 1.89 Å from correlation with other hexafluorides and a valence force constant calculation. The three principal moments of inertia are I_A = I_B = I_C = 4.22572 x 10⁻³⁸ g cm².

References

1. J. Gaunt, Trans. Faraday Soc. **49**, 1122 (1953).
2. T. O. Burke, D. P. Smith and A. H. Nielsen, J. Chem. Phys. **20**, 447 (1952).
3. K. N. Tanner and A. B. P. Duncan, J. Am. Chem. Soc. **73**, 1164 (1951).
4. K. N. Tanner and A. B. P. Duncan, J. Chem. Phys. **30**, 968 (1959).
5. V. Schomaker, M. Kimura and B. Weinstein, Proceedings of 2nd U.N. International Conference on Peaceful Uses of Atomic Energy, Geneva, **28**, 125, (1958).
6. J. Gaunt, Trans. Faraday Soc. **50**, 546 (1954).

Point Group D_{5h}

$$\Delta H_f^\circ = -226.35 \pm 0.6 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -229.7 \pm 0.6 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 83.08 \pm 0.3 \text{ gibbs/mol}$$

Ground State Quantum Weight = [1]

Iodine Heptafluoride (IF₇)

(Ideal Gas) GFW = 259.8932

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	.000	INFINITE	INFINITE	5.610	-226.348	-226.348	INFINITE
100	12.487	59.043	104.243	4.716	-226.251	-219.187	479.033
200	24.777	71.665	85.817	2.826	-226.400	-209.026	229.026
300	32.134	83.084	83.084	.000	-226.700	-199.770	146.441
400	37.235	93.175	84.406	3.504	-229.701	-199.535	145.403
500	38.645	101.553	87.020	7.266	-231.534	-189.494	103.535
600	40.057	108.733	90.055	11.207	-233.369	-178.535	78.034
800	42.001	125.414	96.257	21.388	-235.152	-167.092	40.838
1000	42.552	133.901	104.744	32.099	-236.892	-155.610	26.588
1100	42.876	141.037	109.827	40.574	-238.592	-144.098	18.495
1300	43.082	148.219	112.171	48.171	-239.855	-132.514	12.153
1500	43.158	149.071	112.588	51.883	-240.202	-120.869	7.657
1600	43.174	149.150	112.648	52.457	-240.202	-119.310	6.958
1800	43.274	155.042	120.587	62.127	-242.915	-107.576	4.198
2000	43.319	157.403	122.425	66.457	-247.279	-95.843	2.143
2500	43.466	169.316	132.314	82.157	-261.615	-61.466	.385
3000	43.567	177.251	139.162	114.268	-270.762	-49.274	.172
3100	43.567	178.600	140.414	124.628	-270.762	-49.274	.172
3200	43.567	179.949	141.666	134.989	-270.762	-49.274	.172
3300	43.567	181.298	142.917	145.350	-270.762	-49.274	.172
3400	43.567	182.647	144.168	155.711	-270.762	-49.274	.172
3500	43.567	183.996	145.419	166.072	-270.762	-49.274	.172
3600	43.567	185.345	146.670	176.433	-270.762	-49.274	.172
3700	43.567	186.694	147.921	186.794	-270.762	-49.274	.172
3800	43.567	188.043	149.172	197.155	-270.762	-49.274	.172
3900	43.567	189.392	150.423	207.516	-270.762	-49.274	.172
4000	43.567	190.741	151.674	217.877	-270.762	-49.274	.172
4100	43.567	192.090	152.925	228.238	-270.762	-49.274	.172
4200	43.567	193.439	154.176	238.599	-270.762	-49.274	.172
4300	43.567	194.788	155.427	248.960	-270.762	-49.274	.172
4400	43.567	196.137	156.678	259.321	-270.762	-49.274	.172
4500	43.567	197.486	157.929	269.682	-270.762	-49.274	.172
4600	43.567	198.835	159.180	280.043	-270.762	-49.274	.172
4700	43.567	200.184	160.431	290.404	-270.762	-49.274	.172
4800	43.567	201.533	161.682	300.765	-270.762	-49.274	.172
4900	43.567	202.882	162.933	311.126	-270.762	-49.274	.172
5000	43.567	204.231	164.184	321.487	-270.762	-49.274	.172
5100	43.567	205.580	165.435	331.848	-270.762	-49.274	.172
5200	43.567	206.929	166.686	342.209	-270.762	-49.274	.172
5300	43.567	208.278	167.937	352.570	-270.762	-49.274	.172
5400	43.567	209.627	169.188	362.931	-270.762	-49.274	.172
5500	43.567	210.976	170.439	373.292	-270.762	-49.274	.172
5600	43.567	212.325	171.690	383.653	-270.762	-49.274	.172
5700	43.567	213.674	172.941	394.014	-270.762	-49.274	.172
5800	43.567	215.023	174.192	404.375	-270.762	-49.274	.172
5900	43.567	216.372	175.443	414.736	-270.762	-49.274	.172
6000	43.567	217.721	176.694	425.097	-270.762	-49.274	.172

Mar. 31, 1962; Mar. 31, 1963; Dec. 31, 1963; June 30, 1966; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}	ω_e, cm^{-1}
676 (1)	746 (2)	510 (2)
635 (1)	425 (2)	352 (2)
670 (1)	257 (2)	310 (2)
365 (1)		(340) (2)

$$\text{Bond Distance: I-F(equatorial)} = 1.86 \text{ \AA} \quad \text{I-F(axial)} = 1.76 \text{ \AA}$$

$$\text{Bond Angle: F(eq)-I-F(ax)} = 90^\circ \quad \text{F(eq)-I-F(eq)} = 72^\circ$$

$$\text{Product of the Moments of Inertia: } I_{AB}^2 I_C = 1.1965 \times 10^{-112} \text{ g}^3 \text{ cm}^6$$

Heat of Formation

Settle et al. (1) derived $\Delta H_f^\circ = -229.7 \pm 0.6$ kcal/mol for IF₇(g) at 298.15 K from treatment of their calorimetric data on combustion of iodine in fluorine. The combustion products, consisting of mixtures of IF₅ and IF₇, were expanded, treated to remove excess fluorine, and then hydrolyzed. The solutions were analyzed for iodate and the sum of iodate plus periodate. Since the recovery of iodine was not complete (about 70 to 98%), it was necessary to try various assumptions about the form of the unrecovered iodine. Consistent results were obtained only by assigning the unrecovered iodine to IF₇, the less volatile product. This treatment indicated that IF₇ was formed in yields ranging from about 1 to 70%.

ΔH_f° for the reaction IF₇(g) = IF₅(g) + F₂(g) may be checked via equilibrium data (2). Using six points read from Fig. 2 of Bernstein and Katz, we obtain ΔH_f° (3rd law) = 29.36 ± 0.2 kcal/mol and ΔH_f° (2nd law) = 29.53 ± 0.7 kcal/mol, both at 298.15 K. The entropy test, ΔS_r° (2nd law) = ΔS_r° (JANAF functions) = 0.3 ± 1.4 gibbs/mol, indicates consistency with the JANAF functions. Combination of ΔH_f° (3rd law) with ΔH_f° for IF₅(g) yields ΔH_f° (IF₇, g) = -230.2 ± 0.6 kcal/mol. In deriving the uncertainty, we assume that ΔH_f° (3rd law) is uncertain by ± 0.5 kcal/mol due to an estimated uncertainty of about 1.0 gibbs/mol in the JANAF value of ΔS_r° at 500 K.

Heat Capacity and Entropy

Recent evidence favors D_{5h} symmetry and a pentagonal bipyramidal structure for the heptafluoride. Claassen et al. (3) review the earlier debate about structures of lower symmetry. They provide convincing evidence of D_{5h} symmetry from the first observation of Raman spectra of the vapor state and re-examination of the infrared spectra. Their data-including five fundamentals in Raman (two polarized), five fundamentals in infrared, no coincidences between Raman and infrared, and one fundamental inactive--are consistent only with D_{5h} symmetry. This is confirmed by Falconer et al. (4) who interpret their electric-deflection experiments as indicating a symmetry-forbidden dipole moment. Extended Hückel-molecular-orbital calculations (5) also predict D_{5h} symmetry. The adopted structural parameters are from our approximate analysis of the electron-diffraction data of Thompson and Bartell (6). The authors gave a radial distribution curve and suggested only a gross (unrefined) structure because of the probable presence of a fluorocarbon impurity in their sample. Principal moments of inertia are $I_A = I_B = 46.93 \times 10^{-39}$ and $I_C = 54.57 \times 10^{-39}$ g cm².

Observed vibrational fundamentals are from Claassen et al. (3). The inactive fundamental is estimated from the calculations of Khanna (7).

References

1. J. L. Settle, J. H. E. Jeffes, P. A. G. O'Hare and W. N. Hubbard, presented at the 23rd Annual Calorimetry Conference, Midland, Mich., August, 1968.
2. R. B. Bernstein and J. J. Katz, J. Phys. Chem. **56**, 885 (1952).
3. H. H. Claassen, E. L. Gasner and H. Seelig, J. Chem. Phys. **43**, 1803 (1968).
4. W. E. Falconer, A. Büchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. **48**, 312 (1968).
5. R. L. Oakland and G. H. Duffey, J. Chem. Phys. **45**, 19 (1967).
6. H. B. Thompson and L. S. Bartell, Trans. Amer. Crystallogr. Ass. **2**, 190 (1966).
7. R. K. Khanna, J. Mol. Spectrosc. **9**, 134 (1962).

Iron (Fe)

(Reference State) At. Wt. = 55.85

T. °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	.000	.000	INFINITE	- 1.075	.000	INFINITE
100	2.680	1.465	11.190	-.972	.000	.000
200	5.133	4.302	7.053	-.550	.000	.000
298	5.989	6.529	6.529	-.000	.000	.000
300	6.000	6.564	.011	.000	.000	.000
400	6.500	8.363	6.771	.000	.000	.000
500	7.020	9.868	7.243	1.312	.000	.000
600	7.580	11.197	7.793	2.042	.000	.000
700	8.240	12.412	8.367	3.231	.000	.000
800	8.980	13.540	8.960	4.785	.000	.000
900	10.480	14.718	9.523	4.675	.000	.000
1000	13.560	15.936	10.102	5.832	.000	.000
1100	10.230	17.249	10.697	7.207	.000	.000
1200	8.310	18.595	11.281	8.900	.000	.000
1300	6.460	19.917	12.871	10.032	.000	.000
1400	6.460	19.917	12.871	10.032	.000	.000
1500	8.610	20.125	12.869	10.885	.000	.000
1600	8.760	20.686	13.840	11.754	.000	.000
1700	10.650	21.096	13.791	11.529	.000	.000
1800	10.650	21.096	13.791	11.529	.000	.000
1900	10.540	24.518	14.728	18.569	.000	.000
2000	10.580	25.077	15.251	19.251	.000	.000
2100	10.620	25.595	15.731	20.713	.000	.000
2200	10.700	26.564	16.431	22.845	.000	.000
2300	10.740	27.020	17.045	23.917	.000	.000
2400	10.780	27.460	17.442	24.593	.000	.000
2500	10.820	27.883	17.855	25.073	.000	.000
2600	10.900	28.688	18.620	26.245	.000	.000
2700	10.940	29.071	18.955	29.337	.000	.000
2800	10.980	29.443	19.292	30.433	.000	.000
2900	11.020	29.804	19.631	31.533	.000	.000
3000	6.486	30.486	20.406	115.502	.000	.000
3100	6.565	57.069	22.551	117.360	.000	.000
3200	6.644	57.260	23.440	118.020	.000	.000
3300	6.724	57.449	24.480	118.489	.000	.000
3400	6.889	57.816	24.224	120.050	.000	.000
3500	6.974	57.997	27.037	120.743	.000	.000
3600	7.061	58.174	27.813	121.445	.000	.000
3700	7.151	58.350	28.556	122.155	.000	.000
3800	7.245	58.605	29.050	123.405	.000	.000
3900	7.340	58.864	30.405	124.342	.000	.000
4000	7.437	59.032	31.235	125.090	.000	.000
4100	7.525	59.199	31.641	125.847	.000	.000
4200	7.626	59.528	32.068	126.592	.000	.000
4300	7.928	59.690	33.431	128.180	.000	.000
4400	8.032	59.851	34.056	128.578	.000	.000
4500	8.136	60.011	34.563	129.786	.000	.000
4600	8.345	60.328	34.529	131.436	.000	.000
4700	8.450	60.485	35.990	132.274	.000	.000
4800	8.555	60.641	36.437	133.124	.000	.000
4900	8.660	60.704	36.870	133.946	.000	.000
5000	8.764	60.950	37.701	134.856	.000	.000
5100	8.868	61.104	37.701	135.738	.000	.000
5200	8.970	61.256	38.089	136.630	.000	.000
5300	9.072	61.408	38.480	137.532	.000	.000

Mar. 31, 1965

Fe

IRON (Fe)

AT. WT. = 55.85

(REFERENCE STATE)

0 to 1184°K. Crystal alpha
1184 to 1665°K. Crystal gamma
1665 to 1809°K. Crystal delta
1809 to 3145°K. Liquid
3145 to 6000°K. Ideal Monatomic Gas

See crystal, liquid and monatomic gas for details.

Fe

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	INFINITE	1.075	.000	.000	INFINITE
100	2.860	1.465	11.100	.000	.000	.001
200	5.133	4.302	7.043	.000	.000	.000
298	5.989	6.529	.000	.000	.000	.000
300	6.000	6.566	.011	.000	.000	.000
400	6.500	8.363	6.771	.000	.000	.000
500	7.020	9.868	7.243	.000	.000	.000
600	7.580	11.197	7.793	.000	.000	.000
700	8.240	13.412	8.947	.000	.000	.000
800	9.170	15.564	9.946	.000	.000	.000
900	10.480	14.718	9.523	.000	.000	.000
1000	13.560	15.934	10.102	.000	.000	.000
1100	10.230	17.249	10.497	.000	.000	.000
1200	8.160	18.256	11.581	.000	.000	.000
1300	8.310	18.915	9.184	.000	.000	.000
1400	8.460	19.537	12.371	.000	.000	.000
1500	8.610	20.125	12.869	.000	.000	.000
1600	8.760	20.686	13.340	.000	.000	.000
1700	8.920	21.394	13.790	.000	.000	.000
1800	10.000	21.963	14.230	.000	.000	.000
1900	10.161	22.308	14.651	.000	.000	.000
2000	10.300	23.031	15.057	.000	.000	.000
2100	10.419	23.438	15.449	.000	.000	.000
2200	10.519	24.025	16.031	.000	.000	.000
2300	10.598	24.495	16.194	.000	.000	.000
2400	10.658	24.847	16.550	.000	.000	.000
2500	10.698	25.381	16.894	.000	.000	.000

$S_{298.15}^0 = 6.529 \pm 0.01$ cal. deg.⁻¹ mole⁻¹
 $T_{t1} = 1184^\circ\text{K.}$
 $T_{t2} = 1665^\circ\text{K.}$
 $T_m = 1809^\circ\text{K.}$
 $\Delta H_f^0 = 0$ kcal. mole⁻¹
 $\Delta H_f^0 298.15 = 0$ kcal. mole⁻¹
 $\Delta H_{t1}^0 = 0.225$ kcal. mole⁻¹
 $\Delta H_{t2}^0 = 0.260$ kcal. mole⁻¹
 $\Delta H_m^0 = 3.630$ kcal. mole⁻¹
 $\Delta H_m^0 298.15 = 99.5 \pm 0.4$ kcal. mole⁻¹

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The heat capacity below 298°K. was obtained by smoothing graphically the data of G. Duyckaerts, *Physica* **6**, 401 (1939) and W. H. Keesom and B. Kurrelmeier, *Physica*, **6**, 633 (1939) over the range 1° - 20°K; P. E. Simon and R. C. Swain, *Z. Physik. Chem.* **28B**, 189 (1935) (30-220°K.), A. Eucken and H. Verth, *Z. Anorg. Chem.* **188**, 152 (1930) (17-206°K.) and K. K. Kelley, *J. Chem. Phys.* **11**, 16 (1943) (55-295°K.). This data on integration yielded $S_{298.15}^0 = 6.529$ starting with $S_1^0 = 0.0003$ cal. deg.⁻¹ mole⁻¹. The heat capacity and enthalpy data above room temperature are extensive and the heat capacities and enthalpies chosen by R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys" John Wiley and Sons, Inc., New York 1963, were adopted here. These values have a sharp peak in the heat capacity curve at the Curie point* and through this region follow closely the work of P. R. Pallister, *J. Iron Steel Inst.* **161**, 87 (1949). This data has recently been corroborated using a pulsed heating technique by D. C. Wallace, P. H. Sidles and G. C. Danielson, *J. App. Phys.* **31**, 168 (1960). It should be noted that there is some disagreement between the heat capacities chosen and the enthalpies measured by P. D. Anderson and R. Hultgren, *Trans. Met. Soc. AIME*, **224**, 842 (1962). The measured values lie consistently above the chosen enthalpies in the range 298-900°K. by from 30 to 60 calories, however the chosen values are considered to be the more reliable. The δ -iron heat capacities adopted here have recently been substantiated confirmed by W. A. Dench and O. Kubashchewski, *J. Iron Steel Inst.* (London) **201**, 140 (1963).

Transition Data.

The enthalpies of the α - γ transition at 1184°K. and the δ - γ transition at 1665°K. were also taken from Hultgren et al. loc. cit.

Melting Data.

The temperature and heat of melting were those adopted by Hultgren et al. loc. cit.

Heat of Sublimation.

The value adopted is from a critical second and third law analysis of the data of 14 investigators over gamma-iron and liquid iron. See the $\Delta H_{sub}(g)$ table for details.

*See W. P. Giauque, G. E. Brodale, R. A. Fisher and E. W. Hornung, *J. Chem. Phys.* **42**, 1 (1965) for the definition of "permt".

Iron (Fe)

(Liquid) At. Wt. = 55.85

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100							
200							
298	5.985	8.195	8.195	•000	3.138	2.641	- 1.936
300	6.000	8.232	8.195	•011	3.138	2.638	- 1.922
400	6.500	8.437	8.437	•617	3.138	2.632	- 1.850
500	7.020	10.059	10.059	1.312	3.138	2.505	- 1.608
600	7.580	12.863	9.460	2.042	3.138	2.138	- .779
700	8.240	14.078	10.034	2.631	3.138	1.972	- .616
800	9.170	15.235	10.612	3.699	3.138	1.805	- .493
900	10.460	16.284	11.168	5.615	3.138	1.639	- .398
1000	11.950	17.600	11.768	8.532	3.138	1.472	- .322
1100	10.230	18.914	12.364	7.207	3.138	1.304	- .259
1200	10.260	19.761	12.945	8.179	2.947	1.141	- .208
1300	10.300	20.584	13.502	9.207	3.152	.982	- .165
1400	10.340	21.388	14.035	10.239	3.245	.809	- .126
1500	10.380	22.067	14.547	11.279	3.326	.621	- .090
1600	10.420	22.734	15.038	12.315	3.699	.422	- .058
1700	10.460	23.367	15.509	13.359	3.568	.217	- .028
1800	10.500	23.966	15.963	14.407	3.625	.019	- .002
1900	10.540	24.532	16.399	15.459	•000	•000	•000
2000	10.580	25.077	16.819	16.515	•000	•000	•000
2100	10.620	25.594	17.225	17.575	•000	•000	•000
2200	10.660	26.089	17.617	18.639	•000	•000	•000
2300	10.700	26.564	17.995	19.707	•000	•000	•000
2400	10.740	27.020	18.359	20.780	•000	•000	•000
2500	10.780	27.459	18.717	21.855	•000	•000	•000
2600	10.820	27.881	19.062	22.935	•000	•000	•000
2700	10.860	28.292	19.396	24.019	•000	•000	•000
2800	10.900	28.687	19.721	25.107	•000	•000	•000
2900	10.940	29.067	20.037	26.200	•000	•000	•000
3000	10.980	29.442	20.344	27.295	•000	•000	•000
3100	11.020	29.801	20.643	28.395	•000	•000	•000
3200	11.060	30.153	20.935	29.499	- 83.425	1.448	- .099
3300	11.100	30.494	21.220	30.607	- 82.962	4.092	- .271
3400	11.140	30.827	21.497	31.719	- 82.486	6.822	- .426
3500	11.180	31.156	21.768	32.835	- 82.007	9.538	- .583
3600	11.220	31.465	22.033	33.955	- 81.596	11.946	- .725
3700	11.260	31.773	22.292	35.079	- 81.148	14.537	- .859
3800	11.300	32.074	22.546	36.207	- 80.705	17.114	- .984
3900	11.340	32.368	22.794	37.339	- 80.266	19.680	- 1.100
4000	11.380	32.656	23.037	38.475	- 79.832	22.240	- 1.215
4100	11.420	32.937	23.275	39.615	- 79.402	24.791	- 1.321
4200	11.460	33.214	23.506	40.759	- 78.978	27.324	- 1.422
4300	11.500	33.483	23.737	41.907	- 78.559	29.852	- 1.517
4400	11.540	33.746	23.962	43.059	- 78.146	32.375	- 1.608
4500	11.580	34.008	24.182	44.215	- 77.737	34.871	- 1.693

IRON (Fe)

(LIQUID)

AT. WT. = 55.85

$$\Delta H_f^{298.15} = 3.138 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{298.15} = 3.650 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{298.15} = 83.679 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{298.15} = 8.195 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1809^\circ \text{K.}$$

$$T_b = 3145.4^\circ \text{K.}$$

Heat of Formation.

The $\Delta H_f^{298.15}$ was obtained from that of the crystal by adding ΔH_m and the difference between $H_{1809}^{298.15}$ and $H_{298}^{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase was that chosen by R. Hultgren, R. L. Orr, F. D. Anderson and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys" John Wiley and Sons, Inc., New York (1963).

Melting Data.

See Fe(c) for details.

Vaporization Data.

The boiling point was calculated from the adopted thermodynamic functions and the chosen heat of sublimation at 298°K. so that the free energy function calculated by integration of the crystal liquid data or by statistical methods from the gas phase were equal at the boiling point.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	5.112	36.949	48.330	98.938	98.938	INFINITE
200	5.483	40.713	43.667	95.785	95.785	-209.329
298	6.137	43.112	40.000	92.177	92.177	-100.722
300	6.138	43.113	40.11	92.500	92.500	-64.487
400	6.103	44.914	36.25	90.488	90.488	-46.367
500	5.949	46.263	33.806	88.219	88.219	-35.499
600	5.785	47.332	32.308	86.273	86.273	-28.241
700	5.603	48.211	31.305	84.505	84.505	-23.261
800	5.420	48.929	30.529	82.844	82.844	-19.241
900	5.241	49.665	29.974	81.318	81.318	-16.269
1000	5.075	50.417	29.511	80.000	80.000	-13.669
1100	4.929	51.185	29.125	78.861	78.861	-11.937
1200	4.799	51.967	28.811	77.885	77.885	-10.597
1300	4.681	52.751	28.561	77.043	77.043	-9.601
1400	4.572	53.534	28.372	76.328	76.328	-8.891
1500	4.471	54.314	28.241	75.728	75.728	-8.366
1600	4.376	55.091	28.161	75.231	75.231	-7.924
1700	4.287	55.862	28.120	74.835	74.835	-7.566
1800	4.202	56.628	28.116	74.538	74.538	-7.281
1900	4.121	57.388	28.140	74.338	74.338	-7.066
2000	4.043	58.141	28.181	74.231	74.231	-6.919
2100	3.968	58.887	28.237	74.216	74.216	-6.839
2200	3.895	59.627	28.307	74.291	74.291	-6.824
2300	3.823	60.361	28.389	74.454	74.454	-6.872
2400	3.751	61.089	28.481	74.704	74.704	-6.981
2500	3.679	61.811	28.583	75.039	75.039	-7.150
2600	3.607	62.527	28.694	75.459	75.459	-7.388
2700	3.535	63.237	28.814	75.964	75.964	-7.694
2800	3.463	63.941	28.943	76.554	76.554	-8.068
2900	3.391	64.639	29.081	77.229	77.229	-8.511
3000	3.319	65.331	29.227	77.989	77.989	-9.024
3100	3.247	66.017	29.381	78.834	78.834	-9.608
3200	3.175	66.697	29.542	79.764	79.764	-10.272
3300	3.103	67.371	29.709	80.779	80.779	-11.024
3400	3.031	68.039	29.882	81.879	81.879	-11.864
3500	2.959	68.701	30.061	83.064	83.064	-12.794
3600	2.887	69.357	30.236	84.334	84.334	-13.814
3700	2.815	70.007	30.417	85.689	85.689	-14.924
3800	2.743	70.651	30.603	87.129	87.129	-16.124
3900	2.671	71.289	30.794	88.654	88.654	-17.414
4000	2.600	71.921	30.990	90.264	90.264	-18.794
4100	2.528	72.547	31.191	91.959	91.959	-20.264
4200	2.456	73.167	31.396	93.739	93.739	-21.824
4300	2.384	73.781	31.605	95.604	95.604	-23.474
4400	2.312	74.389	31.818	97.554	97.554	-25.214
4500	2.240	74.991	32.034	99.589	99.589	-27.044
4600	2.168	75.587	32.253	101.709	101.709	-28.964
4700	2.096	76.177	32.475	103.914	103.914	-30.974
4800	2.024	76.761	32.700	106.204	106.204	-33.074
4900	1.952	77.339	32.927	108.579	108.579	-35.264
5000	1.880	77.911	33.156	111.039	111.039	-37.544
5100	1.808	78.477	33.387	113.584	113.584	-40.014
5200	1.736	79.037	33.620	116.214	116.214	-42.674
5300	1.664	79.591	33.855	118.929	118.929	-45.524
5400	1.592	80.139	34.091	121.729	121.729	-48.564
5500	1.520	80.681	34.328	124.614	124.614	-51.794
5600	1.448	81.217	34.566	127.584	127.584	-55.214
5700	1.376	81.747	34.805	130.639	130.639	-58.824
5800	1.304	82.271	35.045	133.779	133.779	-62.624
5900	1.232	82.789	35.286	136.994	136.994	-66.614
6000	1.160	83.301	35.528	140.284	140.284	-70.794
6100	1.088	83.807	35.771	143.649	143.649	-75.164
6200	1.016	84.307	36.015	147.089	147.089	-79.724
6300	0.944	84.801	36.260	150.604	150.604	-84.474
6400	0.872	85.289	36.506	154.194	154.194	-89.414
6500	0.800	85.771	36.753	157.859	157.859	-94.544
6600	0.728	86.247	36.999	161.599	161.599	-99.864
6700	0.656	86.717	37.246	165.414	165.414	-105.374
6800	0.584	87.181	37.493	169.304	169.304	-111.074
6900	0.512	87.639	37.740	173.269	173.269	-116.964
7000	0.440	88.091	37.987	177.309	177.309	-123.044
7100	0.368	88.537	38.234	181.424	181.424	-129.314
7200	0.296	88.977	38.481	185.614	185.614	-135.774
7300	0.224	89.411	38.728	189.879	189.879	-142.424
7400	0.152	89.839	38.974	194.219	194.219	-149.264
7500	0.080	90.261	39.219	198.634	198.634	-156.294
7600	0.008	90.677	39.464	203.124	203.124	-163.514
7700	0.000	91.087	39.709	207.689	207.689	-170.924
7800	0.000	91.491	39.954	212.329	212.329	-178.524
7900	0.000	91.889	40.199	217.044	217.044	-186.314
8000	0.000	92.281	40.443	221.834	221.834	-194.294
8100	0.000	92.667	40.686	226.699	226.699	-202.464
8200	0.000	93.047	40.928	231.639	231.639	-210.824
8300	0.000	93.421	41.169	236.654	236.654	-219.374
8400	0.000	93.789	41.409	241.744	241.744	-228.114
8500	0.000	94.151	41.648	246.909	246.909	-237.034
8600	0.000	94.507	41.886	252.149	252.149	-246.144
8700	0.000	94.857	42.123	257.464	257.464	-255.444
8800	0.000	95.201	42.359	262.854	262.854	-264.934
8900	0.000	95.539	42.594	268.319	268.319	-274.614
9000	0.000	95.871	42.828	273.859	273.859	-284.484
9100	0.000	96.197	43.061	279.474	279.474	-294.544
9200	0.000	96.517	43.293	285.164	285.164	-304.794
9300	0.000	96.831	43.524	290.929	290.929	-315.234
9400	0.000	97.139	43.754	296.769	296.769	-325.864
9500	0.000	97.439	43.983	302.684	302.684	-336.684
9600	0.000	97.733	44.211	308.674	308.674	-347.694
9700	0.000	98.021	44.438	314.739	314.739	-358.894
9800	0.000	98.303	44.664	320.879	320.879	-370.284
9900	0.000	98.579	44.889	327.094	327.094	-381.864
10000	0.000	98.849	45.113	333.384	333.384	-393.634

Mar. 31, 1965

IRON, MONATOMIC (Fe)

(IDEAL GAS)

AT. WT. = 55.85

Ground State Configuration $5D_4$
 $S_{298.15}^0 = 43.112$ cal. mole⁻¹ deg.⁻¹
 $\Delta H_f^0 = 98.9 \pm 0.4$ kcal. mole⁻¹
 $\Delta H_f^0 = 99.5 \pm 0.4$ kcal. mole⁻¹

Electronic Levels and Multiplicities

E , cm. ⁻¹	g_i	E , cm. ⁻¹	g_i	E , cm. ⁻¹	g_i
0	9	12561	7	19913	5
416	7	12969	5	20020	3
604	5	17550	7	19390	13
878	3	17521	11	43022	412
6928	11	17527	3	47182	427
7377	9	18378	5	53761	405
7728	7	18553	3	57651	405
8986	5	20038	1	53782	433
11976	9	21039	5	57421	482
		21949	27		
		21928	49		
		23143	146		

Heat of Formation.

The heat of formation is the heat of sublimation at 298°K. which was obtained by second and third law analysis of the following vapor pressure data.

Method	Points	Ref.	ΔH , 298.15 2nd law kcal. mole ⁻¹	ΔH , 298.15 3rd law kcal. mole ⁻¹	Drift in 3rd law cal. deg. ⁻¹ mole ⁻¹
Boiling	1	1	—	105.6	—
Boiling	1	2	—	88.1	—
Transport	1	3	—	101.5	—
Langmuir	20	5*	100.0 ± 1.1	99.5	-0.2 ± 0.6
Langmuir	12	6	98.4 ± 1.8	97.3	-0.6 ± 1.2
Langmuir	12	7	101.6 ± 1.8	98.0	-1.1 ± 1.3
Langmuir	9	8*	99.4 ± 1.0	99.8	0.3 ± 0.7
Alloy activities	4	9	101.7 ± 13.5	99.1	-6.6 ± 4.5
Knudsen	12	11*	108.8 ± 1.0	96.8	-7.9 ± 0.8
Langmuir	12	12	105.9 ± 1.2	97.2	-5.9 ± 0.9
Isotope Exchange	10	13*	95.6 ± 5.2	97.3	1.0 ± 3.6
Knudsen	—	14**	99.9	99.0	-0.6
Knudsen	—	15**	98.6	101.0	—
Langmuir	4	16	94.5 ± 0.5	96.8	1.5 ± 0.3

*1 point rejected in statistical test. **Data from equations.

- 1 - O. Ruff and W. Bormann, Z. Anorg. Chem. **89**, 365 (1914) [2723°K.]
- 2 - H. C. Greenwood and M. S. B. Fellow, Proc. Roy. Soc. **83A**, 483 (1910) [2723°K.]
- 3 - E. T. Turkdogan and L. E. Leske, Trans. Met. Soc. AIME, **218**, 1136 (1960) [1873°K.]
- 4 - L. S. Darken and R. W. Ourry, J. Am. Chem. Soc. **69**, 798 (1946) [1873°K.]
- 5 - J. P. Morris, O. R. Zellars, S. L. Payne and R. L. Kipp, U.S.B.M. Report Invest. 5364 (1957) [1810-1889°K.]
- 6 - A. L. Marshall, R. W. Dornie, and F. J. Norton, J. Am. Chem. Soc. **59**, 1161 (1937) [1317-1579°K.]
- 7 - Ref. 6 with temperatures increased by 11 degrees suggested by Ref. 8 [1328-1590°K.]
- 8 - J. W. Edwards, H. L. Johnston and W. E. Dittmar, J. Am. Chem. Soc. **76**, 4729 (1951) [1389-1519°K.]
- 9 - R. Spelaer, A. J. Jacoba and J. W. Sprensk, Trans. Met. Soc. AIME, **215**, 185 (1959) [1725-1928°K.]
- 10 - Yu. V. Kornev, Dokl. Akad. Nauk. SSSR, **93**, 467 (1953) [1464-1623°K.]
- 11 - V. D. Burakov, Vis. Metallov i Metalloved. **5**, 90 (1957) (cast specimen) [1292-1529°K.]
- 12 - Ref. 11 using evaporated specimens on different substrates [1302-1505°K.]
- 13 - I. I. Ivanov - Thesis - Inst. of Metallurgy, Acad. Sci. USSR (1957) [1260-1620°K.]
- 14 - K. M. Nyles and A. T. Aldred, J. Phys. Chem. **68**, 64 (1964) [1450-1650°K.]
- 15 - E. Z. Vintalokin, Dokl. Akad. Nauk. SSSR, **117**, 532 (1957) [1400-1600°K.]
- 16 - H. A. Jones, I. Langmuir and O. M. J. Meckay, Phys. Rev. **30**, 201 (1957) [1270-1580°K.]

The adopted value of 99.5 kcal. mole⁻¹ is based mainly on the work of Refs. 5, 8 and 14, which have the best drift analysis and agreement between second and third law.

Heat Capacities and Entropies.

The electronic levels were taken from C. E. Moore, Natl. Bur. Standards Circ. 467 (1949). Levels above 20,000 cm.⁻¹ were averaged.

Iron Dihydroxide (Fe(OH)₂)

(Crystal) GFW = 89.86174

T, °K	Cp°	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
298	23.200	21.040	21.000	•000	-137.200	-117.599	86.203
300	23.220	21.144	21.000	•043	-137.194	-117.478	85.583
400	24.400	27.987	21.925	2.424	-136.844	-110.958	80.625
500	25.520	33.552	23.711	4.921	-136.452	-104.550	75.690
600	26.600	38.302	25.756	7.527	-136.031	-98.186	70.764
700	27.600	42.480	27.853	10.239	-135.588	-91.912	65.896
800	28.430	46.222	29.919	13.042	-135.157	-85.705	61.413
900	29.050	49.608	31.921	15.918	-134.783	-79.545	57.316
1000	29.490	52.693	33.847	18.846	-134.457	-73.422	53.646
1100	29.760	55.517	35.690	21.810	-134.173	-67.305	49.572
1200	29.900	58.113	37.452	24.793	-133.925	-61.209	45.148
1300	29.960	60.509	39.135	27.787	-133.725	-55.142	40.420
1400	29.980	62.730	40.742	30.784	-133.565	-49.117	35.344
1500	30.000	64.799	42.277	33.783	-133.440	-43.129	30.000



GFW = 89.86174

IRON DIHYDROXIDE (Fe(OH)₂) (CRYSTAL)

ΔH_f° = Unknown
 ΔH_f°_{298.15} = -137.2 ± 0.7 kcal/mol
 ΔH_m° = Unknown
 ΔH_{298.15} = 58.2 kcal/mol

S°_{298.15} = [21 ± 2] gibbs/mol

T_m = Unknown

Heat of Formation.

The heat of combustion of Fe(OH)₂(c), according to the chemical reaction Fe(OH)₂(c) + 1/4 O₂(g) = 1/2 Fe₂O₃(c) + H₂O(l), was determined to be -29.8 ± 0.65 kcal/mol by R. Fricke and S. Rühl, Z. anorg. allgem. chem. 251, 414 (1943). From this data the heat of formation (ΔH_f°_{298.15}) was evaluated to be -137.2 ± 0.7 kcal/mol. which was adopted here.

The enthalpy changes for the following three reactions were determined by J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882 - 1886:

Reaction	ΔH _r ° ₂₉₈ , kcal/mol
1. FeCl ₂ (c) = FeCl ₂ (400 H ₂ O)	-17.9
2. FeCl ₂ (200 H ₂ O) + H ₂ SO ₄ (200 H ₂ O) = FeSO ₄ (200 H ₂ O) + 2 HCl(100 H ₂ O)	-3.6
3. FeSO ₄ (aq.) + 2KOH(aq.) = Fe(OH) ₂ (c) + K ₂ SO ₄ (aq.)	-6.34

Using ΔH_f°_{298.15} = -81.7 kcal/mol for FeCl₂(c) and those for the other compounds in aqueous solution (assuming aq. = 200 H₂O in Reaction 3) obtained from D.D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, National Bureau of Standards, 1965, the heat of formation (298.15°K) for Fe(OH)₂(c) was derived as -135.8 kcal/mol which agrees reasonably with the adopted value.

Heat Capacity and Entropy.

The heat capacities, 298.15 - 700°K, and S°_{298.15} were estimated by comparison with those for FeCl₂(c), CaCl₂(c) and Ca(OH)₂(c). The Cp values above 700°K were obtained by graphical extrapolation of the Cp curve plotted using the above Cp values.

Heat of Sublimation.

The value of ΔH_{298.15} was calculated as the difference between ΔH_f°_{298.15} for Fe(OH)₂(g) and Fe(OH)₂(c).

GFW = 89.86174

IRON DIHYDROXIDE (Fe(OH)₂)

(IDEAL GAS)

OPW = 89.86174

Point Group [C_{2h}]
 $S_{298.15}^\circ = [67.58] \text{ gibbs/mol}$
 $\Delta H_f^\circ = [-77.2 \pm 0.5] \text{ kcal/mol}$
 $\Delta H_f^{298.15} = [-79.0 \pm 0.5] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{ cm}^{-1}$	g_i
0	(5)
[700] (10)	
[2500] (5)	
[4000] (5)	

Vibrational Frequencies and Degeneracies

$\omega_j, \text{ cm}^{-1}$	$\omega_j, \text{ cm}^{-1}$	$\omega_j, \text{ cm}^{-1}$
[2300] (1)	[450] (1)	[800] (1)
[750] (1)	[320] (1)	[700] (1)
[400] (1)	[2600] (1)	[570] (1)

Bond Distance: Fe-O = [1.8] Å

Bond Angle: O-Fe-O = [180]°

Product of the Moments of Inertia: $I_A I_B I_C = [9.368 \times 10^{-115}] \text{ g}^3 \text{ cm}^6$

O-H = [0.96] Å

Fe-O-H = [105]°

 $\sigma = 2$

Heat of Formation

The equilibrium constants, at temperatures between 1300 and 1460°C, for the chemical reaction $\text{Fe}(c) + 2\text{H}_2\text{O}(g) = \text{Fe}(\text{OH})_2(g) + \text{H}_2(g)$, were determined by G. R. Belton and F. D. Richardson, Trans. Faraday Soc. 58, 1562 (1962). Using these data, the enthalpy change ($\Delta H_f^{298.15}$) of the reaction is evaluated to be 35.53 ± 3.0 and 35.57 kcal/mol by the second and third law method, respectively. Based on the third law value for $\Delta H_f^{298.15}$, the heat of formation ($\Delta H_f^{298.15}$) for $\text{Fe}(\text{OH})_2(g)$ is calculated to be $-79 \pm 0.5 \text{ kcal/mol}$.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that for $\text{B}(\text{OH})_2(g)$. The Fe-O bond distance is taken from $\text{FeO}(g)$. The O-H bond distance and Fe-O-H bond angle are estimated from those for $\text{H}_2\text{O}(g)$. The vibrational frequencies, and electronic levels and quantum weights are obtained by comparison with those for $\text{B}(\text{OH})_2(g)$ and $\text{FeCl}_2(g)$, respectively. These values are adjusted to give reasonable second and third law agreements. The three principal moments of inertia are: $I_A = 2.658 \times 10^{-40}$, $I_B = 1.864 \times 10^{-36}$ and $I_C = 1.890 \times 10^{-36} \text{ g cm}^2$.

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	-	3.396	-77.222	-77.222	INFINITE
100	8.787	54.182	80.037	-2.366	-77.968	-77.968	167.542
200	13.193	61.525	69.027	-1.501	-78.604	-78.604	82.066
298	17.090	67.577	67.577	0.000	-79.000	-79.000	53.770
300	17.145	67.683	67.577	0.032	-79.005	-79.005	53.363
400	19.362	72.953	68.281	1.869	-79.130	-79.130	38.956
500	20.585	77.416	69.673	3.871	-79.302	-79.302	30.296
600	21.907	81.245	71.291	5.973	-79.385	-79.385	24.516
700	22.030	84.593	72.587	8.144	-79.422	-79.422	20.516
800	22.588	87.573	74.401	10.377	-79.422	-79.422	17.279
900	23.067	90.261	76.194	12.661	-79.480	-79.480	14.859
1000	23.485	92.714	77.725	14.989	-80.214	-80.214	12.916
1100	23.846	94.970	79.192	17.356	-80.797	-80.797	11.316
1200	24.156	97.058	80.595	19.752	-81.132	-81.132	9.977
1300	24.419	99.002	81.937	22.183	-81.127	-81.127	8.840
1400	24.643	100.820	83.221	24.639	-81.130	-81.130	7.866
1500	24.833	102.527	84.452	27.113	-81.146	-81.146	7.021
1600	24.993	104.135	85.632	29.604	-81.179	-81.179	6.283
1700	25.128	105.651	86.762	32.111	-81.111	-81.111	5.647
1800	25.242	107.084	87.856	34.629	-81.675	-81.675	5.047
1900	25.339	108.461	88.904	37.158	-85.524	-85.524	4.503
2000	25.420	109.763	89.915	39.696	-85.757	-85.757	4.010
2100	25.490	111.005	90.890	42.242	-86.000	-86.000	3.563
2200	25.548	112.192	91.826	44.760	-86.522	-86.522	3.163
2300	25.598	113.329	92.742	47.251	-86.801	-86.801	2.783
2400	25.641	114.420	93.632	49.713	-87.094	-87.094	2.440
2500	25.677	115.467	94.475	52.179	-87.094	-87.094	2.123
2600	25.707	116.475	95.268	54.648	-87.397	-87.397	1.830
2700	25.734	117.445	96.013	57.113	-87.715	-87.715	1.563
2800	25.756	118.382	96.683	59.569	-88.043	-88.043	1.303
2900	25.775	119.286	97.272	62.017	-88.384	-88.384	1.056
3000	25.792	120.160	98.377	65.350	-88.739	-88.739	0.843
3100	25.806	121.006	99.093	67.930	-89.104	-89.104	0.634
3200	25.818	121.825	99.831	70.531	-89.487	-89.487	0.430
3300	25.828	122.620	100.470	73.093	-89.886	-89.886	0.232
3400	25.837	123.391	101.133	75.677	-90.297	-90.297	0.035
3500	25.844	124.140	101.780	78.261	-90.728	-90.728	0.073
3600	25.851	124.868	102.411	80.845	-91.174	-91.174	0.016
3700	25.857	125.574	103.025	83.411	-91.635	-91.635	0.006
3800	25.861	126.266	103.600	85.961	-92.111	-92.111	0.001
3900	25.865	126.938	104.219	88.603	-92.603	-92.603	0.000
4000	25.868	127.593	104.796	91.190	-93.110	-93.110	0.000
4100	25.871	128.232	105.359	93.777	-93.633	-93.633	0.000
4200	25.874	128.854	105.912	96.354	-94.170	-94.170	0.000
4300	25.875	129.464	106.442	98.924	-94.722	-94.722	0.000
4400	25.877	130.059	106.982	101.539	-95.290	-95.290	0.000
4500	25.878	130.641	107.501	104.127	-95.873	-95.873	0.000
4600	25.879	131.209	108.011	106.714	-96.471	-96.471	0.000
4700	25.880	131.763	108.500	109.300	-97.083	-97.083	0.000
4800	25.880	132.311	109.000	111.900	-97.709	-97.709	0.000
4900	25.881	132.844	109.481	114.478	-98.350	-98.350	0.000
5000	25.881	133.367	109.954	117.067	-99.006	-99.006	0.000
5100	25.881	133.880	110.418	119.655	-99.677	-99.677	0.000
5200	25.881	134.385	110.863	122.243	-100.362	-100.362	0.000
5300	25.881	134.876	111.292	124.831	-101.061	-101.061	0.000
5400	25.881	135.356	111.703	127.419	-101.774	-101.774	0.000
5500	25.881	135.834	112.166	130.007	-102.500	-102.500	0.000
5600	25.881	136.300	112.623	132.595	-103.242	-103.242	0.000
5700	25.880	136.754	113.065	135.177	-104.000	-104.000	0.000
5800	25.880	137.208	113.495	137.771	-104.773	-104.773	0.000
5900	25.879	137.651	113.961	140.359	-105.561	-105.561	0.000
6000	25.879	138.086	114.421	142.947	-106.364	-106.364	0.000

June 30, 1966; Dec. 31, 1966

Iron Trihydroxide (Fe(OH)₃)
(Crystal) GFW = 106.86911

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0							
100	24.300	25.000	25.000	0.000	-199.000	-168.634	123.612
200	24.400	25.151	25.000	+0.045	-199.005	-168.446	122.713
300	28.200	32.714	26.006	2.683	-199.100	-158.238	86.457
400	31.000	39.312	28.021	5.695	-198.958	-148.034	64.706
500	33.600	45.205	30.403	8.882	-198.634	-137.877	50.222
600	35.400	50.523	32.404	12.333	-198.192	-127.784	39.896
700	37.000	55.357	35.413	15.956	-197.693	-117.762	32.171
800	38.300	59.792	37.879	19.723	-197.191	-107.799	26.177
900	39.400	63.867	40.277	23.610	-196.779	-97.891	21.394
1000	40.250	67.684	42.598	27.594	-196.517	-88.010	17.486
1200	40.900	71.215	44.838	31.653	-195.994	-78.174	14.237
1300	41.400	74.509	46.995	35.769	-195.103	-68.391	11.498
1400	41.750	77.591	49.071	39.927	-194.210	-58.678	9.160
1500	42.000	80.480	51.070	44.115	-193.331	-49.026	7.143

IRON TRIHYDROXIDE (Fe(OH)₃)
(CRYSTAL) GFW = 106.86911

S°_{298.15} = [25 ± 2] gibbs/mol
Tm = Unknown
ΔHf° = Unknown
ΔHf°_{298.15} = -199 ± 3 kcal/mol
ΔHm° = Unknown

Heat of Formation.

P. Schindler, W. Michaelis and W. Feltrecht, *Helv. Chim. Acta*, **46**, 444 (1963), investigated the solubility of aged Fe(OH)₃ precipitates by determining the Fe⁺⁺⁺ and H⁺ ion concentration of solution in contact with the solid phase. The ion concentration was measured by the EMF method at the constant ionic strength 3M NaClO₄ (solution). The precipitates were investigated by X-ray and electron microscope methods. The equilibrium constant was derived as log [Fe⁺⁺⁺] [H⁺]⁻³ = log K = 3.55 ± 0.1 for amorphous inactive hydroxide at 25°C. From these data the quantity log Ka = -39.1 ± 0.2 was evaluated where Ka is the solubility product of Fe(OH)₃. The Gibbs energy change (ΔHf°_{298.15}) of the reaction Fe(OH)₃(c) = Fe⁺⁺⁺(aq) + 3OH⁻(aq) was calculated to be 53.34 ± 0.27 kcal/mol. Using S°_{298.15} = 70.1 and -2.57 gibbs/mol for Fe⁺⁺⁺(aq) and OH⁻(aq), respectively, and an estimated S°_{298.15}(Fe(OH)₃, c) = 25 gibbs/mol, the enthalpy change (ΔHf°_{298.15}) of the reaction is calculated to be 22.69 kcal/mol, according to the relationship ΔH = ΔG + TΔS. The entropy values for Fe⁺⁺⁺ and OH⁻ ions were obtained from "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952, and NBS Technical Note 270-1 by D. D. Wagman and co-workers, 1965, respectively. Based on ΔHf°_{298.15}(Fe⁺⁺⁺, aq) = -11.4 and ΔHf°_{298.15}(OH⁻, aq) = -54.97 kcal/mol, taken from the same source, the heat of formation (ΔHf°_{298.15}) for Fe(OH)₃(c) was evaluated to be -199 ± 3 kcal/mol, which was adopted here.

The divergent values for solubility product (SP) of Fe(OH)₃ found in the literature may be due not only to the various forms of precipitate, but also to the tendency to form colloidal solutions. The SP values for Fe(OH)₃ were also reported by Evans and Pryor, *J. Chem. Soc.* **5157** (1949); Kriukor and Awsejwitsch, *Z. Elektrochem.* **39**, 884 (1935); Ruff and Hirsch, *Z. Anorg. Chem.* **146**, 338 (1925); Britton, *J. Chem. Soc.* **2148** (1925); and Jellinek and Gordan, *Z. Phys. Chem.* **112**, 207 (1924).

The enthalpy changes (ΔHf°_{298.15}) for the reactions: (1) FeCl₃(aq) + 3NaOH(aq) = Fe(OH)₃(c) + 3NaCl(aq) and (2) FeCl₃(c) = FeCl₃(aq) were determined to be -24.50 and -31.68 kcal/mol, respectively, by J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882 - 1886. Assuming the aqueous solutions all contain 200 mol of H₂O, the heat of formation (ΔHf°_{298.15}) for Fe(OH)₃ was calculated as -196.9 kcal/mol from Reactions (1) and (2). The ΔHf°_{298.15} values for NaOH(aq) and NaCl(aq) were obtained from V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBSRD-NBS-2, National Bureau of Standards, 1965, and JANAP ΔHf°_{298.15} values for NaOH(c) and NaCl(c).

Heat Capacity and Entropy.

The heat capacities, 298.15 - 1000°K, were estimated by comparison with those for Fe₂O₃(c), Fe₂O₃(c) and B(OH)₃(c). The Cp values above 1000°K were obtained by graphical extrapolation. The S°_{298.15}(Fe(OH)₃, c) value was estimated by comparison with that for B(OH)₃(c).

Iron Diodide (FeI₂)

(Crystal) GFW = 309.6558

FeI₂IRON DIODIDE (FeI₂)

(CRYSTAL)

OFW = 309.6558

T, °K	Cp°	gkcal/mol S°	-(C°-H°)/T	— kcal/mol H°-H° ₂₉₈	— kcal/mol ΔH°	ΔG°	log Kp
0							
100	20.000	40.000	4.000	•000	- 25•000	- 26•703	19•574
200	20.000	40.000	•037	- 24•998	- 26•714	- 26•714	19•641
300	20.000	40.000	•086	- 24•914	- 27•161	- 27•161	19•840
400	20.000	40.000	•146	- 24•791	- 28•082	- 28•082	19•974
500	20.120	50.368	42•270	4•049	- 38•982	- 25•793	11•274
600	20.178	54.042	43•935	6•064	- 38•594	- 23•104	8•449
700	22.800	57•588	45•633	8•368	- 37•978	- 20•673	6•454
800	26•000	62•517	47•332	11•034	- 37•519	- 18•620	4•586
900	30•000	67•542	49•031	13•713	- 36•224	- 16•713	2•997
1000	32.760	70.716	52.385	20.164	- 34.175	- 11.607	2.306
1100	33.745	74.665	54.037	24.544	- 32.857	- 9.619	1.752
1200	34.000	78.407	55.225	29.540	- 31.186	- 7.918	1.318
1300	34.000	81.252	56.749	33.754	- 29.540	- 6.008	0.938
1400	34.000	81.252	56.749	33.754	- 27.506	- 4.386	0.639

 $\Delta H_f^\circ =$ Unknown $\Delta H_f^\circ_{298.15} = -25 \pm 4$ kcal/mol $\Delta H_f^\circ = 0.2$ kcal/mol $\Delta H_m^\circ = [10.7]$ kcal/mol $\Delta H_{298.15}^\circ$ (to monomer) = [46] kcal/mol $\Delta H_{298.15}^\circ$ (to dimer) = [52] kcal/mol

Heat of Formation.

The chemical equilibrium of the decomposition of FeI₂(c), 771.15 — 958.15°K, has been studied by W. E. Zaugg and N. W. Gregory, J. Phys. Chem. 70, 488 (1966). Using the reported partial pressures for I₂(g), the enthalpy change ($\Delta H_{298.15}^\circ$) for the reaction FeI₂(c) = Fe(c) + I₂(g) was evaluated by both the second and third law methods to be 39.79 ± 1.0 and 39.69 ± 0.3 kcal/mol, respectively. Based on the third law $\Delta H_{298.15}^\circ$ value, the heat of formation ($\Delta H_{298.15}^\circ$) for FeI₂(c) was calculated as -25 kcal/mol which was adopted here.

The enthalpy change for the reaction FeI₂(c) = Fe⁺⁺(aq) + 2 I⁻(aq) was determined to be -19.48 ± 0.03 kcal/mol by P. Paoletti, A. Sabatini and A. Vacca, Trans. Faraday Soc. 61, 2417 (1965), using a solution calorimetric method. Adopting $\Delta H_{298.15}^\circ = -21.3$ and -13.19 kcal/mol for Fe⁺⁺(aq) and I⁻(aq), respectively, the value of $\Delta H_{298.15}^\circ$ (FeI₂, c) was derived as -28.22 ± 1 kcal/mol. The value of $\Delta H_{298.15}^\circ$ (I⁻, aq) was taken from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Part 1, Technical Note 270-1, National Bureau of Standards, 1965. The value of $\Delta H_{298.15}^\circ$ (Fe⁺⁺, aq) was derived from heats of solution and formation for FeCl₂(c).

The heats of solution of Fe(c), I₂(c) and FeI₂(c) in aqueous Br₂-KBr solution were measured by W. Hieber and A. Moerner, Z. Elektrochem. 40, 287 (1936), using an ice calorimeter. From the results obtained the heat of formation for FeI₂(c) was reported as -30.1 kcal/mol.

Heat Capacity and Entropy.

The heat capacities, 343.15 — 773.15°K, were measured by F. L. Oetting and N. W. Gregory, J. Phys. Chem. 65, 173 (1961). The Cp values at temperatures below 343.15 and above 773.15°K were estimated by graphical extrapolation. The low temperature heat capacities, 11-130°K, were determined by O. Miljutin and E. A. Parfenova, Phys. Trans. Ukrain. Acad. Sci. 9, 81 (1940). These data appear to be inadequate for the derivation of the entropy at 298.15°K. The value of S_{298.15} adopted was calculated from the entropy change, $\Delta S_{298.15}^\circ = 28.7$ eu, for the decomposition reaction FeI₂(c) = Fe(c) + I₂(g), obtained by the second law analysis of the equilibrium pressure data reported by W. E. Zaugg and N. W. Gregory, J. Phys. Chem. 70, 486 (1966).

Transition Data.

A minor transition in the vicinity of 370°C (360-385°C) has been reported by F. L. Oetting and N. W. Gregory, loc. cit. Subsequent studies by T. J. Mydven, Ph. D. Thesis, University of Washington, Seattle, Wash., 1964, have shown the magnitude of the transition to be sensitive to trace amounts of impurities, but the nature of the transition has not been clearly established. A magnetic transition at 10°K was reported by H. Bizette, C. Terrier and B. Taal, Compt. rend. 245, 507 (1957). The ΔH_f° value was evaluated from the heat capacity - temperature plot given by F. L. Oetting and N. W. Gregory, loc. cit.

Melting Data.

Tm was reported by W. Fischer and R. Guehr, Z. anorg. allgem. Chem. 222, 303 (1935). ΔH_m° was estimated by comparison with that for FeBr₂(c).

Heat of Sublimation.

$\Delta H_{298.15}^\circ$ (to monomer) is calculated as the difference between $\Delta H_{298.15}^\circ$ for FeI₂(g) and FeI₂(c). $\Delta H_{298.15}^\circ$ (to dimer) was calculated as the difference between those for FeI₄(g) and 2 FeI₂(c).

FeI₂

Sept. 30, 1966

Iron Diodide (FeI₂)

(Liquid) GFW = 309.6558

FeI₂

GFW = 309.6558

(LIQUID)

IRON DIODIDE (FeI₂)

T, °K	C _p	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0							
100							
200							
298	27.000	46.720	46.720	0.000	-16.066	-20.676	15.156
300	27.000	46.887	46.720	0.000	-16.054	-20.680	15.079
400	27.000	54.654	47.779	2.750	-20.052	-21.028	11.603
500	27.000	60.679	49.779	5.450	-20.550	-21.517	9.403
600	27.000	65.602	52.018	8.150	-20.477	-20.013	7.290
700	27.000	69.764	54.264	10.950	-27.465	-18.084	5.833
800	27.000	73.528	56.512	13.750	-25.712	-17.493	4.779
900	27.000	76.944	58.760	16.550	-24.000	-16.903	3.969
1000	27.000	79.994	60.944	18.950	-25.076	-15.417	3.369
1100	27.000	81.967	62.285	21.650	-24.658	-14.467	2.874
1200	27.000	83.517	64.025	24.350	-24.030	-13.574	2.477
1300	27.000	84.776	65.776	26.750	-23.112	-12.683	2.187
1400	27.000	85.776	67.229	28.750	-21.179	-11.793	1.877
1500	27.000	86.341	68.708	32.450	-21.179	-11.293	1.644
1600	27.000	87.084	70.115	35.150	-20.262	-10.662	1.456
1700	27.000	87.721	71.456	40.850	-19.653	-10.085	1.297
1800	27.000	88.261	72.761	43.250	-21.757	-9.864	1.100
1900	27.000	88.724	73.961	45.950	-21.033	-8.207	1.020
2000	27.000	89.109	75.134	45.950	-21.033	-8.207	1.897

ΔH_{f,298.15}° = [16.969] kcal/mol

ΔH_m° = [10.7] kcal/mol

ΔH_v° = [25.0] kcal/mol

S°_{298.15} = [46.720] gibbs/mol

T_m = 860 ± 2° K

T_b = [1366] °K

Heat of Formation.

The heat of formation (ΔH_{f,298.15}°) was obtained from ΔH_{f,298.15}° (c) by adding ΔH_m° and the difference between H_m° - H_l°_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was assumed to be constant in the temperature range from 298.15 to 2000°K. The value of Cp was calculated on an assumption that Cp = 9.0 gibbs/g-atom for FeI₂(l). The entropy was obtained in a manner analogous to that of the heat of formation.

Vaporization Data.

T_b is the temperature at which the vapor pressure of FeI₂(g) and Fe₂I₄(g) over FeI₂(l) equals one atmosphere. The value of ΔH_v° is derived from the vapor composition and the heats of vaporization of FeI₂(l) to monomer and dimer at T_b.

Iron Dioxide (FeI₂)
(Ideal Gas)

GF_W = 309.6558

IRON DIOXIDE (FeI₂) (IDEAL GAS)

GF_W = 309.6558

FeI₂

Point Group [D_{∞h}]

$\Delta H_f^\circ = [21.4 \pm 3] \text{ kcal/mol}$

$\Delta H_f^{298.15} = [21.0 \pm 3] \text{ kcal/mol}$

$S_{298.15}^\circ = [83.5] \text{ gibbs/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{ cm}^{-1}$ g_i

0 [10] [10] [10] [5]

Vibrational Frequencies and Degeneracies

$\omega_i, \text{ cm}^{-1}$

[140] (1) [32] (2) [280] (1)

Bond Distance: Fe - I = [2.43] Å

Bond Angle: I - Fe - I = [180]°

Rotational Constant: B₀ = [0.0124] cm⁻¹

$\sigma = 2$

Heat of Formation

The chemical equilibria for the reactions: (A) $\text{FeI}_2(\text{g}) = \text{FeI}_2(\text{g})$, (B) $\text{FeI}_2(1) = \text{FeI}_2(\text{g})$, and (C) $\text{Fe}(\text{c}) + 2\text{I}(\text{g}) = \text{FeI}_2(\text{g})$, have been studied by several investigators. Based on the equilibrium pressures reported, the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented in the table below. Using the third law $\Delta H_f^{298.15}$ values, the heats of formation for $\text{FeI}_2(\text{g})$ were calculated. The adopted value for $\Delta H_f^{298.15}(\text{FeI}_2, \text{g})$ is 21.0 ± 3 kcal/mol. The disagreement between the sets of second and third law $\Delta H_f^{298.15}$ values listed in the table may be due to the presence of dimer, $\text{Fe}_2\text{I}_4(\text{g})$, which was not accounted for in deriving the partial pressure of $\text{FeI}_2(\text{g})$. The data obtained from Schoonmaker et al. was adjusted for the presence of dimer.

Investigator	Reaction	Temperature, °K	Method	Second Law Value	Third Law Value	Drift $\Delta H_f^{298.15}$ kcal/mol
Schäfer and Hones ¹	(A)	790.15 - 850.15	Transpiration	41.81	46.58	+ 5.78
	(B)	874.15 - 959.15	Transpiration	43.56	35.58	- 8.75
Schoonmaker et al. ²	(A)	714	Mass Spectrometric	-	46.78	- 21.78
Sime and Gregory ³	(A)	670.0 - 740.0	Torsion - Effusion	45.13	45.70	0.85
Zaugg and Gregory ⁴	(C)	865.15 - 1023.15	Transpiration	-32.53	-28.99	3.75
*The vapor pressure data used for evaluation were those adjusted by W. E. Zaugg and N. W. Gregory, J. Phys. Chem. 70, 430 (1966).						

1. H. Schäfer and M. J. Hones, Z. Anorg. Allgem. Chem. 288, 62 (1956).
2. R. C. Schoonmaker, A. H. Friedman and P. R. Porter, J. Chem. Phys. 31, 1586 (1959).
3. R. J. Sime and N. W. Gregory, J. Phys. Chem. 64, 86 (1960). The vapor pressure equation used for calculation is $\log P_{\text{v}} = -(9760/T) + 11.82$. In the original paper, the term A = 960 should be 9760.
4. W. E. Zaugg and N. W. Gregory, J. Phys. Chem. 70, 430 (1966).

Heat Capacity and Entropy

The molecular structure was assumed to be linear. The Fe-I bond distance was estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The vibrational frequencies were estimated so that the derived Gibbs energy functions yielded second and third law $\Delta H_f^{298.15}$ values in reasonable agreement (see the above table). The electronic levels and quantum weights were estimated from those for $\text{FeCl}_2(\text{g})$ reported by C. W. DeKock and D. N. Gruen, J. Chem. Phys. 44, 439 (1966). The moment of inertia is $2.48844 \times 10^{-37} \text{ g cm}^2$.

FeI₂

Sept. 30, 1966

log Kp

ΔG°

ΔH°

$\text{H}^\circ - \text{H}^\circ_{298}$

$S^\circ - S^\circ_{298}$

C_p°

T, °K

INFINITE

21.365

21.365

- 3.864

INFINITE

68.365

96.158

- 2.770

21.618

21.365

84.851

- 1.412

21.000

6.318

- 4.631

21.000

83.530

- 0.000

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

83.530

Wustite (Fe_{0.947}O) (Crystal)

Mol. Wt. = 68.88651

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	5.577	2.938	23.548	-2.061	-63.846	-62.178	INFINITE
200	10.579	5.419	14.793	-1.005	-63.873	-60.289	135.884
298	11.500	5.764	13.764	-0.000	-63.840	-58.595	65.888
300	11.516	5.785	13.764	-0.021	-63.836	-58.594	42.462
400	12.041	6.224	14.223	1.201	-63.405	-56.908	31.092
500	12.392	6.550	15.104	2.423	-63.187	-55.309	24.174
600	12.674	6.795	15.817	3.676	-63.002	-53.752	19.578
700	12.923	6.967	16.407	4.946	-62.844	-52.140	15.404
800	13.155	7.068	16.893	6.240	-62.776	-50.710	11.704
900	13.377	7.110	17.280	7.567	-62.780	-49.201	8.947
1000	13.593	7.120	17.596	8.936	-62.941	-47.686	6.673
1100	13.805	7.100	17.848	10.305	-63.293	-46.160	5.819
1200	14.013	7.057	18.030	11.606	-63.827	-44.610	5.248
1300	14.220	6.993	18.169	12.840	-64.533	-43.037	4.745
1400	14.426	6.908	18.262	14.040	-65.402	-41.470	4.287
1500	14.630	6.800	18.312	15.193	-66.428	-39.938	3.879
1600	14.834	6.669	18.324	16.306	-67.616	-38.451	3.500
1700	15.036	6.519	18.300	17.376	-68.966	-37.011	3.158
1800	15.235	6.357	18.247	18.400	-70.488	-35.621	2.847
1900	15.424	6.178	18.167	19.384	-72.182	-34.281	2.564
2000	15.600	5.981	18.066	20.320	-74.048	-32.991	2.304
2100	15.753	5.770	17.943	21.213	-76.086	-31.751	2.065
2200	15.890	5.542	17.798	22.063	-78.306	-30.561	1.847
2300	16.014	5.300	17.634	22.878	-80.718	-29.421	1.650
2400	16.127	5.047	17.452	23.660	-83.332	-28.331	1.473
2500	16.230	4.786	17.254	24.410	-86.156	-27.291	1.317

June 30, 1965

Melting Data.

T_m and ΔH_f⁰ were taken from J. P. Coughlin, E. O. King and K. R. Bonnickson, et al. T_m was reported as 1372°C. (1645°K.) by L. S. Darken and R. W. Orry, J. Am. Chem. Soc. **68**, 798 (1946) and as 1369°C. (1642°K.) by J. Chipman and S. Marshall, loc. cit.

WUSTITE (Fe_{0.947}O)

(CRYSTAL)

MOL. WT. = 68.88651

$$\Delta H_f^0 = -63.85 \pm 0.20 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -63.64 \pm 0.20 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 7.49 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 13.764 \pm 0.10 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1650^\circ\text{K.}$$

Heat of Formation.

The chemical equilibria in the Fe-C-O and Fe-H-O systems have been studied by many investigators. Using the reported equilibrium constants for the following two reactions (1) $\text{Fe}_{0.947}\text{O}(c) + \text{CO}(g) = 0.947\text{Fe}(c) + \text{CO}_2(g)$ and (2) $\text{Fe}_{0.947}\text{O}(c) + \text{H}_2(g) = 0.947\text{Fe}(c) + \text{H}_2\text{O}(g)$, the corresponding enthalpy changes (ΔH_f⁰) were evaluated by both the second and third law methods. Based on the third law values for ΔH_f⁰, the ΔH_f⁰ 298.15 (Wüstite, c) values were also calculated. The results obtained are presented as follows.

Investigator	Reaction	Temperature, °K.	Second Law Value	Third Law Value	ΔH _f ⁰ 298.15 ¹
Eastman ¹	(1)	873.2-1273.2	-3.80 ± 0.01	-4.01	-63.63
Eastman - Evans ²	(1)	973.2-1273.2	-4.02 ± 0.01	-4.03	-63.61
Eastman ¹	(2)	873.2-1273.2	6.50 ± 0.12	5.90	-63.70
Eastman - Evans ²	(2)	973.2-1273.2	5.81 ± 0.01	5.07	-62.86
Emmett - Schultz ³	(2)	873.2-1273.2	5.95 ± 0.07	5.82	-63.62
Britzke et al. ⁴	(2)	1123.2-1498.2	-2.25 ± 0.03	4.26	-62.06
Joniny - Murphy ⁵	(2)	1360.0-1646.0	5.01 ± 0.61	6.01	-63.81
Chipman - Marshall ⁶	(2)	1438.2-1633.2	5.03 ± 0.34	5.85	-62.83
Joniny - Murphy ⁵	(2)	1653.2-1787.2	-2.61 ± 0.77	-0.02	-61.87
Britzke et al. ⁴	(2)	1698.0-1700.0	—	0.87	-62.72
Britzke et al. ⁴	(3)	1123.0-1473.0	-129.08 ± 0.18	-126.28	-63.14

¹ E. D. Eastman, J. Am. Chem. Soc. **44**, 975 (1922).

² E. D. Eastman and R. W. Evans, J. Am. Chem. Soc. **46**, 888 (1924). The K_p value at 1273.2°K. for reaction (1) is rejected by a statistical criterion.

³ P. H. Emmett and J. P. Schultz, J. Am. Chem. Soc. **52**, 4268 (1930).

⁴ E. V. Britzke, A. F. Kapustin and T. I. Schachkins, Z. anorg. allgem. Chem. **219**, 287 (1954). The K_p value at 1123°K. for reaction (2) is rejected by a statistical criterion.

⁵ W. E. Joniny and D. W. Murphy, Ind. Eng. Chem. **23**, 394 (1931). The K_p values at 1590 and 1645°K. are rejected by a statistical criterion.

⁶ J. Chipman and S. Marshall, J. Am. Chem. Soc. **62**, 299 (1940).

Britzke et al. also determined the equilibrium pressures for the reaction (3) $1.894 \text{ Fe}(c) + \text{O}_2(g) = 2\text{Fe}_{0.947}\text{O}(c)$. The corresponding ΔH_f⁰ 298.15 for Wüstite was evaluated based on the third law value for ΔH_f⁰ 298.15. The adopted value of ΔH_f⁰ 298.15 (Wüstite, c) is the weighted average of the ΔH_f⁰ 298.15 listed in the above table.

Heat Capacity and Entropy.

The low temperature (54.37-298.16°K.) heat capacities (C_p) were measured by S. S. Todd and K. R. Bonnickson, J. Am. Chem. Soc. **73**, 3894 (1951). The high temperature (298-1650°K.) heat capacities were determined by J. P. Coughlin, E. O. King and K. R. Bonnickson, J. Am. Chem. Soc. **73**, 3891 (1951). The two sets of C_p data were plotted and joined smoothly at 298°K. The C_p values above 1650°K. were obtained by graphical extrapolation. The low temperature (70.7-279.8°K.) C_p's were also reported by R. W. Miller, J. Am. Chem. Soc. **51**, 215 (1929). S_{298.15} was derived from the low temperature heat capacities, based on S_{298.15}⁰ = 0.696 cal. deg.⁻¹ mole⁻¹. S. S. Todd and K. R. Bonnickson, loc. cit. added 0.41 e.u., the amount calculated for completely random distribution of the vacant Fe spaces in the Wüstite lattice. However, the free energy functions derived from S_{298.15}⁰ = 0.696 e.u. give better agreement between second and third law values for ΔH_f⁰ than those derived from S_{298.15}⁰ = 1.11 e.u. Therefore the value 0.41 e.u. was not added here.

Fe_{0.947}O

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	$\log K_p$
0							
200	11.930	14.520		0.000	65.020	60.097	44.050
298							
300	11.950	14.594		0.022	65.015	60.067	43.757
400	12.390	18.094		1.240	64.779	58.454	31.936
500	12.760	20.698		2.407	64.562	56.897	24.868
600	13.120	23.257		3.762	64.375	55.382	20.172
700	13.420	25.703		5.119	64.226	53.896	16.826
800	13.680	28.041		6.477	64.103	52.437	13.875
900	13.930	30.274		7.857	64.003	50.964	12.375
1000	14.190	32.422		9.263	64.138	49.495	10.817
1100	14.396	34.584		10.692	64.668	47.991	9.535
1200	14.600	36.655		12.142	64.605	46.474	7.464
1300	14.800	38.645		13.613	64.483	44.943	5.683
1400	15.000	40.557		15.104	64.360	43.453	4.173
1500	15.151	42.397		16.611	64.147	41.968	3.744
1600	15.300	44.150		18.134	63.932	40.496	3.531
1700	15.445	45.822		19.671	64.010	39.033	3.018
1800	15.576	47.420		21.223	64.083	37.581	2.484
1900	15.724	48.945		22.789	67.652	36.021	4.132
2000	15.850	50.425		24.368	67.380	34.266	3.744

June 30, 1965

FeO

$\Delta H^\circ_f 0$ = Unknown
 $\Delta H^\circ_f 298.15$ = [-65.02] kcal. mole⁻¹
 ΔH°_m = [5.75] kcal. mole⁻¹
 $\Delta H^\circ_g 298.15$ = [121.62] kcal. mole⁻¹

$S^\circ_{298.15}$ = [14.52] cal. deg.⁻¹ mole⁻¹
 T_m = [1850]*°K.

Heat of Formation.

The value of $\Delta H^\circ_f 298.15$ for FeO(c) was derived based on an assumption that at 1650°K., ΔH°_f (FeO, c) = ΔH°_f (FeO, l). From the value $\Delta H^\circ_f 1650$ (FeO, c) = -39.77 kcal. mole⁻¹, $\Delta H^\circ_f 1650$ (FeO, c) was calculated to be -63.97 kcal. mole⁻¹, yielding $\Delta H^\circ_f 298.15$ (FeO, c) = -65.02 kcal. mole⁻¹.

Heat Capacity and Entropy.

The C_p values were estimated assuming C_p (FeO, c) = C_p (Wüstite, c) + 0.053 C_p (Fe, c). The C_p values obtained were plotted. The adopted C_p points were taken from the smoothed C_p curve. $S^\circ_{298.15}$ for FeO(c) was calculated as S° (FeO, c) = S° (Wüstite, c) + 0.053 S° (Fe, c) + ΔS° (mixing) where ΔS° is the entropy of mixing (0.41 cal. deg.⁻¹ mole⁻¹).

Melting Data.

T_m is assumed to be the same as that for Wüstite. The difference between $\Delta H^\circ_f 1650$ for FeO(l) and FeO(c) is ΔH°_m .

Heat of Sublimation.

$\Delta H^\circ_g 298.15$ is calculated as the difference between $\Delta H^\circ_f 298.15$ for FeO(g) and FeO(c).

FeO

MOL. WT. = 71,8464

$$\Delta H_{\text{f}}^{\circ} = [5.75] \text{ kcal. mole}^{-1}$$

$$T_2 = [368.7]^\circ\text{K}.$$

T_d is the temperature at which ΔF_p° equals zero.

T, °K.	C _p ^a	S ^a - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ ^a	ΔH _f ^b	ΔF _f ^b	Log K _p
		cal. mole ⁻¹ deg. ⁻¹		— kcal. mole ⁻¹		
0						
100						
200						
298	11.500	18.029	18.029	• 000	— 59.642	— 55.765
300	11.516	18.100	18.029	• 021	— 59.638	— 55.761
400	12.041	21.489	18.048	1.201	— 59.440	— 54.673
500	12.392	24.215	19.370	2.423	— 59.259	— 53.252
600	12.674	26.500	20.373	3.676	— 59.111	— 52.065
700	12.902	28.386	21.386	4.966	— 59.011	— 50.999
800	13.153	30.213	22.382	6.286	— 58.940	— 49.959
900	13.377	31.776	23.346	7.587	— 59.030	— 48.988
1000	13.593	33.196	24.261	8.936	— 59.252	— 47.418
1100	16.300	34.502	25.133	10.306	— 59.676	— 46.210
1200	16.300	37.223	26.700	11.516	— 44.993	— 45.194
1300	16.300	39.433	27.779	12.666	— 59.936	— 44.194
1400	16.300	38.433	27.579	15.196	— 58.936	— 42.012
1500	16.300	39.558	28.341	16.826	— 58.554	— 41.662
1600	16.300	40.610	29.075	18.456	— 58.332	— 40.331
1700	16.300	41.618	30.765	20.086	— 58.238	— 39.710
1800	16.300	42.523	30.765	21.716	— 58.238	— 39.710
1900	16.300	43.411	31.124	23.346	— 61.518	— 36.819
2000	16.300	44.247	31.759	24.976	— 61.594	— 35.524
2100	16.300	45.042	32.373	26.606	— 61.276	— 34.231
2200	16.300	46.522	33.000	28.236	— 61.106	— 32.945
2300	16.300	47.119	33.490	29.866	— 60.936	— 31.659
2400	16.300	47.219	33.950	31.496	— 60.965	— 30.372
2500	16.300	47.884	34.634	33.126	— 60.875	— 29.118
2600	16.300	48.523	35.136	34.756	— 60.791	— 27.849
2700	16.300	49.733	35.632	36.386	— 60.714	— 26.586
2800	16.300	50.733	36.130	38.016	— 60.630	— 25.324
2900	16.300	50.303	36.632	39.646	— 60.580	— 24.060
3000	16.300	50.856	37.097	41.276	— 60.522	— 22.802
3100	16.300	51.390	37.550	42.906	— 60.471	— 21.543
3200	16.300	52.008	37.921	44.536	— 60.451	— 19.846
3300	16.300	52.608	38.292	46.166	— 60.430	— 18.148
3400	16.300	52.894	38.659	47.796	— 60.457	— 16.450
3500	16.300	53.369	39.247	49.426	— 60.437	— 14.752
3600	16.300	53.828	39.646	51.056	— 60.402	— 13.054
3700	16.300	54.705	40.035	52.686	— 60.359	— 11.356
3800	16.300	55.132	40.407	54.316	— 60.344	— 9.658
3900	16.300	55.545	41.751	55.946	— 60.344	— 7.960
4000	16.300	55.948	41.511	57.576	— 60.344	— 6.262
4100	16.300	55.948	41.507	59.206	— 60.344	— 4.564
4200	16.300	56.740	41.856	60.836	— 60.344	— 2.866
4300	16.300	57.099	42.107	62.466	— 60.344	— 1.168
4400	16.300	57.099	42.531	64.096	— 60.344	— 0.470
4500	16.300	57.465	42.849	65.726	— 60.344	— 0.172
4600	16.300	57.823	43.181	67.356	— 60.344	— 0.172
4700	16.300	58.174	43.466	68.986	— 60.344	— 0.172
4800	16.300	58.517	43.710	70.616	— 60.344	— 0.172
4900	16.300	58.853	44.019	72.246	— 60.344	— 0.172
5000	16.300	59.188	44.407	73.876	— 60.344	— 0.172

IRON OXIDE (FeO)

(IDEAL GAS)

GFW = 71.8464

Ground State Configuration [5s]
 $\Delta H_f^\circ = 60 \pm 5 \text{ kcal/mol}$ $S_{298.15}^\circ = [57.8] \text{ gibbs/mol}$
 $\Delta H_f^{298.15} = 60 \pm 5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[10]
[10000]	[10]
[16000]	[5]

 $\omega_e x_e = 5.0 \text{ cm}^{-1}$
 $\sigma = 1$ $\omega_e = 880.0 \text{ cm}^{-1}$
 $\chi_e = [0.4184] \text{ cm}^{-1}$
 $r_e = [1.8] \text{ \AA}$

Heat of Formation

The heat of formation for FeO(g) is not well established at the present time. The values of ΔH_f° (FeO, g) derived from the following reactions: (1) $\text{FeO(g)} = \text{Fe(g)} + \text{O(g)}$, (2) $\text{FeO(g)} = \text{Fe(g)} + 1/2 \text{O}_2(\text{g})$, and (3) $\text{FeO(l)} = \text{FeO(g)}$, are not in agreement. There are three D° (Fe-O) values reported for reaction (1). The enthalpy change for reaction (2) was evaluated based on the partial pressure data ($P_{\text{FeO}}/P_{\text{O}_2}$) = 0.2 at 1600°C, measured by Washburn⁴, using a mass spectrometric method, U. S. Atomic Energy Commission, UCRL-10991, August 1963, and P_{O_2} = 1.66×10^{-6} atm reported by L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 82, 796 (1960). The enthalpy value for reaction (3) was calculated based on the reported value, $\Delta H_f^{298.15} = 96.096 \text{ kcal/mol}$ determined by Burtsev, Karasev and Smirnov⁵. The results obtained are presented as follows. The value of $\Delta H_f^{298.15}$ for FeO(g) adopted is $60 \pm 5 \text{ kcal/mol}$.

Investigator	Reaction	Method	$\Delta H_f^{298.15}$ kcal/mol	$\Delta H_f^{298.15}$ kcal/mol
1. Herzberg (1950)	(1)	Spectroscopic	111.9	47.2
2. Gaydon (1953)	(1)	Spectroscopic	93.4 ± 23.1	65.7 ± 23.1
3. Lagerqvist and Hult (1953)	(1)	Spectroscopic	99.0 ± 11.6	60.1 ± 11.6
4. Washburn et al. (1963)	(2)	Spectroscopic	99.3 ± 5	59.8 ± 5
5. Burtsev et al. (1964)	(3)	transpiration	111.8	52.2

1. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950.

2. A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., London, 1953.

3. A. Lagerqvist and L. Hult, Z. Naturforsch. 8a, 483 (1953). D° was derived from atomic spectra of Fe produced by acetylene-air flame method.

4. J. Washburn UCRL 10991, August 1963, obtained from L. Brewer, private communication, October 18, 1966.

5. V. T. Burtsev, R. A. Karasev and A. M. Samarin, Fiz.-Khim. Osnovy Proizv. Stali, Akad. Nauk SSSR, Inst. Met., Tr. 5-01 (Shestol) Konf., Moscow, 366 (1961); published in 1964.

Heat Capacity and Entropy

Since the ground state configuration is due to Fe^{++} in a ligand field, it was assumed to be the same as that of $\text{FeCl}_2(\text{g})$ reported by C. W. DeLoock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966). The electronic levels and quantum weights were estimated by comparison with those of $\text{FeCl}_2(\text{g})$. The values of ω_e and $\omega_e x_e$ were taken from G. Herzberg, loc. cit. The bond distance was calculated according to the method suggested by K. M. Ouguenheimer, Proc. Phys. Soc. (London) 58, 456 (1946), assuming FeO(g) as a polar molecule. The value of B_e was calculated by use of the relationship $B_e = (2.79976 \times 10^{-19})/I$ where I is the moment of inertia of FeO(g). The value of χ_e was derived from ω_e , $\omega_e x_e$ and B_e by the method suggested by G. Herzberg, loc. cit. The principal moment of inertia is $6.6899 \times 10^{-39} \text{ g cm}^2$.

June 30, 1965; Sept. 30, 1966

Iron Sulfate (FeSO₄)

GFW = 151.9086

(Crystal)

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	-0.000	0.000	INFINITE	4.008	-219.730	-219.730	INFINITE
100	10.534	10.223	46.561	3.634	-213.311	-213.311	466.101
200	18.865	20.319	30.966	2.429	-221.713	-205.305	224.347
298	24.040	28.909	28.909	0.000	-222.000	-197.176	144.534
300	24.140	29.058	28.910	0.015	-222.002	-197.022	143.531
400	32.430	37.453	20.904	2.652	-222.542	-188.668	103.083
500	40.810	43.085	31.898	5.593	-222.676	-180.178	78.756
600	48.990	48.904	34.257	8.788	-222.578	-171.685	62.536
700	56.570	54.113	36.728	12.180	-222.410	-162.413	50.227
800	63.510	59.769	38.260	15.299	-222.183	-152.837	42.627
900	69.910	63.061	41.618	19.299	-221.843	-142.615	35.498
1000	75.760	66.943	43.960	22.983	-221.411	-132.362	29.808
1100	81.100	70.511	46.213	26.727	-220.863	-122.029	25.159
1200	86.200	73.813	48.377	30.523	-220.210	-111.595	20.526
1300	91.040	76.969	50.464	34.260	-219.463	-101.028	16.028
1400	95.640	79.979	52.464	38.250	-218.539	-90.331	11.524
1500	99.920	82.873	54.358	42.173	-217.459	-80.091	12.835
1600	103.800	85.629	56.196	46.133	-216.270	-70.008	10.737
1700	107.451	88.251	57.984	50.159	-214.983	-60.031	8.931
1800	110.880	90.769	59.734	54.269	-213.593	-50.282	7.259
1900	114.100	93.190	61.450	58.219	-212.108	-40.747	5.780
2000	117.100	95.520	63.120	62.313	-210.521	-30.452	4.452

IRON SULFATE (FeSO₄)

(CRYSTAL)

OPW = 151.9086

ΔHf° = -219.7 ± 2 kcal/mol
 ΔHf°_{298.15} = -222.0 ± 2 kcal/mol
 S°_{298.15} = 28.91 ± 0.3 gibbs/mol
 Td = 944°K

Heat of Formation.

The enthalpy change for the reaction $\text{FeSO}_4(c) = \text{FeSO}_4(110 \text{ H}_2\text{O})$ was determined to be -14.9 kcal/mol by R. de Forcrand, Comp. rend. 156, 20 (1914). Using $\Delta H_f^{\circ} 298.15 = -235.85$ kcal/mol for $\text{FeSO}_4(110 \text{ H}_2\text{O})$, the heat of formation (298.15°K) for $\text{FeSO}_4(c)$ was calculated as -221 kcal/mol. The value of $\Delta H_f^{\circ} 298.15$ ($\text{FeSO}_4(c)$) was estimated based on $\Delta H_f^{\circ} 298.15 = 235.9$ kcal/mol for $\text{FeSO}_4(200 \text{ H}_2\text{O})$ which was derived from the enthalpy change for the reaction $\text{FeCl}_2(200 \text{ H}_2\text{O}) + \text{H}_2\text{SO}_4(200 \text{ H}_2\text{O}) = \text{FeSO}_4(200 \text{ H}_2\text{O}) + 2\text{HCl}(100 \text{ H}_2\text{O})$ measured by J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882-1886. See the $\text{Fe}(\text{OH})_2(c)$ table for details.

The decomposition pressures of $\text{FeSO}_4(c)$ at different temperatures were investigated by J. D'Ans and E. Oreulich. Using their reported partial pressures for $\text{SO}_3(g)$ and $\text{SO}_2(g)$, the enthalpy change for the reaction $2 \text{FeSO}_4(c) = \text{Fe}_2\text{O}_3(c) + \text{SO}_3(g) + \text{SO}_2(g)$ was evaluated by both the second and third law methods. The results obtained are presented in the following table.

Investigator	Temperature, °K	Second Law Value	Third Law Value	ΔHf° _{298.15} kcal/mol
1. J. D'Ans (1905)	753.15 - 908.15	83.2 ± 4.6	82.7 ± 1.1	-222.7
2. E. Oreulich (1927)	887.15 - 971.15	84.8 ± 8.8	80.1 ± 1.4	-221.5
3. B. Neumann and O. Heintke (1937)	833.15 - 862.15	72.4 ± 5.4	75.3 ± 0.5	-219.1

1. J. D'Ans, Dissertation, Darmstadt, 1905. Data quoted by B. Neumann and O. Heintke, loc. cit.
2. E. Oreulich, Z. anorg. Chem. 168, 197 (1927). Only the last seven high temperature points were adopted for evaluation.
3. B. Neumann and O. Heintke, Z. Elektrochem. 43, 246 (1937), based on the last 18 high temperature points adopted.

The decomposition pressures assumed for the same reaction have been determined by B. Neumann and O. Heintke. From their data the partial pressures for $\text{SO}_3(g)$ and $\text{SO}_2(g)$ were evaluated. Using the derived $\text{SO}_3(g)$ and $\text{SO}_2(g)$ partial pressures, the corresponding enthalpy changes for the reaction were calculated by both the second and third law methods. The results obtained are also listed in the same table.

The value of $\Delta H_f^{\circ} 298.15$ for $\text{FeSO}_4(c)$ is selected as -222 ± 2 kcal/mol.

Heat Capacity and Entropy.

The low temperature heat capacities, 53.0-294.9°K, were determined by O. E. Moore and K. K. Kelley, J. Am. Chem. Soc., 64, 2949 (1942). Based on $S^{\circ}_{50.12} = 2.10$ eu, the value of $S^{\circ}_{298.15}$ ($\text{FeSO}_4(c)$) was reported to be 25.71 ± 0.2 eu. Using the free energy functions for $\text{FeSO}_4(c)$ based on this $S^{\circ}_{298.15}$ value, to evaluate the vapor pressure data for Reaction (1), the second and third law values of ΔH_f° were derived as 72.35 ± 7.60 and 86.51 ± 1.26 kcal/mol, respectively. Since the report by Moore and Kelley, loc. cit., did not mention the magnetic entropy contribution, an attempt was made to add 3.20 (= $R \ln 5$) eu to $S^{\circ}_{298.15}$ ($\text{FeSO}_4(c)$) and re-evaluate the decomposition pressure data. The results obtained were better than before (see the paragraph on "Heat of Formation," for details). Therefore the value, $S^{\circ}_{298.15} = 25.71 + 3.2 = 28.91$ eu for $\text{FeSO}_4(c)$, was adopted. The heat capacities above 294.9°K were estimated by comparison with those for $\text{MnSO}_4(c)$. The high temperature heat capacities, 870.3-1082.3°K, were determined by J. C. Southard and C. H. Shomate, J. Am. Chem. Soc. 64, 1770 (1942). The two sets of data were joined smoothly at 298.15°K by use of Shomate-function plot.

Temperature of Decomposition.

Td is the temperature at which the vapor pressure of the gaseous decomposition products equals one atmosphere, which was obtained by graphical interpolation of the decomposition pressure data on $\text{FeSO}_4(c)$, reported by E. Oreulich, loc. cit.

Iron Dioxide, Dimeric (Fe_2I_4)
(Ideal Gas) GFW = 619.3116

T, °K	Cp°	S°	$-(G^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	.000	.000	INFINITE	- 8.133	2.325	2.325	INFINITE
100	28.554	96.669	157.341	- 6.067	2.727	- 3.731	8.154
200	30.887	117.422	132.723	- 3.060	2.534	- 10.151	11.093
298	31.577	129.865	129.865	- .000	2.000	- 16.274	11.929
300	31.382	130.059	129.865	-.058	-	-	-
400	31.561	139.115	131.089	3.206	6.460	- 16.387	11.938
500	31.666	146.168	133.433	6.367	27.695	- 22.134	12.083
600	31.699	151.042	136.051	9.595	23.297	- 24.034	10.505
700	31.744	156.832	138.680	12.707	27.781	- 25.535	9.486
800	31.797	161.074	141.220	15.884	27.085	- 27.436	7.936
900	31.861	164.823	143.638	19.066	28.924	- 28.924	5.937
1000	31.939	168.184	145.927	22.256	29.858	- 30.875	4.457
1100	32.029	171.232	148.091	25.445	31.223	- 32.936	3.749
1200	32.129	174.023	150.138	28.633	32.159	- 34.226	3.226
1300	32.235	176.599	152.075	31.881	32.405	- 35.500	2.774
1400	32.343	178.992	153.914	35.110	32.678	- 36.768	2.383
1500	32.450	181.227	155.661	38.349	32.971	- 38.042	2.042
1600	32.554	183.325	157.325	41.600	33.286	- 39.326	1.740
1700	32.653	185.301	158.913	44.890	33.620	- 40.620	1.473
1800	32.744	187.170	160.431	48.130	34.754	- 41.974	1.223
1900	32.826	188.943	161.886	51.408	42.668	- 43.321	.957
2000	32.900	190.628	163.281	54.695	43.333	- 44.650	.710
2100	32.964	192.235	164.627	57.988	44.002	- 45.977	.483
2200	33.019	193.770	165.912	61.287	44.677	- 47.299	.273
2300	33.065	195.230	167.156	64.596	45.356	- 48.619	.079
2400	33.102	196.647	168.355	67.900	46.042	- 50.000	.000
2500	33.131	197.999	169.514	71.212	46.736	- 51.381	.000
2600	33.152	199.299	170.635	74.526	47.438	- 52.762	.000
2700	33.167	200.550	171.720	77.842	48.140	- 54.143	.000
2800	33.175	201.756	172.771	81.159	48.871	- 55.524	.000
2900	33.176	202.921	173.791	84.477	49.601	- 56.905	.000
3000	33.176	204.045	174.781	87.794	50.344	- 58.286	.000
3100	33.169	205.133	175.742	91.112	51.096	- 59.667	.000
3200	33.159	206.186	176.677	94.430	51.858	- 61.048	.000
3300	33.146	207.206	177.587	97.743	52.630	- 62.429	.000
3400	33.130	208.195	178.473	101.057	53.411	- 63.810	.000
3500	33.112	209.156	179.336	104.369	54.200	- 65.191	.000
3600	33.092	210.088	180.177	107.679	55.000	- 66.572	.000
3700	33.068	210.993	181.000	110.988	55.811	- 67.953	.000
3800	33.048	211.876	181.799	114.296	56.633	- 69.334	.000
3900	33.024	212.734	182.581	117.597	57.466	- 70.715	.000
4000	33.000	213.570	183.345	120.898	58.311	- 72.096	.000
4100	32.975	214.385	184.093	124.197	59.166	- 73.477	.000
4200	32.950	215.180	184.826	127.496	60.033	- 74.858	.000
4300	32.925	215.954	185.538	130.797	60.911	- 76.239	.000
4400	32.900	216.711	186.238	134.098	61.800	- 77.620	.000
4500	32.874	217.450	186.924	137.397	62.700	- 79.001	.000
4600	32.849	218.172	187.595	140.693	63.611	- 80.382	.000
4700	32.824	218.876	188.250	143.988	64.533	- 81.763	.000
4800	32.800	219.560	188.899	147.281	65.466	- 83.144	.000
4900	32.776	220.245	189.531	150.577	66.411	- 84.525	.000
5000	32.752	220.907	190.152	153.874	67.366	- 85.906	.000
5100	32.729	221.555	190.762	157.168	68.333	- 87.287	.000
5200	32.699	222.188	191.368	160.463	69.311	- 88.668	.000
5300	32.669	222.811	191.968	163.758	70.300	- 90.049	.000
5400	32.642	223.424	192.555	167.053	71.300	- 91.430	.000
5500	32.614	224.023	193.132	170.348	72.311	- 92.811	.000
5600	32.586	224.611	193.699	173.643	73.333	- 94.192	.000
5700	32.559	225.188	194.256	176.938	74.366	- 95.573	.000
5800	32.532	225.755	194.803	180.233	75.411	- 96.954	.000
5900	32.505	226.312	195.340	183.528	76.466	- 98.335	.000
6000	32.478	226.859	195.867	186.823	77.533	- 99.716	.000

Sept. 30, 1966

IRON DIOXIDE, DIMERIC (Fe_2I_4) (IDEAL GAS) OPW = 619.3116 Fe_2I_4

Point Group [D_{2h}]
 $S^\circ_{298.15} = 129.9 \text{ gibs/mol}$
 $\Delta H^\circ_f = 2.3 \pm 5 \text{ kcal/mol}$
 $\Delta H^\circ_{298.15} = 2.0 \pm 5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

ϵ , cm ⁻¹	g_i
0	(5)
[4200]	(5)
[6800]	(5)

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
[100] (1)	[70] (1)	[80] (2)
[50] (1)	[90] (1)	[20] (2)
[95] (1)	[105] (1)	[160] (2)

Bond Distance: Fe - I = [2.43] Å

Bond Angle: I - Fe - I_{bridge} = [135]°

Product of the Moments of Inertia: $I_A I_B I_C = [8.7771 \times 10^{-110} \text{ g cm}^6]$

Heat of Formation: $\Delta H^\circ_f = 2.3 \pm 5 \text{ kcal/mol}$

Heat Capacity and Entropy: $S^\circ_{298.15} = 129.9 \text{ gibs/mol}$

Heat of Formation

The chemical equilibrium of the interaction of Fe(c) and I(g) has been studied by a transpiration method by W. E. Zeugs and N. W. Gregory, J. Phys. Chem. **70**, 490 (1966). Using the reported equilibrium constants in the temperature range from 591 to 751°K, the enthalpy change ($\Delta H^\circ_{298.15}$) of the reaction $2\text{Fe(c)} + 4 \text{I(g)} = \text{Fe}_2\text{I}_4\text{(g)}$ was evaluated by both the second and third law method to be -85.3 and -103.76 kcal/mol, respectively. The corresponding values of the heat of formation ($\Delta H^\circ_{298.15}$) for $\text{Fe}_2\text{I}_4\text{(g)}$ were calculated as +16.9 and -1.6 kcal/mol.

Mass spectrometric and Knudsen effusion techniques have been used to study the vaporization of $\text{FeI}_2\text{(c)}$ by R. C. Schoonmaker, A. H. Friedman and R. P. Porter, J. Chem. Phys. **31**, 1568 (1959). Using the reported vapor pressure, $P = 1.21 \times 10^{-6}$ atm. at 714°K for $\text{Fe}_2\text{I}_4\text{(g)}$, the enthalpy change ($\Delta H^\circ_{298.15}$) for the reaction $2 \text{FeI}_2\text{(c)} = \text{Fe}_2\text{I}_4\text{(g)}$ was evaluated by the third law method as 52.8 kcal/mol, yielding $\Delta H^\circ_{298.15} = 2.8 \text{ kcal/mol}$ for $\text{Fe}_2\text{I}_4\text{(g)}$. The adopted value of $\Delta H^\circ_{298.15}$ for $\text{Fe}_2\text{I}_4\text{(g)}$ is $2.0 \pm 5 \text{ kcal/mol}$.

Heat Capacity and Entropy

The molecular structure was assumed to be the same as that assumed for $\text{FeBr}_4\text{(g)}$. The Fe-I bond distance was estimated from that in $\text{FeI}_2\text{(g)}$ molecule. Four vibrational frequencies (ν_i), i.e. $i = 2, 4, 5$ and 6 , were estimated by comparison with those for $\text{K}_2\text{I}_2\text{(g)}$, calculated by J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960). The other frequency values were estimated from those for $\text{FeI}_2\text{(g)}$. The electronic levels and quantum weights were estimated from those for $\text{FeI}_2\text{(g)}$. The three principal moments of inertia are: $I_A = 1.2442 \times 10^{-5}$, $I_B = 7.7996 \times 10^{-37}$ and $I_C = 9.0439 \times 10^{-37} \text{ g cm}^2$.

Fe_2I_4

Hematite (Fe₂O₃)

(Crystal) Mol. Wt. = 159.6922

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	7.528	3.492	12.256	38.192	-3.719	-195.757	-195.757	INFINITE
200	18.300	12.256	22.976	34.470	-196.783	-196.783	-196.783	416.560
298	24.800	20.889	30.889	22.976	-197.321	-197.321	-197.321	201.255
300	24.900	21.043	20.889	20.889	∞	-197.300	-177.719	130.265
400	28.710	28.752	21.915	2.735	-197.296	-197.296	-197.296	129.374
500	31.500	35.469	23.968	2.735	-196.925	-196.925	-196.925	93.470
600	33.740	41.713	26.390	9.014	-196.855	-196.855	-196.855	57.697
700	35.715	47.513	28.404	12.470	-196.804	-196.804	-196.804	57.697
800	37.485	51.679	31.466	16.171	-196.764	-196.764	-196.764	30.923
900	39.792	56.248	34.968	20.051	-196.735	-196.735	-196.735	34.035
1000	42.000	60.440	38.415	24.025	-196.719	-196.719	-196.719	29.364
1100	44.200	64.260	41.713	27.505	-196.688	-196.688	-196.688	25.522
1200	46.400	67.692	44.968	30.968	-196.622	-196.622	-196.622	22.316
1300	48.600	70.713	48.171	34.470	-196.577	-196.577	-196.577	19.084
1400	50.800	73.429	51.429	37.578	-196.538	-196.538	-196.538	15.279
1500	53.000	75.850	54.686	41.105	-196.524	-196.524	-196.524	11.872
1600	55.200	77.977	57.977	44.550	-196.512	-196.512	-196.512	8.858
1700	57.400	79.800	61.171	47.977	-196.500	-196.500	-196.500	6.157
1800	59.600	81.429	64.429	51.429	-196.488	-196.488	-196.488	3.841
1900	61.800	82.850	67.686	54.886	-196.484	-196.484	-196.484	1.895
2000	64.000	84.293	71.171	58.429	-196.477	-196.477	-196.477	0.157
2100	66.200	85.713	74.686	61.968	-196.468	-196.468	-196.468	7.157
2200	68.400	87.129	78.171	65.523	-196.458	-196.458	-196.458	5.354
2300	70.600	88.543	81.686	69.058	-196.448	-196.448	-196.448	3.859
2400	72.800	90.000	85.171	72.599	-196.437	-196.437	-196.437	2.316
2500	75.000	91.429	88.686	76.147	-196.427	-196.427	-196.427	0.859

Fe₂O₃HEMATITE (Fe₂O₃)

(CRYSTAL)

MOL. WT. = 159.6922

$$\Delta H_f^o = -195.8 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o \text{ 298.15} = -197.3 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 20.889 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_d = 1735^\circ\text{K.}$$

Heat of Formation.

The chemical equilibria for the reaction $4\text{Fe}_3\text{O}_4(c) + \text{O}_2(g) = 6\text{Fe}_2\text{O}_3(c)$ have been studied by several investigators. From the reported data the corresponding values of ΔH_f^o 298.15 and ΔH_f^o 298.15 (Fe₂O₃, c) were evaluated. The results obtained are given as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	ΔH_f^o 298.15 [*] kcal. mole ⁻¹
Tretyskov and Khomyakov ¹	1373-1728	-106.32 ± 0.19	-111.05	-197.11
Schmahl ²	1583-1683	-123.95 ± 1.37	-112.94	-197.42
Smitten ³	1373-1673	-117.68 ± 0.38	-114.25	-197.64
Darkey and Gurry ⁴	1725	-110.29	—	-196.98

^{*}Calculation based on the third law values for ΔH_f^o 298.15^{*}.

¹ Y.D. Tretyskov and K. O. Khomyakov, Russ. J. Inorg. Chem. **7**, 628 (1962).

² N. G. Schmahl, Z. Elektrochem. **47**, 821 (1941).

³ J. Smitten, J. Am. Chem. Soc. **73**, 4877 (1951).

⁴ L. S. Darkey and R. W. Gurry, J. Am. Chem. Soc. **68**, 798 (1946). ΔH_f^o 298.15 was calculated based on ΔH_f^o 1725 = -54.5 kcal. mole⁻¹.

The value of ΔH_f^o 298.15 adopted for Fe₂O₃(c) is the weighted average of the ΔH_f^o 298.15 values listed in the above table.

Heat Capacity and Entropy.

The low temperature (5.58-345.42°K.) heat capacities were determined by F. Gronvold and E. F. Westrum, Jr., J. Am. Chem. Soc. **81**, 1780 (1959). The high temperature (298-1750°K.) C_p values were obtained from J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Am. Chem. Soc. **73**, 3691 (1951). The two sets of data were plotted and joined smoothly at 298°K. The C_p values above 1750°K. were obtained by graphical extrapolation. The heat capacities of Fe₂O₃(c) have also been reported by G. G. Brown and C. C. Furnas, Trans. Am. Inst. Chem. Eng. **18**, 309 (1926), 0-650°C, and G. S. Parks and K. K. Kelley, J. Phys. Chem. **30**, 47 (1926), 68-289°K. $S_{298.15}^o$ for Fe₂O₃(c) was derived from the smoothed C_p data, based on $S_5^o = 0.0003$ e.u. J. P. Coughlin, E. G. King and K. R. Bonnickson, loc. cit. measured the heat-content for hematite and found two anomalies, presumably of magnetic nature, at about 950 and 1050°K., respectively. Both appear to involve maxima in the heat-capacity curves rather than isothermal heats of transformation. The complex magnetic properties at low temperatures were discussed by F. Gronvold and E. F. Westrum, Jr., loc. cit. No heat capacity anomaly was observed at the magnetic transition about 250°K. The Curie points of the antiferromagnetic α -Fe₂O₃ were reported by A. Aharoni, E. H. Frei and M. Schieber, Phys. Rev. **127**, 439 (1962) and J. Liekeza and A. C. D. Chaklader, Phys. Rev. Letters, **13**, 866 (1965).

Temperature of Decomposition.

T_d is the temperature at which $\Delta F_f^o = 0$ for the reaction $6\text{Fe}_3\text{O}_4(c) = 4\text{Fe}_2\text{O}_3(c) + \text{O}_2(g)$. In other words, Fe₂O₃(c) decomposes into Fe₃O₄(c) and O₂(g) at 1735°K.

Fe₂O₃

(CRYSTAL)

DIIRON TRISULFATE (Fe₂(SO₄)₃)

OFW = 399.8788

T, °K	Cp°	S°	-(G°-H° _{298.15})/T	H°-H° _{298.15}	ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	63.270	73.500	73.500	•000	- 617.350	- 340.882	396.477
300	63.540	73.892	73.501	.117	- 617.363	- 340.408	393.686
400	73.380	93.570	76.117	6.981	- 619.314	- 314.624	281.178
500	81.090	110.809	91.967	14.721	- 626.124	- 286.343	213.454
600	86.830	126.125	87.575	32.130	- 620.276	- 261.962	168.270
700	90.990	139.837	94.079	52.031	- 620.021	- 235.521	135.976
800	93.990	152.193	100.584	41.287	- 658.764	- 413.004	112.827
900	96.090	163.388	106.950	50.794	- 657.407	- 382.362	92.850
1000	97.810	173.604	113.112	60.492	- 656.308	- 351.860	76.899
1100	99.250	182.995	119.044	70.346	- 655.567	- 321.449	63.866
1200	100.540	191.687	124.740	80.337	- 654.322	- 291.136	53.023
1300	101.700	199.781	130.205	90.450	- 652.332	- 260.847	43.869
1400	102.750	207.357	135.448	100.672	- 650.313	- 230.619	36.049
1500	103.750	214.480	140.487	110.968	- 648.283	- 201.038	29.241
1600	104.700	221.207	145.319	121.421	- 646.184	- 171.287	23.397
1700	105.600	227.581	149.972	131.936	- 644.658	- 141.657	18.211
1800	106.490	233.642	154.453	142.541	- 642.719	- 112.124	13.614
1900	107.330	239.422	158.774	153.232	- 640.102	- 82.326	9.470
2000	108.180	244.944	162.946	164.007	- 636.192	- 52.610	5.749

ΔHf° = Unknown

ΔHf°_{298.15} = -617.35 ± 0.40 kcal/mol

S°_{298.15} = [73.5 ± 2] gibbs/mol

Td = 1451°K

Heat of Formation.

The enthalpy change (ΔHf°_{298.15}) for the chemical reaction Fe₂O₃(c) + 3H₂SO₄(14.855 H₂O) = Fe₂(SO₄)₃(c) + 3H₂O(l) was measured to be 8.54 ± 0.18 kcal/mol by solution calorimetry by R. Barany and L. H. Idami, U. S. Bur. Mines RI 6887, 1955. Using ΔHf°_{298.15} = -211.178 kcal/mol for H₂SO₄(14.855 H₂O) and -68.315 kcal/mol for H₂O(l), obtained from "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, by D. D. Wagman and coworkers, National Bureau of Standards, 1965, and -197.3 kcal/mol for Fe₂O₃(c), the heat of formation (ΔHf°_{298.15}) for Fe₂(SO₄)₃(c) was evaluated as -617.35 ± 0.40 kcal/mol which was adopted here.

The equilibrium pressures for the decomposition of Fe₂(SO₄)₃(c) have been determined by several investigators at different temperatures. The chemical reactions involved are: (1) Fe₂(SO₄)₃(c) = Fe₂O₃(c) + 3SO₃(g) and (2) SO₃(g) = SO₂(g) + 0.5 O₂(g). However, the measured pressure of the chemical equilibrium is the total pressure of three partial pressures, namely, P_{SO₃}, P_{SO₂}, and P_{O₂}. In order to calculate the enthalpy change of Reaction (1), the partial pressures of SO₃(g) were evaluated from the total vapor pressure data at each temperature. Based on the derived values for P_{SO₃}, the ΔHf°_{298.15} value for Reaction (1) was calculated by both the second and third law methods. The results obtained are presented in the following table. The ΔHf°_{298.15} (Fe₂(SO₄)₃, c) values were derived, using the third law ΔHf°_{298.15}. These determinations were not given any weight.

Investigator	Temperature, °K	Second Law Value	Third Law Value	Drift	ΔHf° _{298.15} kcal/mol
1. Keppeler and D'Ana (1908)	753.15 - 1013.15	136.8 ± 0.5	139.9 ± 0.5	3.4 ± 0.6	-621.0
2. Wöhler, et al. (1908)	826.15 - 980.15	114.2 ± 6.2	133.1 ± 2.3	19.2 ± 6.9	-614.2
3. Bodenstern and Suzuki (1910)	903.65 - 997.15	140.7 ± 6.6	139.1 ± 1.3	-1.2 ± 7.1	-620.2
4. Wöhler and Ordnzweig (1913)	909.15 - 984.15	155.1 ± 1.3	135.5 ± 1.3	-20.4 ± 1.4	-616.6
5. Neumann and Heintke (1937)	793.15 - 973.15	136.4 ± 2.3	136.2 ± 1.2	-1.2 ± 2.6	-617.3
6. Warner and Ingraham (1960)	903.15 - 997.15	133.9 ± 2.6	135.4 ± 0.5	1.7 ± 2.7	-616.5

1. O. Keppeler and J. D'Ana, Z. physik. Chem. 82, 89 (1908).
2. L. Wöhler, W. Plüddemann and P. Wöhler, Ber. Deut. Chem. Gesell. 41, 703 (1908).
3. M. Bodenstern and T. Suzuki, Z. Elektrochem. 16, 912 (1910).
4. L. Wöhler and M. Ordnzweig, Ber. Deut. Chem. Gesell. 43, 1587 (1913).
5. B. Neumann and O. Heintke, Z. Elektrochem. 43, 246 (1937).
6. N. A. Warner and T. R. Ingraham, Can. J. Chem. 38, 2196 (1960).

The decomposition pressures of Fe₂(SO₄)₃(c) have also been investigated by: M. Ordnzweig, Ph. D. dissertation, Darmstadt, Germany, 1913, 793-994°K; R. P. Blanka, Ph. D. dissertation, University of Melbourne, Australia, 1961, 845 - 978°K; and T. R. Ingraham, Internal Rept. EMT-53-17, Department of Mines and Technical Surveys, Ottawa, Canada, 1963, 856-995°K. These data together with some of the data mentioned previously were critically reviewed by H. H. Kellogg, Trans. AIME, 230, 1622 (1964).

Heat Capacity and Entropy.

The heat capacities were estimated by comparison with those for FeSO₄(c), assuming their average specific heats, Gibbs/g, to be the same. The value of S°_{298.15} was estimated so that the second and third law ΔHf°_{298.15} values, derived from decomposition pressure data, are in reasonable agreement.

June 30, 1966

Temperature of Decomposition.

Td is the temperature at which the total pressure of the gaseous products equals one atmosphere, which was obtained by graphical extrapolation of the decomposition pressure data measured by Warner and Ingraham, loc. cit.

Magnetite (Fe₃O₄)

(Crystal)

Mol. wt. = 231.5386

Fe₃O₄

MOL. WT. = 231.5386

(CRYSTAL)

MAGNETITE (Fe₃O₄)

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	(H° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔG _f ⁰	Log K _p
0	0.000	INFINITE	INFINITE	5.873	-266.398	-266.398	-266.398	INFINITE
100	13.464	6.599	60.756	5.416	-267.676	-267.676	-259.592	567.310
200	27.172	17.772	17.772	5.151	-268.017	-268.017	-251.358	274.659
298	35.190	34.720	34.720	5.000	-268.150	-268.150	-243.151	178.225
300	35.300	34.938	34.720	0.655	-267.894	-267.894	-243.038	177.044
400	40.900	45.878	36.174	3.881	-267.378	-267.378	-234.820	128.294
500	45.980	55.555	39.100	8.228	-266.518	-266.518	-228.772	99.117
600	50.800	64.364	42.586	13.067	-265.370	-265.370	-218.926	79.760
700	55.620	72.557	46.789	18.388	-263.981	-263.981	-211.790	65.945
800	60.440	80.299	50.060	24.191	-262.378	-262.378	-205.674	55.653
900	65.260	87.696	53.834	30.476	-260.649	-260.649	-199.661	47.754
1000	68.000	92.751	57.477	37.276	-260.974	-260.974	-189.541	41.422
1100	68.000	97.328	60.895	40.076	-261.977	-261.977	-182.336	36.225
1200	68.000	101.504	64.108	44.876	-262.362	-262.362	-175.906	31.888
1300	68.000	105.347	67.134	49.676	-261.745	-261.745	-167.849	28.217
1400	68.000	108.904	69.992	54.476	-261.190	-261.190	-160.646	25.077
1500	68.000	112.215	72.668	59.276	-260.691	-260.691	-153.483	22.361
1600	68.000	115.311	75.266	64.076	-260.252	-260.252	-146.350	19.989
1700	68.000	118.223	77.708	68.876	-260.741	-260.741	-139.227	17.898
1800	68.000	120.967	80.036	73.676	-260.492	-260.492	-132.076	16.036
1900	68.000	123.562	82.259	78.476	-260.411	-260.411	-124.930	14.306
2000	68.000	126.024	84.386	83.276	-260.481	-260.481	-117.827	12.744
2100	68.000	128.366	86.435	88.076	-260.701	-260.701	-109.853	11.328
2200	68.000	130.599	88.383	92.876	-261.077	-261.077	-101.077	10.041
2300	68.000	132.733	90.265	97.676	-261.523	-261.523	-93.296	8.865
2400	68.000	134.776	92.077	102.476	-262.033	-262.033	-85.497	7.785
2500	68.000	136.735	93.825	107.276	-262.607	-262.607	-77.685	6.791
2600	68.000	138.618	95.512	112.076	-263.241	-263.241	-69.867	5.873
2700	68.000	140.429	97.142	116.876	-263.939	-263.939	-62.033	5.021
2800	68.000	142.175	98.719	121.676	-264.699	-264.699	-54.185	4.229
2900	68.000	143.859	100.247	126.476	-265.521	-265.521	-46.325	3.491
3000	68.000	145.486	101.728	131.276	-266.405	-266.405	-38.448	2.801

1 R. Prigogine, K. Walter and W. Lohrer, Z. Elektrochem. 47, 487 (1941). The two ΔH_f⁰ 298.15 values listed are the average values of three separate results derived from three sets of experimental data.

2 E. D. Eastman, J. Am. Chem. Soc. 44, 975 (1922).

3 E. D. Eastman and R. M. Evans, J. Am. Chem. Soc. 46, 888 (1924).

4 P. H. Emmett and J. P. Schultz, J. Am. Chem. Soc. 52, 4268 (1930).

5 O. N. Salomon, J. Phys. Chem. 65, 550 (1961).

The enthalpy change of the reaction Fe₃O₄(c) + 0.8215 Fe(c) + 0.5787 O₂(g) = 0.5895 Fe₃O₄(c) has been determined by O. L. Humphrey, E. O. King and K. K. Kelley, U. S. Bur. Mines RI 4870 (1952). Based on ΔH_f⁰ 298.15 = -93.45 kcal. mole⁻¹ (average of two separate values derived from two experimental determinations) and ΔH_f⁰ 298.15 (Wüster, c) = -63.64 kcal. mole⁻¹, the value of ΔH_f⁰ 298.15 (Fe₃O₄, c) was calculated as -266.5 kcal. mole⁻¹. The enthalpy change, ΔH_f⁰ 298.15 = 4.33 kcal. mole⁻¹, for the reaction 3Fe(c) + 4CO₂(g) = Fe₃O₄(c) + 4CO(g) was reported by L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 68, 798 (1946). The corresponding ΔH_f⁰ 298.15 (Fe₃O₄, c) was evaluated as -266.22 kcal. mole⁻¹. The adopted value of ΔH_f⁰ 298.15 for Fe₃O₄(c) is selected as -267.9 ± 0.2 kcal. mole⁻¹.

Heat Capacity and Entropy.

The low temperature (60.5-299.7°K.) heat capacities were reported by R. W. Millar, J. Am. Chem. Soc. 51, 215 (1929). The high temperature (298-1800°K.) heat capacities were obtained from J. P. Coughlin, E. O. King and K. R. Bonnickson, J. Am. Chem. Soc. 73, 3891 (1951). These two sets of data were plotted and joined smoothly at 298°K. The C_p values above 1800°K. were obtained by graphical extrapolation. Heat capacities (90-295°K.) for Fe₃O₄(c) were also reported by O. S. Parks and K. K. Kelley, J. Phys. Chem. 50, 47 (1926). S_{298.15} (Fe₃O₄, c) was derived from the smoothed C_p data mentioned previously, using S_{4.7} = 0.969 e.u. J. P. Coughlin, E. O. King and K. R. Bonnickson, loc. cit. measured the heat-content for magnetite and found a magnetic anomaly around 880°K., corresponding to a maximum in heat capacity. A maximum heat capacity of 37.1 cal. deg.⁻¹ mole⁻¹ at 114.15°K. was also reported by R. W. Millar, loc. cit.

Melting Data.

T_m and ΔH_m⁰ were obtained from L. S. Darken and R. W. Gurry, loc. cit.

June 30, 1965

Fe₃O₄

HYDROGEN, MONATOMIC (H)

(IDEAL GAS)

AT. WT. = 1.00797

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H°)/T	III°-H° ₂₉₈ Kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0	∞	∞	∞	∞	∞	∞
100	4.968	21.965	1.481	51.631	51.631	INFINITE
200	4.968	21.965	1.481	51.631	51.631	INFINITE
300	4.968	21.965	1.481	51.631	51.631	INFINITE
400	4.968	21.965	1.481	51.631	51.631	INFINITE
500	4.968	21.965	1.481	51.631	51.631	INFINITE
600	4.968	21.965	1.481	51.631	51.631	INFINITE
700	4.968	21.965	1.481	51.631	51.631	INFINITE
800	4.968	21.965	1.481	51.631	51.631	INFINITE
900	4.968	21.965	1.481	51.631	51.631	INFINITE
1000	4.968	21.965	1.481	51.631	51.631	INFINITE
1100	4.968	21.965	1.481	51.631	51.631	INFINITE
1200	4.968	21.965	1.481	51.631	51.631	INFINITE
1300	4.968	21.965	1.481	51.631	51.631	INFINITE
1400	4.968	21.965	1.481	51.631	51.631	INFINITE
1500	4.968	21.965	1.481	51.631	51.631	INFINITE
1600	4.968	21.965	1.481	51.631	51.631	INFINITE
1700	4.968	21.965	1.481	51.631	51.631	INFINITE
1800	4.968	21.965	1.481	51.631	51.631	INFINITE
1900	4.968	21.965	1.481	51.631	51.631	INFINITE
2000	4.968	21.965	1.481	51.631	51.631	INFINITE
2100	4.968	21.965	1.481	51.631	51.631	INFINITE
2200	4.968	21.965	1.481	51.631	51.631	INFINITE
2300	4.968	21.965	1.481	51.631	51.631	INFINITE
2400	4.968	21.965	1.481	51.631	51.631	INFINITE
2500	4.968	21.965	1.481	51.631	51.631	INFINITE
2600	4.968	21.965	1.481	51.631	51.631	INFINITE
2700	4.968	21.965	1.481	51.631	51.631	INFINITE
2800	4.968	21.965	1.481	51.631	51.631	INFINITE
2900	4.968	21.965	1.481	51.631	51.631	INFINITE
3000	4.968	21.965	1.481	51.631	51.631	INFINITE
3100	4.968	21.965	1.481	51.631	51.631	INFINITE
3200	4.968	21.965	1.481	51.631	51.631	INFINITE
3300	4.968	21.965	1.481	51.631	51.631	INFINITE
3400	4.968	21.965	1.481	51.631	51.631	INFINITE
3500	4.968	21.965	1.481	51.631	51.631	INFINITE
3600	4.968	21.965	1.481	51.631	51.631	INFINITE
3700	4.968	21.965	1.481	51.631	51.631	INFINITE
3800	4.968	21.965	1.481	51.631	51.631	INFINITE
3900	4.968	21.965	1.481	51.631	51.631	INFINITE
4000	4.968	21.965	1.481	51.631	51.631	INFINITE
4100	4.968	21.965	1.481	51.631	51.631	INFINITE
4200	4.968	21.965	1.481	51.631	51.631	INFINITE
4300	4.968	21.965	1.481	51.631	51.631	INFINITE
4400	4.968	21.965	1.481	51.631	51.631	INFINITE
4500	4.968	21.965	1.481	51.631	51.631	INFINITE
4600	4.968	21.965	1.481	51.631	51.631	INFINITE
4700	4.968	21.965	1.481	51.631	51.631	INFINITE
4800	4.968	21.965	1.481	51.631	51.631	INFINITE
4900	4.968	21.965	1.481	51.631	51.631	INFINITE
5000	4.968	21.965	1.481	51.631	51.631	INFINITE
5100	4.968	21.965	1.481	51.631	51.631	INFINITE
5200	4.968	21.965	1.481	51.631	51.631	INFINITE
5300	4.968	21.965	1.481	51.631	51.631	INFINITE
5400	4.968	21.965	1.481	51.631	51.631	INFINITE
5500	4.968	21.965	1.481	51.631	51.631	INFINITE
5600	4.968	21.965	1.481	51.631	51.631	INFINITE
5700	4.968	21.965	1.481	51.631	51.631	INFINITE
5800	4.968	21.965	1.481	51.631	51.631	INFINITE
5900	4.968	21.965	1.481	51.631	51.631	INFINITE
6000	4.968	21.965	1.481	51.631	51.631	INFINITE

Dec. 31, 1980; Sept. 30, 1985

Ground State Configuration $1s^2$

$S_{298.15}^\circ = 27.392 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^\circ = 51.631 \pm 0.001 \text{ kcal. mole}^{-1}$

$\Delta H_f^\circ = 52.100 \pm 0.001 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

E_1	E_2
0.000	2
82258.907	2
82258.942	2
82259.272	4
97492.198	2
97492.208	2
97492.306	4
97492.342	6

Heat of Formation

The heat of formation was calculated from $D_0^\circ(\text{H}_2) = 36113.0 \pm 0.3 \text{ cm.}^{-1}$, reported by G. Herzberg and A. Monfilla, J. of Molecular Spectroscopy 5, 482 (1960). This value was measured more precisely than the value $D_0^\circ(\text{H}_2) = 36116 \pm 6 \text{ cm.}^{-1}$ by H. Boulier, Z. Phys. Chem. B23, 315 (1935).

Heat Capacity and Entropy

Electronic levels taken from C. E. Moore, Natl. Bur. Standards (U. S.) Circ. 467 (1949).

Proton (H⁺)
(Ideal Gas)

GF_W = 1.00742

T, °K	C _p ^o	S ^o - (C _p ^o - H ^o ₂₉₈)/T	H ^o - H ^o ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0						
100	4.968	26.012	26.012	367.186	362.596	-265.790
200	4.968	26.043	26.012	367.198	362.567	-264.130
300	4.968	26.072	26.012	367.184	362.567	-264.130
400	4.968	26.097	26.012	367.184	362.567	-264.130
500	4.968	26.117	26.012	367.184	362.567	-264.130
600	4.968	26.133	26.012	367.184	362.567	-264.130
700	4.968	26.145	26.012	367.184	362.567	-264.130
800	4.968	26.153	26.012	367.184	362.567	-264.130
900	4.968	26.157	26.012	367.184	362.567	-264.130
1000	4.968	26.158	26.012	367.184	362.567	-264.130
1100	4.968	26.158	26.012	367.184	362.567	-264.130
1200	4.968	26.157	26.012	367.184	362.567	-264.130
1300	4.968	26.155	26.012	367.184	362.567	-264.130
1400	4.968	26.152	26.012	367.184	362.567	-264.130
1500	4.968	26.148	26.012	367.184	362.567	-264.130
1600	4.968	26.143	26.012	367.184	362.567	-264.130
1700	4.968	26.137	26.012	367.184	362.567	-264.130
1800	4.968	26.130	26.012	367.184	362.567	-264.130
1900	4.968	26.122	26.012	367.184	362.567	-264.130
2000	4.968	26.113	26.012	367.184	362.567	-264.130
2100	4.968	26.103	26.012	367.184	362.567	-264.130
2200	4.968	26.092	26.012	367.184	362.567	-264.130
2300	4.968	26.080	26.012	367.184	362.567	-264.130
2400	4.968	26.067	26.012	367.184	362.567	-264.130
2500	4.968	26.053	26.012	367.184	362.567	-264.130
2600	4.968	26.039	26.012	367.184	362.567	-264.130
2700	4.968	26.024	26.012	367.184	362.567	-264.130
2800	4.968	26.009	26.012	367.184	362.567	-264.130
2900	4.968	25.993	26.012	367.184	362.567	-264.130
3000	4.968	25.977	26.012	367.184	362.567	-264.130
3100	4.968	25.960	26.012	367.184	362.567	-264.130
3200	4.968	25.943	26.012	367.184	362.567	-264.130
3300	4.968	25.925	26.012	367.184	362.567	-264.130
3400	4.968	25.907	26.012	367.184	362.567	-264.130
3500	4.968	25.888	26.012	367.184	362.567	-264.130
3600	4.968	25.869	26.012	367.184	362.567	-264.130
3700	4.968	25.849	26.012	367.184	362.567	-264.130
3800	4.968	25.828	26.012	367.184	362.567	-264.130
3900	4.968	25.807	26.012	367.184	362.567	-264.130
4000	4.968	25.785	26.012	367.184	362.567	-264.130
4100	4.968	25.763	26.012	367.184	362.567	-264.130
4200	4.968	25.740	26.012	367.184	362.567	-264.130
4300	4.968	25.717	26.012	367.184	362.567	-264.130
4400	4.968	25.693	26.012	367.184	362.567	-264.130
4500	4.968	25.669	26.012	367.184	362.567	-264.130
4600	4.968	25.644	26.012	367.184	362.567	-264.130
4700	4.968	25.619	26.012	367.184	362.567	-264.130
4800	4.968	25.593	26.012	367.184	362.567	-264.130
4900	4.968	25.567	26.012	367.184	362.567	-264.130
5000	4.968	25.540	26.012	367.184	362.567	-264.130
5100	4.968	25.513	26.012	367.184	362.567	-264.130
5200	4.968	25.485	26.012	367.184	362.567	-264.130
5300	4.968	25.457	26.012	367.184	362.567	-264.130
5400	4.968	25.428	26.012	367.184	362.567	-264.130
5500	4.968	25.399	26.012	367.184	362.567	-264.130
5600	4.968	25.369	26.012	367.184	362.567	-264.130
5700	4.968	25.338	26.012	367.184	362.567	-264.130
5800	4.968	25.307	26.012	367.184	362.567	-264.130
5900	4.968	25.275	26.012	367.184	362.567	-264.130
6000	4.968	25.243	26.012	367.184	362.567	-264.130

June 30, 1966

PROTON (H⁺)

(IDEAL GAS)

GF_W = 1.00742

ΔH_{f,0}^o = 365.236 ± 0.01 kcal/mol

ΔH_{f,298.15}^o = 367.186 ± 0.01 kcal/mol

S_{298.15}^o = 26.012 gibbs/mol

Heat of Formation

The heat of formation was calculated from the equation H(g) → H⁺(g) + e⁻ with the JANAF auxiliary data for H(g), using an ionization potential = 13.598 eV (313.605 kcal/mol) for H(g) obtained from C. W. Beckett, National Bureau of Standards Report 8628, Jan. 1, 1965.

Heat Capacity and Entropy

Calculated by assuming the proton to be an ideal monatomic gas. The enthalpy between 298° and 0°K is 1.481 kcal/mol as for all unexcited monatomic gases.

Hydrogen Uninegative Ion (H⁻)
(Ideal Gas) At. Wt. = 1.00852

H⁻

HYDROGEN UNINEGATIVE ION (H⁻) (IDEAL GAS) AT. WT. = 1.00852

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
100	4.968	26.015	26.015	0.000	33.200	31.583	-23.150
200	4.968	26.045	26.045	0.009	33.194	31.574	-23.000
250	4.968	27.475	26.210	1.506	31.085	31.085	-16.983
300	4.968	28.583	26.578	1.003	32.497	30.685	-13.412
400	4.968	29.489	26.990	1.500	32.147	30.356	-11.057
500	4.968	30.255	27.403	1.996	31.796	30.086	-9.393
600	4.968	30.918	27.802	2.493	31.443	29.865	-8.158
700	4.968	31.503	28.181	2.990	31.087	29.689	-7.209
800	4.968	32.027	28.540	3.487	30.728	29.553	-6.458
900	4.968	32.500	28.879	3.984	30.365	29.453	-5.851
1000	4.968	32.933	29.199	4.481	29.998	29.385	-5.351
1100	4.968	33.330	29.502	4.977	29.626	29.352	-4.934
1200	4.968	33.699	29.788	5.474	29.249	29.341	-4.580
1300	4.968	34.041	30.061	5.971	28.866	29.364	-4.278
1400	4.968	34.362	30.320	6.468	28.477	29.409	-4.017
1500	4.968	34.663	30.566	6.965	28.083	29.480	-3.790
1600	4.968	34.947	30.802	7.461	27.685	29.574	-3.591
1700	4.968	35.216	31.027	7.958	27.282	29.688	-3.415
1800	4.968	35.471	31.243	8.455	26.875	29.825	-3.259
1900	4.968	35.713	31.450	8.952	26.462	29.984	-3.120
2000	4.968	35.944	31.649	9.449	26.046	30.161	-2.996
2100	4.968	36.165	31.841	9.945	25.627	30.359	-2.885
2200	4.968	36.376	32.025	10.442	25.204	30.574	-2.784
2300	4.968	36.579	32.204	10.939	24.776	30.805	-2.693
2400	4.968	36.774	32.376	11.436	24.346	31.055	-2.610
2500	4.968	36.962	32.542	11.933	23.912	31.318	-2.535
2600	4.968	37.142	32.703	12.430	23.476	31.603	-2.467
2700	4.968	37.317	32.859	12.926	23.037	31.900	-2.404
2800	4.968	37.485	33.011	13.423	22.595	32.215	-2.347
2900	4.968	37.648	33.158	13.920	22.151	32.542	-2.294
3000	4.968	37.806	33.300	14.417	21.704	32.881	-2.246
3100	4.968	37.959	33.439	14.914	21.254	33.238	-2.201
3200	4.968	38.107	33.574	15.410	20.803	33.608	-2.160
3300	4.968	38.251	33.706	15.907	20.349	33.992	-2.122
3400	4.968	38.391	33.834	16.404	19.892	34.387	-2.088
3500	4.968	38.527	33.959	16.901	19.432	34.800	-2.055
3600	4.968	38.659	34.081	17.398	18.971	35.222	-2.026
3700	4.968	38.788	34.200	17.895	18.507	35.655	-1.998
3800	4.968	38.914	34.316	18.391	18.042	36.102	-1.972
3900	4.968	39.037	34.430	18.888	17.574	36.559	-1.949
4000	4.968	39.157	34.541	19.385	17.103	37.024	-1.926
4100	4.968	39.274	34.650	19.882	16.630	37.502	-1.906
4200	4.968	39.388	34.756	20.379	16.156	37.983	-1.887
4300	4.968	39.499	34.860	20.875	15.679	38.469	-1.870
4400	4.968	39.609	34.962	21.372	15.201	38.968	-1.853
4500	4.968	39.715	35.062	21.869	14.720	39.476	-1.838
4600	4.968	39.820	35.160	22.366	14.237	40.008	-1.824
4700	4.968	39.922	35.257	22.863	13.752	40.561	-1.811
4800	4.968	40.023	35.351	23.359	13.266	41.159	-1.799
4900	4.968	40.121	35.444	23.856	12.778	41.778	-1.788
5000	4.968	40.218	35.534	24.353	12.288	42.424	-1.777
5100	4.968	40.312	35.624	24.850	11.795	43.093	-1.768
5200	4.968	40.405	35.711	25.347	11.301	43.782	-1.759
5300	4.968	40.496	35.798	25.844	10.806	44.492	-1.751
5400	4.968	40.586	35.882	26.340	10.309	45.222	-1.744
5500	4.968	40.674	35.966	26.837	9.810	45.977	-1.738
5600	4.968	40.760	36.047	27.334	9.309	46.753	-1.730
5700	4.968	40.845	36.128	27.831	8.806	47.553	-1.725
5800	4.968	40.929	36.207	28.328	8.302	48.376	-1.719

Sept. 30, 1965

H⁻

Ground State Configuration 1s₀
S°_{298.15} = 26.015 cal. deg.⁻¹ mole⁻¹
ΔH°_f 0 = 34.2 ± 0.5 kcal. mole⁻¹
ΔH°_f 298.15 = 33.2 ± 0.5 kcal. mole⁻¹

Electronic Levels and Quantum Weight

E ₁ cm. ⁻¹	E ₁
0	1

Heat of Formation.

The heat of formation was calculated from the equation: H(g) + e⁻ → H⁻(g) with the JANAF auxiliary value for H(g) (this supplement), using an I.P. = 6.083098 X 10³ cm.⁻¹ (.754 e.v. or 17.39 kcal/mole) for H⁻(g) obtained from C. L. Pekeris, Phys. Rev. 125, 1470 (1962). The I.P. value for H⁻(g) reported by C. W. Scherr and R. E. Knight, Rev. Mod. Phys. 35, 436 (1963) is in agreement with the value of Pekeris.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, U. S. National Bureau of Standards Circular 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Helium. The electronic levels above 1 X 10⁵ cm.⁻¹ were omitted because their contribution is negligible below 6000°K. The H⁻ H₂₉₈ value at 0°K. is -1.481 kcal/mole.

Mercury Monohydride (HgH)

(Ideal Gas) Mol. Wt. = 201.618

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	∞.000	INFINITE	-2.082	58.163	58.163	INFINITE
100	6.695	46.683	58.746	-1.391	59.066	59.066	-121.708
200	6.995	48.584	58.746	-1.000	59.583	59.583	-121.708
298	7.181	52.486	52.486	∞.000	57.000	51.421	-37.693
300	7.186	52.530	52.486	-0.13	56.995	51.387	-37.634
400	7.509	54.940	52.772	1.748	56.721	49.560	-27.077
500	7.845	56.353	53.322	1.515	56.487	47.798	-20.891
600	8.140	57.810	53.951	2.315	56.288	46.078	-16.783
700	8.386	59.084	54.595	3.142	56.089	45.062	-14.349
800	8.588	60.217	55.228	3.991	55.888	44.515	-12.707
900	8.757	61.238	55.840	4.858	55.683	43.709	-11.429
1000	8.899	62.164	56.427	5.741	55.474	42.713	-10.407
1100	9.022	63.023	56.980	6.637	55.260	41.566	-9.569
1200	9.130	63.813	57.525	7.545	55.041	40.281	-8.871
1300	9.227	64.547	58.037	8.463	54.818	38.859	-8.279
1400	9.314	65.234	58.527	9.390	54.591	37.303	-7.771
1500	9.395	65.880	58.996	10.326	54.359	35.618	-7.331
1600	9.471	66.488	59.445	11.269	54.126	33.894	-6.945
1700	9.541	67.065	59.877	12.220	53.891	32.130	-6.604
1800	9.609	67.612	60.291	13.177	53.653	30.333	-6.300
1900	9.673	68.133	60.690	14.141	53.413	28.503	-6.028
2000	9.735	68.631	61.075	15.112	53.170	26.647	-5.783
2100	9.796	69.108	61.446	16.088	52.924	24.767	-5.560
2200	9.854	69.565	61.805	17.071	52.676	22.861	-5.358
2300	9.911	70.004	62.152	18.059	52.426	20.931	-5.173
2400	9.967	70.427	62.488	19.053	52.173	18.976	-5.003
2500	10.022	70.834	62.814	20.053	51.918	17.003	-4.846
2600	10.076	71.229	63.130	21.058	51.663	15.013	-4.702
2700	10.130	71.610	63.437	22.068	51.408	13.003	-4.567
2800	10.182	71.980	63.736	23.083	51.153	10.976	-4.442
2900	10.235	72.338	64.026	24.104	50.898	8.933	-4.326
3000	10.286	72.686	64.309	25.130	50.643	6.876	-4.217
3100	10.338	73.024	64.585	26.162	50.388	4.803	-4.114
3200	10.388	73.353	64.853	27.198	50.133	2.716	-4.018
3300	10.439	73.673	65.116	28.239	49.878	0.613	-3.928
3400	10.489	73.986	65.372	29.286	49.623	-1.493	-3.843
3500	10.539	74.290	65.623	30.337	49.368	-3.603	-3.762
3600	10.589	74.588	65.868	31.393	49.113	-5.713	-3.686
3700	10.638	74.879	66.107	32.455	48.858	-7.813	-3.614
3800	10.688	75.163	66.342	33.521	48.603	-9.903	-3.545
3900	10.737	75.441	66.572	34.592	48.348	-11.983	-3.480
4000	10.786	75.714	66.797	35.669	48.093	-14.053	-3.417
4100	10.835	75.981	67.018	36.750	47.838	-16.123	-3.358
4200	10.884	76.243	67.234	37.836	47.583	-18.193	-3.301
4300	10.932	76.499	67.447	38.926	47.328	-20.263	-3.247
4400	10.981	76.751	67.655	40.022	47.073	-22.333	-3.195
4500	11.029	76.998	67.860	41.123	46.818	-24.403	-3.146
4600	11.078	77.241	68.065	42.228	46.563	-26.473	-3.098
4700	11.126	77.480	68.259	43.338	46.308	-28.543	-3.052
4800	11.174	77.715	68.454	44.453	46.053	-30.613	-3.008
4900	11.222	77.946	68.645	45.573	45.798	-32.683	-2.966
5000	11.270	78.173	68.833	46.698	45.543	-34.753	-2.925
5100	11.318	78.397	69.019	47.827	45.288	-36.823	-2.886
5200	11.366	78.617	69.201	48.961	45.033	-38.893	-2.848
5300	11.414	78.834	69.381	50.100	44.778	-40.963	-2.812
5400	11.462	79.048	69.558	51.244	44.523	-43.033	-2.776
5500	11.510	79.258	69.732	52.393	44.268	-45.103	-2.742
5600	11.558	79.466	69.904	53.546	44.013	-47.173	-2.709
5700	11.605	79.671	70.074	54.704	43.758	-49.243	-2.677
5800	11.653	79.873	70.241	55.867	43.503	-51.313	-2.646
5900	11.701	80.073	70.406	57.035	43.248	-53.383	-2.616
6000	11.748	80.270	70.569	58.207	43.000	-55.453	-2.587

June 30, 1963

Mercury Monohydride (HgH)

(Ideal Gas)

MOL. WT. = 201.618

Ground State Configuration [$^2\Sigma^+$]
 $\Delta H_f^0 = 58 \pm 4$ kcal. mole⁻¹
 $S_{298.15}^0 = [52.486]$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^0 = 298.15 = 57 \pm 4$ kcal. mole⁻¹

Electronic Levels and Multiplicities

$$\frac{\epsilon_1 \text{ cm.}^{-1}}{0} \quad \frac{g_1}{[2]}$$

$$\omega_e = 1387 \text{ cm.}^{-1}$$

$$\omega_e x_e = 83.01 \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$B_e = 5.549 \text{ cm.}^{-1}$$

$$\alpha_e = 0.312 \text{ cm.}^{-1}$$

$$r_e = 1.74 \text{ \AA}$$

Heat of Formation.

The heat of formation was calculated from D_0 , 8.671 kcal. mole⁻¹, taken from G. Herzberg, "Spectra of Diatomic Molecules," 2nd Edition, D. Van Nostrand Company, Inc., New York (1950).

Heat Capacity and Entropy.

Molecular constants were taken from G. Herzberg, loc. cit.

HHg

HHg

(Ideal Gas) Mol. Wt. = 127.918

MOL. WT. = 127.918

(IDEAL GAS)

HYDROGEN IODIDE (HI)

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	6.000	0.000	INFINITE	2.069	6.420	6.420	INFINITE
100	6.954	41.746	55.541	1.379	6.766	6.439	0.420
200	7.901	66.570	82.980	0.683	7.071	6.571	2.509
298	8.949	89.351	97.351	0.000	7.376	6.736	4.276
300	8.969	89.394	97.321	0.013	7.380	6.740	4.287
400	7.010	51.403	62.625	1.711	6.060	5.332	0.837
500	7.107	52.977	50.163	1.817	5.146	4.413	1.055
600	7.283	54.285	50.777	2.134	4.427	3.620	0.954
700	7.524	56.419	51.898	3.620	3.907	3.097	0.819
800	7.800	58.419	52.448	4.368	3.585	3.176	0.771
900	7.767	57.324	52.448	4.368	3.585	3.176	0.771
1000	7.920	58.150	52.977	5.172	3.351	3.351	0.732
1100	8.050	58.911	53.493	5.971	3.125	3.125	0.700
1200	8.166	60.276	54.425	7.403	2.899	2.899	0.660
1300	8.263	60.894	54.866	8.439	2.673	2.673	0.613
1400	8.346	61.474	55.287	9.281	2.446	2.446	0.561
1500	8.414	62.023	55.691	10.131	2.219	2.219	0.508
1600	8.469	62.562	56.079	10.981	1.992	1.992	0.456
1700	8.516	63.035	56.452	11.850	1.765	1.765	0.403
1800	8.554	63.436	56.811	12.718	1.538	1.538	0.350
1900	8.583	63.767	57.157	13.591	1.311	1.311	0.297
2000	8.604	64.030	57.480	14.464	1.084	1.084	0.244
2100	8.618	64.236	57.781	15.350	0.857	0.857	0.191
2200	8.625	64.394	58.067	16.235	0.630	0.630	0.138
2300	8.625	64.516	58.327	17.124	0.403	0.403	0.085
2400	8.618	64.602	58.567	18.016	0.176	0.176	0.032
2500	8.604	64.657	58.780	18.911	0.000	0.000	0.000
2600	8.583	64.677	58.964	19.811	-0.176	-0.176	-0.032
2700	8.554	64.664	59.129	20.719	-0.351	-0.351	-0.085
2800	8.516	64.618	59.276	21.635	-0.526	-0.526	-0.138
2900	8.469	64.540	60.784	22.551	-0.701	-0.701	-0.191
3000	8.414	64.436	61.236	23.474	-0.876	-0.876	-0.244
3100	8.346	64.306	61.655	24.403	-1.051	-1.051	-0.297
3200	8.263	64.151	62.035	25.335	-1.226	-1.226	-0.350
3300	8.166	63.974	62.474	26.274	-1.401	-1.401	-0.403
3400	8.050	63.774	62.874	27.219	-1.576	-1.576	-0.456
3500	7.920	63.549	63.233	28.174	-1.751	-1.751	-0.508
3600	7.767	63.294	63.551	29.139	-1.926	-1.926	-0.561
3700	7.524	62.999	63.827	30.119	-2.101	-2.101	-0.613
3800	7.283	62.664	64.061	31.109	-2.276	-2.276	-0.666
3900	7.010	62.289	64.251	32.114	-2.451	-2.451	-0.719
4000	6.954	62.241	64.251	32.114	-2.451	-2.451	-0.719
4100	7.283	62.664	64.401	32.114	-2.451	-2.451	-0.719
4200	7.524	62.999	64.551	32.114	-2.451	-2.451	-0.719
4300	7.767	63.324	64.701	32.114	-2.451	-2.451	-0.719
4400	7.920	63.549	64.851	32.114	-2.451	-2.451	-0.719
4500	8.050	63.774	64.999	32.114	-2.451	-2.451	-0.719
4600	8.166	63.974	65.149	32.114	-2.451	-2.451	-0.719
4700	8.263	64.151	65.299	32.114	-2.451	-2.451	-0.719
4800	8.346	64.306	65.449	32.114	-2.451	-2.451	-0.719
4900	8.414	64.436	65.599	32.114	-2.451	-2.451	-0.719
5000	8.469	64.540	65.749	32.114	-2.451	-2.451	-0.719
5100	8.516	64.618	65.899	32.114	-2.451	-2.451	-0.719
5200	8.554	64.664	66.049	32.114	-2.451	-2.451	-0.719
5300	8.583	64.684	66.199	32.114	-2.451	-2.451	-0.719
5400	8.604	64.694	66.349	32.114	-2.451	-2.451	-0.719
5500	8.618	64.694	66.499	32.114	-2.451	-2.451	-0.719
5600	8.625	64.694	66.649	32.114	-2.451	-2.451	-0.719
5700	8.625	64.694	66.799	32.114	-2.451	-2.451	-0.719
5800	8.618	64.694	66.949	32.114	-2.451	-2.451	-0.719
5900	8.604	64.694	67.099	32.114	-2.451	-2.451	-0.719
6000	8.583	64.694	67.249	32.114	-2.451	-2.451	-0.719

September 30, 1961

$$\Delta H_f^\circ = 6.82 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\text{Ground State} = \sum$$

$$\Delta H_f^\circ 298 = 6.30 \text{ kcal. mole}^{-1}$$

$$S_{298}^\circ = 49.351$$

$$\omega_e = 2309.06 \text{ cm}^{-1}$$

$$\omega_e x_e = 39.73 \text{ cm}^{-1}$$

$$B_e = 8.512 \text{ cm}^{-1}$$

$$\alpha_e = 0.1715 \text{ cm}^{-1}$$

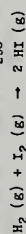
$$G = 1$$

Thermodynamic Functions.

Molecular constants are from M. Cowan and W. Gordy [Phys. Rev. 104, 551 (1956)] and D. R. J. Boyd and H. W. Thompson [Spectrochim. Acta 5, 308 (1952)]. The calculated functions are in reasonable agreement with the compilation of K. K. Kelley [U. S. Bur. Mine Bull. 504 (1960)].

Heat of Formation.

Using the calculated functions derived above and functions for H₂(g) and I₂(g) given in the JANAP tables, equilibrium data from the literature were used to calculate ΔH₂₉₈° for the reaction



$$\Delta H_{298}^\circ, \text{ kcal. mole}^{-1}$$

$$\begin{aligned} & \text{Taylor and Crist}^1 (667^\circ \text{ to } 764^\circ \text{K}) \\ & \text{Bodenstein}^2 (556^\circ \text{ to } 781^\circ \text{K}) \\ & \text{Bright and Hagerly}^3 (696^\circ \text{ and } 779^\circ \text{K}) \\ & \text{Rittenberg and Urey}^4 (671^\circ \text{ and } 741^\circ \text{K}) \end{aligned}$$

The data of Taylor and Crist are the most concordant and are given the most weight. Converting to the solid state of iodine, which has been adopted as a JANAP reference state gives the standard heat of formation of hydrogen iodide.

References

- (1) A. H. Taylor and R. H. Crist, *J. Am. Chem. Soc.* **65**, 1377 (1941).
- (2) M. Bodenstein, *Z. physikal. Chem.* **29**, 295 (1899).
- (3) N. P. H. Bright and R. P. Hagerly, *Trans. Faraday Soc.* **43**, 697 (1947).
- (4) D. Rittenberg and H. C. Urey, *J. Am. Chem. Soc.* **56**, 1885 (1934).

Potassium Hydride (KH)

(Crystal) Mol. Wt. = 40.108

HK

POTASSIUM HYDRIDE (KH)

(CRYSTAL)

MOL. WT. = 40.108

T, °K.	C _p	$S^\circ - (F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0						
100						
200						
298	9.050	12.000	0.000	-13.819	-8.136	5.964
300						
400	9.406	12.056	-0.017	-13.822	-8.101	5.901
500	11.450	12.906	1.011	-14.469	-6.069	3.316
600	11.600	17.378	2.120	-16.472	-3.964	1.732
700	14.810	19.568	3.123	-17.345	-1.672	0.892
800	13.051	21.530	4.567	-14.136	2.562	0.007
900	14.990	23.833	7.812	-13.559	4.214	1.023
1000	14.300	26.425	17.700	-13.223	6.170	1.348
1100	14.571	27.401	18.550	-10.169	9.117	1.811
1200	14.400	28.079	19.191	-11.639	12.868	2.245
1300	14.200	28.587	20.548	-10.574	16.806	2.735
1400	15.129	31.187	20.435	-14.636	20.041	3.128
1500	15.230	32.435	21.667	-16.152	23.588	3.437

 $\Delta H^\circ_f O = \text{Unknown}$ $\Delta H^\circ_f 298.15 = -13.819 \pm 0.011 \text{ kcal. mole}^{-1}$ $S^\circ_{298.15} = [12] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $T_d = [590]^\circ K.$

Heat of Formation.

The value of $\Delta H^\circ_f 298.15$ was taken from S. R. Gunn and L. G. Green, J. Am. Chem. Soc. **80**, 4782 (1958). The corresponding value reported by C. E. Measer, L. O. Pasolino and C. E. Thalmeier, J. Am. Chem. Soc. **77**, 4524 (1955) was $-15.16 \pm 0.6 \text{ kcal. mole}^{-1}$. In this paper the results of the previous investigations were also reviewed.

Heat Capacity and Entropy.

C_p and $S^\circ_{298.15}$ were estimated by comparison with those for NaH(c) and LiH(c).

Temperature of Decomposition.

T_d was assumed to be the temperature at which the value of ΔF°_f changes from negative to positive.

March 31, 1963

HK

POTASSIUM HYDRIDE (KH) (IDEAL GAS) MOL. WT. = 40.108

POTASSIUM HYDRIDE (KH)

(IDEAL GAS)

Ground State Configuration $1s^2 +$
 $S_{298.15}^\circ = 47.304 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ 0 = 30.0 \pm 3.5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = 29.4 \pm 3.5 \text{ kcal. mole}^{-1}$

$\omega_e = 985.0 \text{ cm.}^{-1}$
 $\omega_e x_e = 14.65 \text{ cm.}^{-1}$
 $B_e = 3.407 \text{ cm.}^{-1}$
 $\alpha_e = 0.0673 \text{ cm.}^{-1}$
 $\sigma = 1$

Heat of Formation.

$\Delta H_f^\circ 298.15$ was calculated from $D_0^\circ = 1.86 \pm 0.15 \text{ e.v.}$ reported by A. G. Daydon, "Dissociation Energies," Chapman and Hall, Ltd., 1953.

Heat Capacity and Entropy.

All molecular and spectroscopic constants were obtained from O. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., 1950.

March 31, 1963

T, °K.	C_p°	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	.000	INFINITE	2.102	30.003	30.003	INFINITE
100	6.944	39.575	1.409	29.592	28.015	61.223
200	7.414	47.304	.000	29.000	24.557	10.000
298	7.414	47.304	.000	29.000	24.557	10.000
300	7.426	47.350	.014	29.394	24.527	17.867
400	7.414	49.541	.778	29.486	23.062	12.600
500	6.134	51.121	1.575	29.402	21.738	9.501
600	6.370	52.026	2.401	27.952	20.470	7.456
700	6.545	53.130	3.247	27.731	19.241	6.007
800	6.674	53.280	4.108	27.527	18.041	4.928
900	6.782	53.308	4.981	27.332	16.868	4.096
1000	6.867	53.278	5.864	27.135	15.715	3.434
1100	6.937	53.087	6.754	26.925	15.407	3.101
1200	6.996	52.867	7.651	26.708	15.295	2.968
1300	7.048	52.619	8.553	26.486	16.979	2.854
1400	7.095	52.350	9.460	26.257	17.663	2.757
1500	7.137	52.060	10.372	26.020	18.343	2.673
1600	7.174	51.751	11.288	25.776	19.021	2.598
1700	7.206	51.424	12.207	25.525	19.697	2.532
1800	7.233	51.081	13.130	25.268	20.372	2.473
1900	7.257	50.720	14.056	24.995	21.045	2.421
2000	7.278	50.343	14.985	24.716	21.718	2.373
2100	7.297	50.000	15.917	24.431	22.389	2.330
2200	7.314	49.643	16.853	24.140	23.060	2.291
2300	7.329	49.275	17.791	23.842	23.729	2.255
2400	7.342	48.900	18.731	23.537	24.399	2.222
2500	7.353	48.516	19.675	23.226	25.066	2.191
2600	7.362	48.124	20.621	22.909	25.738	2.163
2700	7.369	47.724	21.569	22.586	26.406	2.137
2800	7.375	47.316	22.521	22.257	27.075	2.113
2900	7.379	46.900	23.474	21.924	27.748	2.091
3000	7.381	46.476	24.431	21.587	28.417	2.070
3100	7.381	46.044	25.389	21.246	29.091	2.051
3200	7.379	45.604	26.351	20.900	29.766	2.033
3300	7.375	45.156	27.314	20.549	30.440	2.016
3400	7.369	44.700	28.280	20.194	31.116	2.000
3500	7.362	44.236	29.248	19.835	31.798	1.985
3600	7.353	43.764	30.219	19.470	32.482	1.972
3700	7.342	43.284	31.192	19.100	33.166	1.959
3800	7.329	42.796	32.168	18.725	33.855	1.947
3900	7.314	42.300	33.146	18.346	34.548	1.936
4000	7.297	41.796	34.126	17.961	35.247	1.926
4100	7.278	41.284	35.108	17.570	35.949	1.916
4200	7.257	40.764	36.093	17.176	36.658	1.906
4300	7.233	40.236	37.080	16.779	37.372	1.899
4400	7.206	39.700	38.070	16.376	38.091	1.892
4500	7.174	39.156	39.062	15.969	38.821	1.885
4600	7.137	38.604	40.056	15.558	39.557	1.879
4700	7.095	38.044	41.052	15.143	40.303	1.874
4800	7.048	37.476	42.051	14.724	41.040	1.869
4900	7.000	36.900	43.052	14.300	41.825	1.865
5000	6.952	36.316	44.055	13.871	42.599	1.862
5100	6.904	35.724	45.060	13.438	43.393	1.859
5200	6.856	35.124	46.068	12.999	44.193	1.857
5300	6.807	34.516	47.078	12.556	45.010	1.856
5400	6.758	33.900	48.090	12.109	45.838	1.855
5500	6.709	33.276	49.105	11.658	46.684	1.855
5600	6.660	32.644	50.122	11.203	47.548	1.856
5700	6.611	32.004	51.141	10.744	48.429	1.856
5800	6.562	31.356	52.162	10.281	49.327	1.859
5900	6.513	30.700	53.186	9.814	50.248	1.861
6000	6.464	30.044	54.212	9.343	51.187	1.864

POTASSIUM HYDROXIDE (KOH) (CRYSTAL) MOL. WT. = 56.10937

T, °K	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	0.000	0.000	INFINITE	-2.926	-100.694	-100.694	INFINITE
100	8.164	5.705	31.303	-2.560	-101.477	-97.901	213.953
200	12.978	12.857	20.368	-1.502	-101.681	-94.220	102.959
298	15.746	18.949	18.949	0.000	-101.510	-90.594	66.407
300	15.769	19.046	18.949	0.079	-101.507	-90.526	65.948
400	17.400	23.798	19.586	1.085	-101.461	-85.468	36.448
500	19.020	27.853	20.843	3.505	-101.505	-85.055	30.453
600	18.800	34.206	22.685	6.909	-99.555	-79.632	29.009
700	18.800	38.408	24.543	10.789	-96.131	-76.345	23.836
800	18.800	39.609	25.543	12.543	-93.115	-73.120	19.975
900	18.800	41.823	27.680	12.549	-90.315	-69.813	14.802
1000	18.800	43.804	29.375	14.429	-87.923	-66.813	10.533
1100	18.800	45.596	30.769	16.309	-85.463	-62.697	8.914
1200	18.800	47.732	32.074	18.189	-82.671	-57.834	6.523
1300	18.800	49.736	33.242	20.069	-79.468	-52.022	4.3525
1400	18.800	50.130	34.252	21.949	-75.814	-45.525	
1500	18.800	51.427	35.541	23.829	-71.150	-43.525	

Heat of Formation. The standard enthalpy of formation, ΔH_f° 298 (KOH, c) = -101.5 ± 0.1 kcal. mole⁻¹, was calculated from the heat of solution of KOH(c), the heat of hydrolysis of potassium metal and the appropriate auxiliary data.

N. A. Peshetnikov¹ has measured the heat of solution KOH(c) $\rightarrow$ KOH(650 H₂O) as -13.665 ± 0.009 kcal. mole⁻¹ at 298.15°K. in the solution calorimeter. Using the auxiliary heat of dilution reported by V. B. Parker², the selected heat of solution of KOH(c) at infinite dilution is -13.770 kcal. mole⁻¹. The heat of solution KOH(c) $\rightarrow$ KOH(25 H₂O) has also been measured as -13.80 ± 0.10 kcal. mole⁻¹ in the solution calorimeter by W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull³. Both results are in good agreement.

The heat of hydrolysis of potassium metal, ΔH_f° 298, has been measured in the solution calorimeter by the following investigators.

K(c) + H₂O(l) $\rightarrow$ KOH(nH₂O) + 1/2 H₂(g) ΔH_f° 298

Source Number of Moles of H₂O ΔH_f° 298 kcal. mole⁻¹ ΔH_f° 298 (KOH, c) kcal. mole⁻¹

Gunn et al.⁴ 1000 -46.877 $\pm$ 0.01 -115.281 -101.511

Messer et al.⁵ ∞ -47.02 $\pm$ 0.15 -115.345 -101.565

Ketchen et al.⁶ ∞ -46.894 $\pm$ 0.24 -115.209 -101.439

The values of ΔH_f° 298 (KOH(∞ H₂O)) were calculated from the heats of reaction, ΔH_f° 298, using ΔH_f° 298 (H₂O, l) = -68.315 kcal. mole⁻¹. Combination of the selected heat of solution of KOH(c) at infinite dilution with the heat of formation of KOH(∞ H₂O)) gives the heat of formation of KOH(c) in the last column of the table. A weighted average of these three measurements was taken for the selected heat of formation of KOH(c).

The earlier investigations have been reviewed by F. R. Bichowsky and F. D. Rossini⁸ and C. E. Messer et al.⁵, and these earlier reported data are not adopted in the tabulation.

Heat Capacity and Entropy.

The low temperature heat capacities of KOH(c) from 15° to 340°K. have been measured by W. E. Hatton et al.³ who have also observed a sharp peak in the heat capacity curve in the temperature range from 210° to 230°K. These values of C_p were adopted in the calculation. W. D. Powers and G. C. Blalock⁹ have measured the high temperature enthalpy changes of the solid KOH in the α and β phases by the drop method. Their enthalpy data are scattered and not precise enough to accurately define the heat capacities in the α phase. Therefore, the selected heat capacities between 340° and 522°K. were estimated from a graphical extrapolation of the low temperature heat capacity curve, and the tabulated H° - H° 298 functions are in agreement with their enthalpy measurements within the experimental uncertainty. The heat capacities of KOH(c) in the β phase were obtained from Powers and Blalock⁹.

The entropy (S° 298 = 18.95 cal. deg.⁻¹ mole⁻¹) was taken from Hatton et al.³, based on an extrapolation of S° 15 = 0.054 cal. deg.⁻¹ mole⁻¹.

Transition and Melting Data.

Hatton et al.³ have found a lambda transition at 227.4°K. in the heat capacity measurement. The adopted heat of α - β transition at 522°K. and heat of melting at 673°K. were obtained from Powers and Blalock⁹. P. S. Seward and K. E. Martin¹⁰ found ΔH_m° = 1.83 kcal. mole⁻¹ at 693°K. In phase diagram studies of the system KOH-K₂CO₃.

Heat of Sublimation.

See KOH(g) table for details.

References:

- 1 N. A. Peshetnikov, Zhur. Neorg. Khim., **6**, 682 (1961).
- 2 V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NBS-NBS 2, Apr., 1965.
- 3 W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull, unpublished work, Dow Thermal Research Lab., 1959.
- 4 S. R. Gunn and L. G. Green, J. Am. Chem. Soc., **80**, 4782 (1958).
- 5 S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking-Bomb Solution Calorimeter, UOHL-7992, Oct. 1965."
- 6 E. E. Ketchen and W. E. Wallace, J. Am. Chem. Soc., **76**, 4736 (1954).
- 7 D. D. Ketchen, W. H. Evans, I. Hallow, V. B. Parker, S. W. Bailey and R. H. Schumm, NBS Technical Note 270-1, Oct. 1965.
- 8 F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, 1956.
- 9 W. D. Powers and G. C. Blalock, "Enthalpies and Specific Heats of Alkali and Alkaline Hydroxides at High Temperatures," J. Am. Chem. Soc., **71**, 3564 (1949).
- 10 P. S. Seward and K. E. Martin, J. Am. Chem. Soc., **71**, 3564 (1949).

Potassium Hydroxide (KOH)

(Liquid) Mol. Wt. = 56.10937

HKO

MOL. WT. = 56.10937

POTASSIUM HYDROXIDE (KOH)

(LIQUID)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(R°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _f
0						
100						
200						
298	19.860	23.518	23.518	0.000	- 98.433	- 88.679
300						
400	19.860	23.641	23.518	0.037	- 98.422	- 88.820
500	19.860	23.768	23.518	0.099	- 97.923	- 87.441
600	19.860	23.897	23.518	0.195	- 97.392	- 86.303
700	19.860	24.028	23.518	0.321	- 96.862	- 85.419
800	19.860	24.161	23.518	0.477	- 96.340	- 84.786
900	19.860	24.297	23.518	0.662	- 95.817	- 84.397
1000	19.860	24.436	23.518	0.877	- 95.293	- 84.156
1100	19.860	24.578	23.518	1.122	- 94.768	- 84.063
1200	19.860	24.723	23.518	1.397	- 94.243	- 84.117
1300	19.860	24.871	23.518	1.702	- 93.718	- 84.326
1400	19.860	25.021	23.518	2.037	- 93.193	- 84.691
1500	19.860	25.173	23.518	2.402	- 92.668	- 85.216
1600	19.860	25.327	23.518	2.797	- 92.143	- 85.801
1700	19.860	25.483	23.518	3.222	- 91.618	- 86.446
1800	19.860	25.641	23.518	3.677	- 91.093	- 87.151
1900	19.860	25.801	23.518	4.162	- 90.568	- 87.916
2000	19.860	25.963	23.518	4.677	- 90.043	- 88.741
2100	19.860	26.127	23.518	5.222	- 89.518	- 89.626
2200	19.860	26.293	23.518	5.797	- 88.993	- 90.571
2300	19.860	26.461	23.518	6.402	- 88.468	- 91.576
2400	19.860	26.631	23.518	7.037	- 87.943	- 92.641
2500	19.860	26.803	23.518	7.702	- 87.418	- 93.766

Dec. 31, 1961; Mar. 31, 1962; Sep. 30, 1962; Mar. 31, 1966

$S_{298.15}^o = 23.518$ cal. deg.⁻¹ mole⁻¹
 $T_m = 673^{\circ}\text{K.}$
 T_b (monomeric gas) = 1600°K.

ΔH_f^o 298.15 = -98.433 kcal. mole⁻¹
 $\Delta H_m^o = 2.240$ kcal. mole⁻¹
 ΔH_v^o (to monomer) = 32.0 kcal. mole⁻¹

Heat of Formation.

The heat of formation of KOH(l) at 298°K. was obtained from that of the crystal by adding ΔH_m^o and the difference between H_{298}^o - H_{298}^o for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase, $C_p = 19.86$ cal. deg.⁻¹ mole⁻¹, was obtained from the enthalpy measurements in the drop calorimeter by W. D. Powers and O. C. Blalock, ORNL-1653, Oak Ridge Nat'l. Lab., Jan. 1954. The constant C_p was extrapolated below the melting point and up to 2500°K.

The entropy, $S_{298.15}^o = 23.51$ cal. deg.⁻¹ mole⁻¹, was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See KOH(c) table for details.

Vaporization Data.

The boiling point 1600°K. was calculated as the temperature at which the free energies of formation (ΔF_f^o) for both KOH(l) and KOH(g) are equal. The difference in the heats of formation (ΔH_f^o) of KOH(l) and KOH(g) at the boiling point is the heat of vaporization. If $K_2(OH)_2(g)$ is also considered as a minor component in the vapor mixture (approximately 2% of total vapor pressure at the boiling point) the calculated boiling point is unchanged as 1600°K. (see KOH(c) table for details).

H. von Wertenberg and P. Albrecht, Z. Elektrochem. 27, 182 (1921), have studied the vapor pressures of liquid KOH and reported the boiling point as 1597°K.

HKO

Potassium Hydroxide (KOH)

(Ideal Gas) Mol. Wt. = 56.10937

HKO

MOL. WT. = 56.10937

(IDEAL GAS)

POTASSIUM HYDROXIDE (KOH)

Point Group C_s
 $S_{298.15}^\circ = [56.4] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = 1

$\Delta H_f^\circ 0 = -54.3 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -55.4 \pm 5 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

$\omega_e, \text{ cm.}^{-1}$
 $408 (1)$
 $[1300](1)$
 $[3700](1)$
 Bond Distance: K-O = $[2.21] \text{ \AA}$ O-H = $[0.96] \text{ \AA}$
 Bond Angle: K-O-H = $[110]^\circ$
 Product of the Moments of Inertia: $I_A I_B I_C = [1.2325] \times 10^{-116} \text{ g.}^3 \text{ cm.}^6$
 $\sigma^\circ = 1$

Heat of Formation

R. P. Porter and R. C. Schoonmaker, J. Phys. Chem. 62, 234 and 466 (1958), have investigated the potassium hydroxide vapor by the mass-spectrometric method and found that the KOH vaporizes mainly as gaseous dimer in the temperature range from 573° to 723°K. Later, Schoonmaker and Porter, J. Chem. Phys. 31, 830 (1959), found the activity of molten alkali hydroxide had been reduced in the presence of MgO in their sample container. Using the reported partial pressures of KOH(g) and $K_2(OH)_2(g)$ at 641° and 666°K. and JANAF free energy functions, the third law calculations give $\Delta H_{298}^\circ = -45.4 \pm 5 \text{ kcal. mole}^{-1}$ for $2KOH(g) \rightarrow K_2(OH)_2(g)$, and $\Delta H_{298}^\circ = 45.41 \pm 3.5 \text{ kcal. mole}^{-1}$ for $KOH(g) \rightarrow KOH(c)$, and $\Delta H_{298}^\circ = 45.6 \pm 5 \text{ kcal. mole}^{-1}$ for $2KOH(c) \rightarrow K_2(OH)_2(g)$. The uncertainties given were derived by assuming I_B to be good to a factor of 5 as stated by the authors and including an extra factor of 2 as a possible error in activity. To this was added an estimate of the uncertainty due to functions used. In order to have good agreement between the calculated total pressures of monomeric and dimeric KOH(g) and the observed vapor pressures measured by H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 182 (1921), the heat of sublimation to monomeric gas was adjusted to $\Delta H_{298}^\circ = 46.08 \text{ kcal. mole}^{-1}$. (The heat of sublimation to dimeric gas was unchanged as $\Delta H_{298}^\circ = 45.64 \text{ kcal. mole}^{-1}$). The calculated boiling point is 1600°K. which is in good agreement with 1597 $\pm 10^\circ$ K. reported by Wartenberg and Albrecht. The heats of formation were calculated from the selected heats of sublimation as $\Delta H_{298}^\circ(KOH, g) = -55.4$ and $\Delta H_{298}^\circ(K_2(OH)_2, g) = -157.4 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy

The bond distance K-O was estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-F(g) to the bond distance K-F(g) (2.1746 Å) which has been accurately measured by R. K. Ritchie and H. Lew, Can. J. Phys. 42, 43 (1964). The bond distance O-H was estimated from that in $H_2O(g)$. The bent molecular configuration with the bond angle of 110° has also been proposed by S. H. Bauer, R. M. Diner and R. F. Porter, J. Chem. Phys. 23, 931 (1956), but a linear model has also been suggested by R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959). The bent model has been adopted in the tabulation. The three principal moments of inertia are: $I_A = [0.1256] \times 10^{-39}$, $I_B = [9.8070] \times 10^{-39}$ and $I_C = [9.9326] \times 10^{-39} \text{ g. cm.}^2$.

The K-O stretching frequency (408 cm.^{-1}) was obtained from L. H. Spinar and J. L. Margrave, Spectrochim. Acta 12, 244 (1957) in the infrared spectroscopic studies. The O-H stretching and the bending frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rapid convergence to a constant as a heavier atom is attached.

L. Brewer and D. P. Matick, J. Am. Chem. Soc. 73, 2045 (1951), have calculated theoretically the bond distances of gaseous alkali oxides ($I_1 O = 1.52 \text{ \AA}$, $Na O = 1.94 \text{ \AA}$ and $K O = 2.27 \text{ \AA}$) which have been quoted by Bauer, Diner and Porter, loc. cit., and many other authors.

T, °K.	C_p°	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	8.000	INFINITE	2.566	-54.258	-	INFINITE
100	8.978	48.900	1.711	-54.258	-	1.00000
200	9.559	59.269	0.911	-55.014	-	61.107
298	9.550	58.392	0.000	-55.434	-56.277	41.252
300	9.559	58.451	0.018	-55.442	-56.283	41.002
400	10.028	61.267	0.186	-56.479	-56.365	30.607
500	10.440	63.549	2.021	-56.914	-56.511	24.614
600	10.743	65.478	6.036	-57.309	-56.152	20.454
700	11.012	67.155	11.201	-57.677	-55.930	17.462
800	11.247	68.641	16.204	-58.027	-55.658	15.205
900	11.459	69.978	21.049	-58.367	-55.340	13.438
1000	11.634	71.195	25.762	-58.705	-54.986	12.017
1100	11.834	72.315	30.346	-59.050	-54.574	10.644
1200	12.000	73.352	34.807	-59.398	-54.125	9.353
1300	12.153	74.318	39.146	-59.746	-53.653	8.259
1400	12.294	75.224	43.369	-60.092	-53.167	7.320
1500	12.422	76.077	47.484	-60.436	-52.668	6.500
1600	12.539	76.882	51.500	-60.775	-52.155	5.792
1700	12.645	77.646	55.416	-61.112	-51.630	5.162
1800	12.741	78.371	59.231	-61.446	-51.096	4.602
1900	12.827	79.062	62.946	-61.775	-50.553	4.099
2000	12.906	79.722	66.561	-62.100	-50.000	3.647
2100	12.978	80.354	70.079	-62.421	-49.437	3.238
2200	13.043	80.959	73.500	-62.738	-48.864	2.865
2300	13.101	81.540	76.831	-63.051	-48.281	2.525
2400	13.155	82.099	80.071	-63.360	-47.688	2.212
2500	13.204	82.637	83.221	-63.665	-47.085	1.928
2600	13.248	83.156	86.281	-63.966	-46.472	1.658
2700	13.289	83.656	89.251	-64.263	-45.849	1.412
2800	13.326	84.140	92.131	-64.556	-45.216	1.183
2900	13.361	84.609	94.921	-64.844	-44.573	0.969
3000	13.392	85.062	97.631	-65.128	-43.920	0.769
3100	13.421	85.502	100.261	-65.408	-43.257	0.582
3200	13.448	85.928	102.821	-65.684	-42.584	0.406
3300	13.472	86.342	105.301	-65.956	-41.901	0.240
3400	13.495	86.745	107.711	-66.224	-41.208	0.085
3500	13.516	87.137	110.051	-66.488	-40.505	0.000
3600	13.536	87.518	112.331	-66.748	-39.792	-0.085
3700	13.554	87.889	114.561	-67.003	-39.069	-0.203
3800	13.571	88.250	116.751	-67.253	-38.336	-0.335
3900	13.587	88.603	118.901	-67.500	-37.593	-0.461
4000	13.602	88.947	121.011	-67.743	-36.840	-0.581
4100	13.616	89.283	123.081	-67.982	-36.077	-0.695
4200	13.628	89.612	125.111	-68.217	-35.304	-0.804
4300	13.641	89.932	127.101	-68.448	-34.521	-0.908
4400	13.652	90.246	129.051	-68.675	-33.728	-1.008
4500	13.663	90.553	130.961	-68.898	-32.925	-1.104
4600	13.673	90.853	132.831	-69.117	-32.112	-1.196
4700	13.682	91.148	134.661	-69.332	-31.290	-1.285
4800	13.691	91.436	136.451	-69.543	-30.459	-1.370
4900	13.699	91.718	138.201	-69.750	-29.616	-1.453
5000	13.707	91.995	139.921	-69.953	-28.763	-1.532
5100	13.715	92.266	141.611	-70.152	-27.900	-1.609
5200	13.722	92.533	143.271	-70.347	-27.027	-1.684
5300	13.729	92.794	144.901	-70.538	-26.144	-1.756
5400	13.735	93.051	146.501	-70.725	-25.251	-1.827
5500	13.741	93.303	148.071	-70.908	-24.348	-1.895
5600	13.747	93.551	149.611	-71.087	-23.435	-1.962
5700	13.752	93.794	151.121	-71.262	-22.512	-2.027
5800	13.758	94.033	152.601	-71.433	-21.580	-2.091
5900	13.762	94.269	154.051	-71.599	-20.638	-2.153
6000	13.767	94.500	155.481	-71.762	-19.685	-2.214

Mar. 31, 1962; June 30, 1962; Mar. 31, 1966

HKO

Lithium Hydride (LiH)
(Crystal)

LITHIUM HYDRIDE (LiH)

CRYSTAL

GFW = 7.94697

GFW = 7.94697

T, °K	Cp ^a	$-(C^a - H^a_{298})/T$	$H^a - H^a_{298}$	ΔH^a	ΔG^a	Log Kp
0	-0.00	INFINITE	- .903	- 20.446	- 20.446	INFINITE
100	1.525	9.165	- .861	- 20.903	- 19.563	42.755
200	4.488	5.336	- .555	- 21.338	- 18.050	19.724
298	6.682	4.789	.000	- 21.660	- 16.362	11.994
300	6.712	4.789	.012	- 21.665	- 16.330	11.896
400	8.316	6.988	.766	- 21.879	- 14.515	7.931
500	9.736	8.988	1.669	- 22.744	- 12.583	5.500
600	11.085	10.803	2.711	- 22.745	- 10.546	3.842
700	12.399	12.700	3.485	- 22.642	- 8.518	2.640
800	13.694	14.481	5.190	- 22.362	- 6.517	1.780
900	14.980	16.126	6.624	- 21.995	- 4.556	1.109
1000	16.259	17.773	8.186	- 21.662	- 2.645	.576
1100	17.534	19.362	9.874	- 20.843	- .791	.137
1200	18.805	20.902	11.699	- 19.990	1.120	- .322
1300	20.075	22.518	13.637	- 19.195	2.720	- .687
1400	21.343	24.052	15.708	- 18.166	4.370	- .962
1500	22.610	25.568	17.805	- 17.055	5.942	- .966

Sept. 30, 1962; Sept. 30, 1967

Heat of Formation

The heats of solution of Li(c) and LiH(c) in water have been measured by Cuntz (1) and Hoers (2) using an open Dewar flask calorimeter and by Messer (3) and Gunn (4) using closed bomb calorimetry. Based on the reported values of the enthalpy changes (ΔH^a) for the reaction (A) $\text{Li(c)} + \text{H}_2\text{O(l)} = \text{LiOH(aq)} + 1/2\text{H}_2\text{(g)}$, and (B) $\text{LiH(c)} + \text{H}_2\text{O(l)} = \text{LiOH(aq)} + \text{H}_2\text{(g)}$, the corresponding ΔH^a_{298} for LiH(c) are calculated. The results are presented in the table below.

The decomposition pressures of LiH(c) have been determined by Hurd (5), at temperatures 782 - 926°K. By use of the second and third law methods, the enthalpy changes for the decomposition reaction (C) $\text{LiH(c)} = \text{Li(c)} + 1/2\text{H}_2\text{(g)}$ are evaluated as 21.87 ± 0.3 and 22.34 kcal/mol, respectively. Based on the third law ΔH^a_{298} and $\Delta H^a_{298}(\text{Li, l}) = 0.569$ kcal/mol, we derive the value $\Delta H^a_{298}(\text{LiH, c}) = -21.77 \pm 0.2$ kcal/mol, which is in good agreement with the values obtained by calorimetric method. Gunts (1) measured the decomposition pressure at 953°K for the same reaction. The third law ΔH^a_{298} and $\Delta H^a_{298}(\text{LiH, c})$ are evaluated as 21.86 and -21.79 kcal/mol, respectively.

Johnson (6) has determined the standard Gibbs energy of formation (ΔG^a) for LiH(c) from emf measurements over the temperature range 875 - 885°K. The cell utilized an Amoco Iron flag over which H_2 was passed as the cathode and a molten Li anode. LiCl, LiBr and LiI, each saturated with LiH were used as electrolytes. Using the reported emf values at different temperatures (47 data points) for reaction (C), we derive a $\Delta H^a_{298} = -21.81$ kcal/mol for LiH(c). The $\Delta H^a_{298}(\text{LiH, c})$ value reported by Gunn (4) is adopted.

Investigator	Reaction A	Reaction B	Reaction C	Drift eu	ΔH^a_{298} kcal/mol
1. Cuntz (1896)	-53.2	-31.6	-	-	-21.6
2. Hoers (1920)	-52.7±0.2	-31.1±0.1	21.86	-	-21.29
3. Messer (1955)	-53.10±0.11	-31.76±0.10	-	-	-21.6±0.25
4. Gunn (1958)	-53.14±0.02	-31.48±0.02	-	-	-21.34±0.15
5. Hurd (1935)	-	-	22.34	0.5±0.3	-21.66±0.03
6. Johnson (1966)	-	-	22.38	1.0±0.2	-21.81±0.15

Heat Capacity and Entropy

The low temperature heat capacities are obtained from the data of Kostyukov (7), 3.72 - 295.5°K. The cp data reported by Gunther (8) are consistently lower than the adopted ones in the temperature range 74.0 - 90.5°K but considerably higher at 292.7°K. The high temperature enthalpies have been determined by Fieldhouse (9), 413.2 - 914.3°K, and Vogt (10), 878.15 - 953.15°K. The derived high temperature heat capacities are joined smoothly with the low temperature values and extrapolated smoothly above 953.15°K.

S^a_{298} is calculated based on the adopted low temperature heat capacities, using $S^a_0 = 0.0002$ eu.

Melting Data

The value of T_m has been reported as 953 (1), 961 ± 1 (10, 12), 959.6 (11), and 961.8 ± 0.3 (13). The value reported by Messer (13) is adopted. The heat of melting (ΔH_m) has been determined as 5.095 ± 0.46 (13) and 5.237 ± 0.040 kcal/mol (14). The first ΔH_m value was evaluated cryogenically from the lowering of melting point in the systems LiH-Li₂O and LiH-CaH₂. The second value was derived from enthalpy data measured with copper block calorimeter. The adopted ΔH_m value is derived from the enthalpy data of Vogt (10) using the adopted heat capacities for LiH(c) and LiH(l).

Heat of Sublimation

The value of ΔH^a_{298} is calculated as the difference between ΔH^a_{298} for LiH(g) and LiH(c).

References

1. A. Cuntz, *Compt. Rend.*, 123, 694 (1896).
2. K. Hoers, *Z. Anorg. Chem.*, 113, 179 (1920).
3. C. E. Messer, L. G. Fasolino and C. E. Thalmyer, *J. Am. Chem. Soc.*, 77, 4524 (1955).
4. S. R. Gunn and L. G. Green, *J. Am. Chem. Soc.*, 80, 4782 (1958); S. R. Gunn, UCL-7992, Univ. of California, July 29, 1964.
5. C. B. Hurd and G. A. Moore, Jr., *J. Am. Chem. Soc.*, 57, 332 (1935).
6. C. Johnson, R. Heifrich, and C. E. Croftman, *J. Phys. Chem.*, 70, 242 (1966).
7. V. N. Kostyukov, *Russk. Khim. Rev.*, 35, 885 (1956).
8. P. Gunther, *Ann. Physik*, 63, 476 (1920).
9. I. B. Fieldhouse, J. C. Hedge and J. I. Lang, *Armour Research Foundation*, PB 151583, November 1958.
10. C. E. Messer, E. B. Damon, P. C. Maybury, J. H. Hollar and R. A. Seales, *J. Phys. Chem.*, 62, 220 (1958).
11. C. E. Messer and J. Mellor, *J. Phys. Chem.*, 64, 503 (1960).
12. C. E. Messer, *Rutherford App. Sci. Res.*, 10, 360 (1962).
13. C. E. Messer, J. H. Hollar, and I. S. Lewis, *Chem. Eng. Data*, 6, 328 (1961).
14. J. W. Vogt, *Thompson Ramo Wooldridge Inc.*, Cleveland, Ohio, NASA N63-22167, June 1962.

Lithium Hydride (LiH)

(Liquid)

GFW = 7.94697

T, °K	Cp*	$\frac{\text{kcal/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
300	14.900	5.314	5.314	.000	- 18.573	- 13.432	9.846
400	14.900	5.406	5.314	.028	- 18.563	- 13.400	9.762
500	14.900	5.493	5.493	1.518	- 18.041	- 11.756	8.425
600	14.900	5.577	5.577	3.006	- 18.316	- 10.166	7.444
700	14.900	5.658	5.658	4.498	- 17.891	- 8.578	6.424
800	14.900	5.734	5.734	5.988	- 17.452	- 7.060	5.424
900	14.900	5.805	5.805	7.478	- 17.007	- 5.607	4.424
1000	14.900	5.871	5.871	8.968	- 16.564	- 4.268	3.424
1100	14.900	5.932	5.932	10.456	- 16.123	- 3.030	2.424
1200	14.900	5.988	5.988	11.948	- 15.684	- 1.853	1.424
1300	14.900	6.040	6.040	13.438	- 15.249	- .728	.424
1400	14.900	6.087	6.087	14.928	- 14.817	.341	-.576
1500	14.900	6.130	6.130	16.418	- 14.389	1.437	-1.576
1600	14.900	6.168	6.168	17.908	- 13.965	2.533	-2.576
1700	14.900	6.202	6.202	19.398	- 13.545	3.630	-3.576
1800	14.900	6.232	6.232	20.888	- 13.129	4.727	-4.576
1900	14.900	6.258	6.258	22.378	- 12.717	5.824	-5.576
2000	14.900	6.280	6.280	23.868	- 12.309	6.921	-6.576
2100	14.900	6.298	6.298	25.358	- 11.907	8.018	-7.576
2200	14.900	6.313	6.313	26.848	- 11.510	9.115	-8.576
2300	14.900	6.325	6.325	28.338	- 11.117	10.212	-9.576
2400	14.900	6.334	6.334	29.828	- 10.729	11.309	-10.576
2500	14.900	6.340	6.340	31.318	- 10.346	12.406	-11.576
2600	14.900	6.344	6.344	32.808	- 9.968	13.503	-12.576
2700	14.900	6.346	6.346	34.298	- 9.595	14.600	-13.576
2800	14.900	6.346	6.346	35.788	- 9.227	15.697	-14.576
2900	14.900	6.344	6.344	37.278	- 8.864	16.794	-15.576
3000	14.900	6.340	6.340	38.768	- 8.506	17.891	-16.576

HL i

LITHIUM HYDRIDE (LiH)

(LIQUID)

GFW = 7.94697

 $S^\circ_{298.15} = 5.314 \text{ gibbs/mol}$ $\Delta H^\circ_{298.15} = -18.573 \text{ kcal/mol}$ $T_m = 961.8 \pm 0.3^\circ\text{K}$ $\Delta H_m^\circ = 5.40 \pm 0.10 \text{ kcal/mol}$ $T_d = 1223^\circ\text{K}$

Heat of Formation

 $\Delta H^\circ_{298}(l)$ is obtained from $\Delta H^\circ_{298}(c)$ by adding ΔH_m° and the difference between $H^\circ_{961.8} - H^\circ_{298}$ for crystal and liquid.

The decomposition pressures of LiH(l) at different temperatures have been investigated by Hill (1), Perlow (2), Johnson, and Gibb (3). Based on their reported equilibrium pressures, the enthalpy changes for the reaction $\text{LiH}(l) = \text{Li}(l) + 1/2\text{H}_2(g)$ are evaluated by the second and third law methods. The results are presented in the table below. It should be noted that the measured decomposition pressures are highly sensitive to composition and change extremely rapidly between 99 and 100 percent purity. Therefore we give no weight to the equilibrium data.

Investigator	Temperature, °K	No. of Points	ΔH°_{298} , kcal/mol		ΔH°_{298} , kcal/mol
			Second Law	Third Law	
Hill (1938)	973.2	1	—	16.93	—
Perlow (1941)	1043-1098	2	20.10	17.69	-2.2
Johnson*	1050-1090	—	24.69	18.36	-5.9
Gibb (1951)	1073-1173	2	5.66	15.2	+8.5

*The vapor pressure values are calculated from an equation quoted by Gibb (3), but derived from the vapor pressures measured by W. C. Johnson, University of Chicago.

**Based on the third law ΔH°_{298} .

Heat Capacity and Entropy

The enthalpies of LiH(l) in the temperature range 975.15-1075.15°K have been measured by Vogt (5). Using the reported enthalpy values, the heat capacity of LiH(l) is derived as 14.9 gibbs/mol. This Cp value is adopted and extrapolated above and below the measured range.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See LiH(c) table for details.

Decomposition Temperature

T_d is calculated as the temperature at which LiH(l) decomposes into Li(l) and $\text{H}_2(g)$ where the partial pressure of $\text{H}_2(g)$ equals one atmosphere.

References

1. L. L. Hill, Ph. D. Thesis, University of Chicago, 1936.
2. M. R. J. Perlow, Ph. D. Thesis, University of Chicago, 1941.
3. T. R. P. Gibb, J. Electrochem. Soc. 93, 198 (1946).
4. T. R. P. Gibb, NEPA-1841, Apr. 30, 1951.
5. J. W. Vogt, Thompson Ramo Wooldridges Inc., Cleveland, Ohio, NASA N63-22167, June 1962.

HL i

(IDEAL GAS)

LITHIUM HYDRIDE (LiH)

GFW = 7.94697

Ground State Configuration $1s^2$

$\Delta H_f^\circ = 33.65 \pm 0.01$ kcal/mol

$\Delta H_{298.15}^\circ = 33.61 \pm 0.01$ kcal/mol

$S_{298}^\circ = 40.821$ gibbs/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	1
26513.7	1
30912.0	2
$\omega_e x_e = 23.24$ cm ⁻¹	
$\omega_e = 1406.73$ cm ⁻¹	
$\sigma = 1$	
$\nu_e = 1.595 \text{ } \mu$	
$\nu_e = 0.2137$ cm ⁻¹	

Heat of Formation

R. Velasco, Can. J. Phys. **35**, 1704 (1957), observed the absorption spectra of LiH(g) in the near ultraviolet with high dispersion and absorbing path lengths up to 16 meters. He found a new band system involving the ground state and a $^1\Pi$ excited state. Rotational and vibrational analyses of this system were carried out and the observed breaking off of the rotational structure of the bands was interpreted as due to predissociation by rotation. With this assumption very accurate dissociation limits of the $B^1\Pi$ state were obtained. From these dissociation limits the dissociation energy (D_0) of the ground state of LiH was found to be 2.4288 ± 0.0002 eV. Based on this D_0 value, we adopt $\Delta H_f^\circ = 33.61$ kcal/mol for LiH(g).

M. Kemperer, J. Chem. Phys. **23**, 2452 (1955), observed the infrared spectrum of LiH(g) in emission in the frequency region 1500 to 970 cm⁻¹, using a Perkin-Elmer double-pass monochromator with NaCl optics. Estimating the minimum LiH pressure as 10 mm and assuming the maximum possible Li pressure, he reported $K = 0.005$ (atm) at 1400°K for the reaction $2Li(g) + H_2(g) = 2LiH(g)$. We calculate the corresponding enthalpy change, ΔH_{1400}° , to be -9.63 kcal/mol, employing $\Delta S_{1400}^\circ = -17.407$ eu. Incorporating this ΔH_{1400}° value with $\Delta H_f^\circ = 35.601$ kcal/mol for Li(g), we obtain $\Delta H_{298}^\circ = 33.92$ kcal/mol for LiH(g), which is in good agreement with the adopted value.

A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953, derived the value $D_0(LiH) = 2.5 \pm 0.2$ eV from earlier spectroscopic data.

Heat Capacity and Entropy

The third electronic level and quantum weight are obtained from Velasco, loc. cit. All the other constants are taken from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., and corrected to the average isotopic species. The moment of inertia is 3.7183×10^{-40} g cm².

Dec. 31, 1960; Sept. 30, 1967

T, °K	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	- 2.076	33.651	33.651	INFINITE
100	6.964	33.183	47.056	- 1.367	33.641	33.641	69.757
200	16.644	36.015	47.865	- 0.860	33.799	33.799	32.776
298	7.106	40.821	48.521	- 0.000	33.610	28.105	20.645
300	7.109	40.865	48.621	.013	33.606	28.131	20.493
400	7.364	42.983	41.102	7.364	33.361	26.343	16.393
500	7.655	44.617	42.640	14.887	32.944	24.694	10.784
600	7.921	46.037	42.240	22.464	32.606	23.192	8.488
700	8.165	47.276	42.680	30.070	31.813	21.736	6.786
800	8.399	48.376	43.508	37.736	31.592	20.309	5.588
900	8.624	49.366	44.105	45.435	31.366	18.911	4.592
1000	8.861	50.265	44.677	53.191	31.191	17.535	3.832
1100	9.038	51.090	45.223	61.054	31.005	16.170	3.215
1200	9.185	51.851	45.764	69.029	30.825	14.839	2.703
1300	9.312	52.558	46.291	77.121	30.650	13.513	2.272
1400	9.429	53.217	46.816	85.330	30.477	12.202	1.905
1500	9.537	53.835	47.327	93.657	30.307	10.903	1.589
1600	9.638	54.417	47.825	10.898	30.138	9.615	1.313
1700	9.734	54.966	48.302	12.715	29.966	8.346	1.079
1800	9.826	55.487	48.762	14.715	29.795	7.100	0.879
1900	9.914	55.981	49.207	16.849	29.624	5.873	0.700
2000	10.000	56.452	49.638	19.149	29.453	4.668	0.549
2100	10.084	56.902	50.055	21.571	29.283	3.489	0.420
2200	10.165	57.333	50.453	24.121	29.113	2.342	0.310
2300	10.244	57.746	50.835	26.796	28.943	1.226	0.216
2400	10.321	58.143	51.201	29.596	28.773	0.143	0.136
2500	10.396	58.525	51.551	32.521	28.603	- 0.882	0.070
2600	10.468	58.893	51.889	35.571	28.433	- 1.907	0.013
2700	10.538	59.248	52.217	38.746	28.263	- 2.932	- 0.034
2800	10.606	59.591	52.535	42.046	28.093	- 3.957	- 0.087
2900	10.672	59.923	52.843	45.471	27.923	- 4.982	- 0.140
3000	10.737	60.245	53.141	49.021	27.753	- 5.997	- 0.193
3100	10.801	60.557	53.429	52.696	27.583	- 6.992	- 0.246
3200	10.864	60.860	53.707	56.506	27.413	- 7.967	- 0.299
3300	10.926	61.154	53.975	60.451	27.243	- 8.922	- 0.352
3400	10.987	61.438	54.234	64.531	27.073	- 9.857	- 0.405
3500	11.048	61.712	54.483	68.746	26.903	- 10.772	- 0.458
3600	11.108	61.976	54.723	73.096	26.733	- 11.667	- 0.511
3700	11.167	62.230	54.958	77.581	26.563	- 12.540	- 0.564
3800	11.225	62.474	55.188	82.196	26.393	- 13.388	- 0.617
3900	11.282	62.708	55.413	86.941	26.223	- 14.211	- 0.670
4000	11.338	62.932	55.633	91.816	26.053	- 15.009	- 0.723
4100	11.393	63.147	55.848	96.821	25.883	- 15.782	- 0.776
4200	11.447	63.352	56.058	101.956	25.713	- 16.530	- 0.829
4300	11.500	63.548	56.263	107.221	25.543	- 17.253	- 0.882
4400	11.552	63.735	56.463	112.616	25.373	- 17.951	- 0.935
4500	11.604	63.912	56.658	118.141	25.203	- 18.624	- 0.988
4600	11.655	64.080	56.848	123.796	25.033	- 19.272	- 1.041
4700	11.706	64.238	57.033	129.581	24.863	- 19.899	- 1.094
4800	11.756	64.387	57.213	135.496	24.693	- 20.504	- 1.147
4900	11.806	64.528	57.388	141.541	24.523	- 21.089	- 1.199
5000	11.856	64.660	57.558	147.716	24.353	- 21.654	- 1.252
5100	11.906	64.783	57.723	154.021	24.183	- 22.199	- 1.305
5200	11.956	64.898	57.883	160.456	24.013	- 22.724	- 1.358
5300	12.006	64.999	58.038	167.021	23.843	- 23.229	- 1.411
5400	12.056	65.096	58.188	173.716	23.673	- 23.714	- 1.464
5500	12.106	65.188	58.333	180.541	23.503	- 24.179	- 1.517
5600	12.156	65.275	58.473	187.496	23.333	- 24.624	- 1.570
5700	12.206	65.358	58.608	194.581	23.163	- 25.049	- 1.623
5800	12.256	65.437	58.738	201.796	22.993	- 25.454	- 1.676
5900	12.306	65.512	58.863	209.141	22.823	- 25.839	- 1.729
6000	12.356	65.583	58.983	216.616	22.653	- 26.204	- 1.782
6100	12.406	65.650	59.103	224.221	22.483	- 26.549	- 1.835
6200	12.456	65.715	59.218	231.956	22.313	- 26.874	- 1.888
6300	12.506	65.776	59.328	239.821	22.143	- 27.189	- 1.941
6400	12.556	65.833	59.433	247.816	21.973	- 27.484	- 1.994
6500	12.606	65.888	59.533	255.941	21.803	- 27.759	- 2.047
6600	12.656	65.938	59.628	264.196	21.633	- 28.014	- 2.100
6700	12.706	65.983	59.718	272.581	21.463	- 28.249	- 2.153
6800	12.756	66.028	59.803	281.096	21.293	- 28.464	- 2.206
6900	12.806	66.068	59.883	289.741	21.123	- 28.659	- 2.259
7000	12.856	66.103	59.958	298.516	20.953	- 28.834	- 2.312
7100	12.906	66.138	60.028	307.421	20.783	- 28.989	- 2.365
7200	12.956	66.168	60.093	316.456	20.613	- 29.124	- 2.418
7300	13.006	66.193	60.153	325.621	20.443	- 29.239	- 2.471
7400	13.056	66.218	60.208	334.916	20.273	- 29.334	- 2.524
7500	13.106	66.238	60.258	344.341	20.103	- 29.409	- 2.577
7600	13.156	66.253	60.303	353.896	19.933	- 29.464	- 2.630
7700	13.206	66.268	60.343	363.581	19.763	- 29.499	- 2.683
7800	13.256	66.278	60.378	373.396	19.593	- 29.514	- 2.736
7900	13.306	66.283	60.408	383.341	19.423	- 29.509	- 2.789
8000	13.356	66.288	60.433	393.416	19.253	- 29.484	- 2.842
8100	13.406	66.288	60.453	403.621	19.083	- 29.439	- 2.895
8200	13.456	66.283	60.468	413.956	18.913	- 29.374	- 2.948
8300	13.506	66.273	60.468	424.421	18.743	- 29.289	- 2.999
8400	13.556	66.258	60.453	434.916	18.573	- 29.184	- 3.052
8500	13.606	66.238	60.428	445.541	18.403	- 29.059	- 3.105
8600	13.656	66.213	60.393	456.296	18.233	- 28.914	- 3.158
8700	13.706	66.183	60.353	467.181	18.063	- 28.749	- 3.211
8800	13.756	66.148	60.308	478.196	17.893	- 28.564	- 3.264
8900	13.806	66.108	60.258	489.341	17.723	- 28.359	- 3.317
9000	13.856	66.063	60.203	500.616	17.553	- 28.134	- 3.370
9100	13.906	66.013	60.143	512.021	17.383	- 27.889	- 3.423
9200	13.956	65.958	60.078	523.556	17.213	- 27.624	- 3.476
9300	14.006	65.898	60.008	535.221	17.043	- 27.339	- 3.529
9400	14.056	65.833	59.933	547.016	16.873	- 27.034	- 3.582
9500	14.106	65.763	59.853	558.941	16.703	- 26.709	- 3.635
9600	14.156	65.688	59.768	571.096	16.533	- 26.364	- 3.688
9700	14.206	65.608	59.678	583.481	16.363	- 25.999	- 3.741
9800	14.256	65.523	59.583	596.096	16.193	- 25.614	- 3.794
9900	14.306	65.433	59.483	608.941	16.023	- 25.209	- 3.847
10000	14.356	65.338	59.378	622.016	15.853	- 24.784	- 3.899

Lithium Hydroxide (LiOH)

(Crystal)

Mol. Wt. = 23.94637

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	Log K _p
0	0.000	0.000	INFINITE	1.770	-114.456	INFINITE
100	3.092	2.044	18.116	1.637	-111.911	244.581
200	8.600	6.124	11.218	1.019	-108.442	118.600
298	11.850	10.225	10.225	0.000	-104.858	76.863
300	11.900	10.299	10.225	0.022	-104.700	76.339
400	13.900	14.020	10.719	2.760	-101.535	42.546
500	15.250	17.272	11.712	2.760	-97.937	42.546
600	16.300	20.143	12.882	4.357	-93.507	34.060
700	17.370	22.737	14.101	6.040	-89.709	28.008
800	18.165	25.117	15.337	7.824	-85.953	23.491
900	18.740	27.248	16.586	9.698	-82.548	19.422
1000	19.336	29.303	17.723	11.580	-79.578	15.173
1100	19.807	31.168	18.661	13.538	-74.961	14.693
1200	20.234	32.910	19.560	15.540	-71.390	13.002
1300	20.630	34.546	21.020	17.583	-67.863	11.409
1400	21.004	36.098	22.042	19.763	-64.984	10.050
1500	21.360	37.550	23.027	21.963	-62.578	8.880
1600	21.704	38.939	23.979	23.937	-57.546	7.860
1700	22.038	40.265	24.898	26.124	-52.862	6.796
1800	22.364	41.534	25.787	28.344	-47.412	5.757
1900	22.684	42.755	26.645	30.584	-42.142	4.757
2000	23.000	43.923	27.483	32.881	-36.059	4.006

LITHIUM HYDROXIDE (LiOH)

(CRYSTAL)

MOL. WT. = 23.94637

HLiO

S_{298.15} = 10.225 cal. deg.⁻¹ mole⁻¹
 T_m = 744.3°K.

Heat of Formation.

The standard enthalpy of formation, ΔH_f⁰ 298 (LiOH, c) = -115.84 ± 0.1 kcal. mole⁻¹, was calculated from the heat of solution of lithium hydroxide (c), the heat of hydrolysis of lithium metal and the appropriate auxiliary data. N. A. Peabody⁷ has measured the heat of solution LiOH(c) → LiOH(400 H₂O) as -5.479 ± 0.007 kcal. mole⁻¹ at 298.15°K. by solution calorimetry. Using the auxiliary heat of dilution reported by V. B. Parker⁸, the selected heat of solution of lithium hydroxide (c) at infinite dilution is -5.632 kcal. mole⁻¹.

The heat of hydrolysis of lithium metal, ΔH_f⁰ 298, has been measured in the solution calorimeter by the following investigators.

Source	Number of moles of H ₂ O	ΔH _f ⁰ 298 kcal. mole ⁻¹	ΔH _f ⁰ 298 (LiOH(c)) kcal. mole ⁻¹
Gunn et al. ³	1000	-53.115 ± 0.019	-121.532
Messer et al. ⁴	OO	-53.075 ± 0.20	-121.390
			-115.900
			-115.758

The values of ΔH_f⁰ 298 (LiOH(c)) were calculated from the heats of reaction ΔH_f⁰ 298, using the ΔH_f⁰ 298 (H₂O, l) = -68.315 kcal. mole⁻¹.⁵ Combination of the selected heat of solution of LiOH(c) at infinite dilution with the heat of formation of LiOH(c) gives the heat of formation of LiOH(c) in the last column of the table. A weighted average of these measurements was taken for the adopted heat of formation of lithium hydroxide (c).

The earlier calorimetric investigations have been reviewed by P. R. Bichowsky and F. D. Rossini⁶, and C. E. Messer et al.⁴, and these data are not adopted in the tabulation.

Heat Capacity and Entropy.

The low temperature heat capacities of lithium hydroxide (c) from 15.91° to 302.85°K. have been measured by T. W. Bauer, H. L. Johnston and E. C. Kerr⁷. The high temperature heat capacities which were determined from the enthalpy measurements in the temperature range from 418° to 878°K. by the drop method have been reported by C. H. Shomate and A. J. Cohen⁸. The low temperature and the high temperature heat capacities have been joined smoothly by the Shomate method⁹. The smooth values of heat capacity of LiOH(c) were adopted in the tabulation.

W. D. Powers and G. C. Blalock¹⁰ have also measured the high temperature enthalpy changes of LiOH(c) by the drop method. Their results are in agreement with the tabulated H_m-H₂₉₈ values within the experimental uncertainty.

The entropy (S₂₉₈ = 10.225 cal. deg.⁻¹ mole⁻¹) was obtained from Bauer et al.⁷, based on an extrapolation of S₁₆ = 0.028 cal. deg.⁻¹ mole⁻¹.

Melting Data.

The adopted heat of melting and the melting point were obtained from the enthalpy measurements by Shomate and Cohen⁸. Powers and Blalock¹⁰ also found the heat of melting ΔH_m⁰ = 5.029 kcal. mole⁻¹ at 746°K. which is in good agreement with the adopted value.

Reference:

1. N. A. Peabody, Zhur. Neorg. Khim., **6**, 682 (1961).
2. V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-NBS 2, Apr. 1965.
3. S. R. Gunn and L. O. Green, J. Am. Chem. Soc., **80**, 4782 (1958).
4. S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking-Bomb Solution Calorimeters," J. Am. Chem. Soc., **77**, 4524 (1955).
5. C. E. Messer, L. O. Green, and C. E. Thalmayer, J. Am. Chem. Soc., **77**, 4524 (1955).
6. P. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, 1955.
7. T. W. Bauer, H. L. Johnston and E. C. Kerr, J. Am. Chem. Soc., **72**, 5174 (1950).
8. C. H. Shomate and A. J. Cohen, J. Am. Chem. Soc., **77**, 285 (1955).
9. W. D. Powers, J. Phys. Chem., **59**, 568 (1955).
10. W. D. Powers and G. C. Blalock, "Enthalpy and Specific Heats of Alkali and Alkaline Earth Hydroxides at High Temperatures," ORNL-1653, Oak Ridge Nat'l. Lab., Jan. 1954.

Dec. 31, 1960; Mar. 31, 1966

HLiO

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0								
100	20.740	11.574	11.574		0.000	-113.263	-102.683	75.269
200	20.740	11.702	11.702		0.038	-113.249	-102.618	74.757
300	20.740	11.769	11.769		2.112	-112.498	-99.189	54.194
400	20.740	12.297	13.024		4.186	-112.557	-95.866	41.903
500	20.740	15.464	15.464		6.260	-111.924	-92.587	33.725
600	20.740	26.078	17.369		8.434	-111.290	-89.415	27.916
700	20.740	32.045	19.036		10.408	-110.660	-86.334	23.585
800	20.740	34.488	20.618		12.482	-110.040	-83.330	20.235
900	20.740	36.673	22.117		14.556	-109.428	-80.395	17.570
1000	20.740	38.650	23.531		16.630	-108.825	-77.521	15.402
1100	20.740	40.450	24.867		18.704	-108.230	-74.702	13.605
1200	20.740	42.114	26.131		20.778	-107.642	-71.932	12.093
1300	20.740	43.651	27.328		22.852	-107.062	-69.206	10.804
1400	20.740	45.082	28.465		24.926	-106.490	-66.522	9.692
1500	20.740	46.421	29.566		27.000	-105.924	-63.877	8.725
1600	20.740	47.678	30.578		29.074	-105.378	-61.270	7.905
1700	20.740	48.864	31.559		31.148	-104.842	-58.697	7.205
1800	20.740	49.985	32.499		33.222	-104.316	-56.155	6.615
1900	20.740	51.049	33.401		35.296	-103.793	-53.641	6.038
2000	20.740	52.061	34.265		37.370	-103.272	-51.151	5.471
2100	20.740	53.025	35.096		39.444	-102.752	-48.684	4.910
2200	20.740	53.947	35.896		41.518	-102.234	-46.242	4.354
2300	20.740	54.830	36.667		43.592	-101.719	-43.822	3.802
2400	20.740	55.677	37.410		45.666	-101.206	-41.422	3.254
2500	20.740	56.490	38.129		47.740	-100.693	-39.042	2.710
2600	20.740	57.273	38.823		49.814	-100.182	-36.682	2.170
2700	20.740	58.027	39.496		51.888	-99.672	-34.342	1.634
2800	20.740	58.755	40.147		53.962	-99.162	-32.022	1.104
2900	20.740	59.458	40.779		56.036	-98.652	-29.722	0.578
3000	20.740	60.138	41.393		58.110	-98.142	-27.442	0.052
3100	20.740	60.797	41.989		60.184	-97.632	-25.182	-0.474
3200	20.740	61.435	42.569		62.258	-97.122	-22.942	-0.998
3300	20.740	62.054	43.133		64.332	-96.612	-20.722	-1.522
3400	20.740	62.655	43.682		66.406	-96.102	-18.522	-2.046
3500	20.740							

Dec. 31, 1960; Mar. 31, 1966

 $S_{298.15}^0 = 11.574 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $T_m = 744.3^\circ\text{K.}$ $T_b(\text{monomeric gas}) = 1803^\circ\text{K.}$ $\Delta H_f^0 298.15 = -113.263 \text{ kcal. mole}^{-1}$ $\Delta H_m^0 = 5.010 \text{ kcal. mole}^{-1}$ $\Delta H_v^0(\text{to monomer}) = 40.1 \text{ kcal. mole}^{-1}$ Heat of Formation.

The heat of formation of LiOH(1) at 298.15°K. was obtained from that of the crystal by adding ΔH_m^0 and the difference between $H_{744.3}^0 298.15$ for crystal and liquid.

Heat Capacity and Entropy.

The selected heat capacity of the liquid phase, $C_p = 20.74 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, was obtained from the enthalpy measurements in the drop calorimeter by C. H. Shomate and A. J. Cohen, *J. Am. Chem. Soc.* **77**, 285 (1955).

W. D. Powers and O. C. Blalock, ORNL-1653, Oak Ridge Nat'l. Lab., have also determined the heat capacity of lithium hydroxide (1), $C_p = 22.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, from the enthalpy measurements by the drop method.

The entropy ($S_{298.15}^0 = 11.574 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See LiOH(c) table for details.

Vaporization Data.

The boiling point was calculated as the temperature at which the free energies of formation (ΔF_f^0) for both LiOH(1) and LiOH(g) are equal. The difference in the heats of formation (ΔH_f^0) of LiOH(1) and LiOH(g) at the boiling point is the heat of vaporization (ΔH_v^0).

Lithium Hydroxide (LiOH)

(Ideal Gas) Mol. Wt. = 23.94637

LITHIUM HYDROXIDE (LiOH)

(IDEAL GAS)

MOL. WT. = 23.94637

T, K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	7.949	43.240	58.089	-2.400	-58.089	-58.089	INFINITE
200	8.041	48.764	58.149	-1.605	-58.149	-59.001	128.947
298	8.474	52.044	58.433	-808	-58.433	-60.329	65.305
300	8.485	52.097	58.451	-806	-58.451	-60.339	63.957
400	9.07	52.822	58.851	-805	-58.851	-60.767	33.202
500	9.686	56.718	59.426	-805	-59.426	-61.008	26.666
600	10.163	58.228	60.435	-805	-60.435	-61.068	22.244
700	10.551	60.124	61.339	-805	-61.339	-61.058	19.063
800	10.85	62.255	62.153	-805	-62.153	-60.882	16.583
900	11.08	64.585	62.885	-805	-62.885	-60.733	13.273
1000	11.400	66.941	63.466	-805	-63.466	-60.568	8.679
1100	11.620	69.138	63.818	-805	-63.818	-60.551	12.030
1200	11.818	71.157	64.024	-805	-64.024	-60.340	10.989
1300	12.000	73.000	64.100	-805	-64.100	-60.266	10.342
1400	12.157	74.600	64.157	-805	-64.157	-60.206	9.842
1500	12.302	76.000	64.198	-805	-64.198	-60.156	9.409
1600	12.432	77.200	64.230	-805	-64.230	-60.116	8.996
1700	12.550	78.300	64.250	-805	-64.250	-60.084	8.600
1800	12.657	79.300	64.260	-805	-64.260	-60.056	8.218
1900	12.755	80.200	64.260	-805	-64.260	-60.032	7.848
2000	12.837	81.000	64.250	-805	-64.250	-60.011	7.490
2100	12.915	81.700	64.230	-805	-64.230	-60.000	7.143
2200	12.985	82.300	64.200	-805	-64.200	-60.000	6.807
2300	13.047	82.800	64.160	-805	-64.160	-60.000	6.481
2400	13.105	83.200	64.110	-805	-64.110	-60.000	6.164
2500	13.159	83.500	64.050	-805	-64.050	-60.000	5.856
2600	13.207	83.700	63.980	-805	-63.980	-60.000	5.557
2700	13.251	83.800	63.900	-805	-63.900	-60.000	5.267
2800	13.291	83.800	63.810	-805	-63.810	-60.000	4.985
2900	13.327	83.700	63.710	-805	-63.710	-60.000	4.710
3000	13.361	83.500	63.600	-805	-63.600	-60.000	4.443
3100	13.392	83.200	63.480	-805	-63.480	-60.000	4.184
3200	13.420	82.800	63.350	-805	-63.350	-60.000	3.933
3300	13.446	82.300	63.210	-805	-63.210	-60.000	3.689
3400	13.470	81.700	63.060	-805	-63.060	-60.000	3.452
3500	13.493	81.000	62.900	-805	-62.900	-60.000	3.221
3600	13.514	80.200	62.730	-805	-62.730	-60.000	2.995
3700	13.533	79.300	62.560	-805	-62.560	-60.000	2.774
3800	13.552	78.300	62.380	-805	-62.380	-60.000	2.557
3900	13.568	77.200	62.200	-805	-62.200	-60.000	2.343
4000	13.584	76.000	62.010	-805	-62.010	-60.000	2.132
4100	13.599	74.700	61.810	-805	-61.810	-60.000	1.924
4200	13.612	73.300	61.600	-805	-61.600	-60.000	1.719
4300	13.623	71.800	61.380	-805	-61.380	-60.000	1.517
4400	13.632	70.200	61.150	-805	-61.150	-60.000	1.317
4500	13.639	68.500	60.910	-805	-60.910	-60.000	1.119
4600	13.659	66.700	60.660	-805	-60.660	-60.000	0.924
4700	13.669	64.800	60.400	-805	-60.400	-60.000	0.732
4800	13.688	62.800	60.130	-805	-60.130	-60.000	0.542
4900	13.696	60.700	59.850	-805	-59.850	-60.000	0.354
5000	13.696	58.500	59.560	-805	-59.560	-60.000	0.168
5100	13.704	56.200	59.260	-805	-59.260	-60.000	-0.016
5200	13.711	53.800	58.950	-805	-58.950	-60.000	-0.200
5300	13.717	51.300	58.630	-805	-58.630	-60.000	-0.384
5400	13.725	48.700	58.300	-805	-58.300	-60.000	-0.568
5500	13.732	46.000	57.960	-805	-57.960	-60.000	-0.752
5600	13.738	43.200	57.610	-805	-57.610	-60.000	-0.936
5700	13.744	40.300	57.250	-805	-57.250	-60.000	-1.120
5800	13.750	37.300	56.880	-805	-56.880	-60.000	-1.304
5900	13.754	34.200	56.500	-805	-56.500	-60.000	-1.488
6000	13.759	31.000	56.110	-805	-56.110	-60.000	-1.672

ΔH_f⁰ = -58.1 ± 4 kcal. mole⁻¹

ΔH_f⁰ 298.15 = -59.8 ± 4 kcal. mole⁻¹

Point Group C_s

S_{298.15} = [52.0] cal. deg⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_i cm⁻¹

[1000](1)

[1300](1)

[3700](1)

Bond Distance: Li-O = [1.60] Å O-H = [0.96] Å

Bond Angle: Li-O-H = [110]°

Product of the Moments of Inertia: I_AI_BI_C = [0.6156 × 10⁻¹¹] g.³ cm.⁶

σ = 1

Heat of Formation

J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 535 (1960), have studied the equilibrium of Li₂O(c) - H₂O(g) system by the mass-spectrometric method. Using the reported equilibrium constants in the temperature range from 1100° to 1450°K, the heat of reaction Li₂O(c) + H₂O(g) → 2LiOH(g) at 298.15°K. has been calculated by both the second and the third law methods as 86.1 and 83.2 kcal. mole⁻¹, respectively. (The third law drift is -2.2 ± 2.6 e.u.) The third law value was taken for the calculation of the heat of formation of LiOH(g) at 298.15°K.

Heat Capacity and Entropy

Since the bond distance Li-F(g) (r_e = 1.56389 Å) was accurately measured from the microwave studies by L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagh and V. E. Derr, J. Chem. Phys. 39, 1203 (1963), the bond distance Li-O in LiOH(g) was estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-F(g) to the bond distance Li-F(g). Also the bond distance Li-O(g) was estimated as 1.62 Å from the matrix-isolated infrared spectrum by D. White, K. S. Seshadri, D. P. Dever, D. E. Mann, M. J. Linevsky, J. Chem. Phys. 39, 2463 (1963). These two are in good agreement. The bond distance O-H was estimated from that in H₂O(g). The adopted bent molecular configuration with bond angle of 110° was proposed by S. H. Bauer, R. M. Diner and P. F. Porter, J. Chem. Phys. 29, 991 (1958). The three principal moments of inertia are I_A = [0.1237] × 10⁻³⁸, I_B = [2.1699] × 10⁻³⁹ and I_C = [2.2936] × 10⁻³⁹ g. cm.²

The Li-O stretching frequency was estimated to be the same as that in Li₂O(g) (ν = 987 cm.⁻¹, see Li₂O(g) table). The bending and the O-H stretching frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rapid convergence to a constant as a heavier atom is attached.

MAGNESIUM MONOHYDRIDE (MgH) (IDEAL GAS) GFW = 25.31997

T, °K

C_p^oS^o- (G° - H°₂₉₈)/TH° - H°₂₉₈

Kcal/mol

ΔH^oΔG^oLog K_p

INFINITE

- 2.075

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

40.533

Dec. 31, 1960; Dec. 31, 1966

Ground State Configuration 2Σ⁺S^o298.15 = 46.15 gibbs/molΔH_f^o = 40.5 ± 11.5 kcal/molΔH_f^o298.15 = 40.4 ± 11.5 kcal/mol

Electronic Levels and Quantum Weights

ε_i, cm⁻¹ω_e = 1495.7 cm⁻¹B_e = 5.8181 cm⁻¹ω_ex_e = 31.5 cm⁻¹

σ = 1

r_e = 1.73 Åα_e = 0.1668 cm⁻¹

Heat of Formation.

The heat of formation is calculated using D₀^o = 2.0 ± 0.5 e.v. derived from a graphical extrapolation of the V(0-3) energy levels of the X²Σ⁺ state reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Edition, Chapman and Hall Ltd., London, 1953. G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," 2nd Edition, D. Van Nostrand Co., Inc., New York, 1950, reported D₀^o ≤ 2.49 e.v. assuming predissociation of the C²Π state of MgH into Mg(³P) and H(²S).

Heat Capacity and Entropy.

The molecular constants and electronic levels are obtained from Herzberg, loc. cit., except for the electronic levels 35000 and 48000 obtained from M. A. Khan, Proc. Phys. Soc. (London) B₂, 209 - 21 (1962).

Magnesium Monohydroxide (MgOH)
(Ideal Gas) $\text{GFW} = 41.31937$

T, °K	C_p^0	S^0	$-(G^0 - H^0_{298})/T$	$H^0 - H^0_{298}$	ΔH^0	ΔG^0	Log Kp
0	-0.000	-0.000	INFINITE	-2.169	-50.923	-50.923	INFINITE
100	6.958	44.924	59.540	-1.474	-51.109	-52.085	113.831
200	7.320	49.812	53.444	-0.767	-51.613	-52.995	57.910
298	8.1360	52.916	52.916	0.000	-52.009	-53.499	39.209
300	8.382	52.968	52.916	-0.015	-52.009	-53.499	38.074
400	9.485	55.535	53.259	0.810	-52.430	-53.931	29.467
500	10.342	57.748	53.940	1.804	-52.793	-54.262	23.718
600	10.970	59.632	54.740	2.871	-53.123	-54.526	19.861
700	11.413	61.253	55.543	3.957	-53.427	-54.749	16.843
800	11.817	62.674	56.253	5.057	-53.707	-54.931	14.398
900	12.128	64.384	57.213	6.254	-54.074	-55.023	13.361
1000	12.334	65.676	57.995	7.681	-54.539	-55.029	12.005
1100	12.528	66.899	58.749	9.332	-54.872	-54.754	10.879
1200	12.709	68.011	59.472	11.255	-55.177	-54.405	9.910
1300	12.871	69.012	60.172	13.409	-55.455	-54.000	9.130
1400	13.019	69.942	60.833	15.809	-55.707	-53.563	8.362
1500	13.130	70.797	61.474	18.434	-55.930	-53.101	7.442
1600	13.262	71.561	62.090	21.274	-56.124	-52.614	6.639
1700	13.416	72.243	62.686	24.439	-56.290	-52.110	5.789
1800	13.585	72.850	63.255	27.934	-56.428	-51.594	4.935
1900	13.779	73.380	63.807	31.763	-56.540	-51.063	4.235
2000	13.964	73.841	64.339	35.934	-56.628	-50.514	3.688
2100	14.141	74.230	64.854	40.454	-56.697	-50.000	3.269
2200	14.301	74.563	65.343	45.324	-56.748	-49.510	2.924
2300	14.443	74.843	65.807	50.544	-56.782	-49.040	2.642
2400	14.579	75.077	66.249	56.114	-56.800	-48.590	2.422
2500	14.710	75.265	66.670	62.034	-56.805	-48.154	2.232
2600	14.827	75.400	67.079	68.304	-56.797	-47.734	2.085
2700	14.930	75.493	67.463	74.924	-56.777	-47.324	1.971
2800	15.020	75.547	67.833	81.894	-56.748	-46.924	1.874
2900	15.097	75.577	68.189	89.214	-56.702	-46.534	1.794
3000	15.178	75.587	68.533	96.884	-56.642	-46.154	1.724
3100	15.253	75.577	68.867	104.904	-56.567	-45.784	1.664
3200	15.323	75.547	69.189	113.274	-56.477	-45.424	1.614
3300	15.388	75.493	69.500	122.004	-56.372	-45.074	1.574
3400	15.448	75.413	69.797	131.094	-56.252	-44.744	1.544
3500	15.512	75.300	70.079	140.544	-56.117	-44.424	1.524
3600	15.580	75.153	71.021	150.354	-55.967	-44.114	1.514
3700	15.653	74.970	71.733	160.524	-55.802	-43.814	1.514
3800	15.730	74.753	72.313	171.054	-55.622	-43.524	1.524
3900	15.812	74.500	72.763	181.944	-55.427	-43.244	1.544
4000	15.898	74.213	73.083	193.194	-55.217	-42.974	1.574
4100	15.988	73.893	73.283	204.804	-54.992	-42.724	1.614
4200	16.083	73.533	73.353	216.774	-54.752	-42.494	1.664
4300	16.183	73.133	73.283	229.104	-54.497	-42.284	1.724
4400	16.288	72.693	73.073	241.794	-54.227	-42.094	1.794
4500	16.400	72.213	72.723	254.844	-53.942	-41.824	1.874
4600	16.518	71.693	72.223	268.254	-53.642	-41.474	1.964
4700	16.643	71.133	71.583	282.024	-53.327	-41.144	2.064
4800	16.775	70.533	70.823	296.154	-52.997	-40.734	2.174
4900	16.915	69.893	69.923	310.644	-52.652	-40.244	2.294
5000	17.063	69.213	68.853	325.494	-52.292	-39.674	2.424
5100	17.218	68.493	67.583	340.704	-51.917	-39.024	2.564
5200	17.380	67.733	66.173	356.274	-51.527	-38.294	2.714
5300	17.548	66.933	64.623	372.204	-51.122	-37.484	2.874
5400	17.723	66.093	62.933	388.494	-50.692	-36.594	3.044
5500	17.905	65.213	61.103	405.144	-50.237	-35.624	3.224
5600	18.095	64.293	59.133	422.154	-49.757	-34.574	3.414
5700	18.293	63.333	57.023	439.524	-49.252	-33.444	3.614
5800	18.498	62.333	54.773	457.254	-48.722	-32.234	3.824
5900	18.710	61.293	52.483	475.344	-48.167	-30.954	4.044
6000	18.928	60.213	50.153	493.794	-47.587	-29.604	4.274

Dec. 31, 1960; June 30, 1967

MAGNESIUM MONOHYDROXIDE (MgOH) $\text{GFW} = 41.31937$

(IDEAL GAS)

Point Group [C_{2v}]

$\Delta H^0_{298.15} = [-51 \pm 20] \text{ kcal/mol}$

$\Delta H^0_{298.15} = [-52.9] \text{ gibbs/mol}$

$\Delta H^0_{298.15} = [-52 \pm 20] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$

g_i

[27000]

[0]

[14]

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}

[3600] (1)

[1000] (2)

[800] (1)

Bond Distances: O-Mg = [1.80] Å

O-H = [0.97] Å

Bond Angle: Mg-O-H = [180°]

Rotational Constant: B_e = 0.47595 cm⁻¹

Heat of Formation

The heat of formation is based on the following estimates. The relation $D^0(\text{M-X})/D^0(\text{X-M-X}) = 0.46 \pm 0.03$ for several alkaline earth dihalides has been reported by R. A. Kent, J. D. McDonald and J. L. Margrave, J. Phys. Chem. 70, 874 (1966). Assuming that this relation applies to hydroxides, we may estimate $D^0(\text{Mg-OH}) = 87 \pm 12 \text{ kcal/mol}$. A value of $D^0(\text{Mg-OH}) = 105 \pm 12 \text{ kcal/mol}$ is obtained by comparison with $D^0(\text{Be-OH}) \leq 111 \pm 10$, $D^0(\text{Ca-OH}) = 100 \pm 10$ and $D^0(\text{Sr-OH}) = 95 \pm 10 \text{ kcal/mol}$. The value for BeOH is from the JANAF tables, while those for CaOH and SrOH are from flame studies of L. V. Gurvich, private communication, High Temperature Institute, Moscow, 1966. The average value of $D^0(\text{Mg-OH}) = 96 \text{ kcal/mol}$ is used to calculate the heat of formation.

A value of $D^0(\text{Mg-OH}) = 56 \pm 5 \text{ kcal/mol}$ was derived from intensity measurements on the flame spectrum of magnesium by E. M. Bulevich and T. M. Sugden, Trans. Faraday Soc. 55, 770 (1959). This appears to be too small.

Heat Capacity and Entropy

The ground state is assumed to be $^2\Sigma$ by analogy with isoelectronic MgF. Ultraviolet emission spectra near 3800 Å were observed for MgOH and MgOD by D. Pesic and A. G. Gaydon, Proc. Phys. Soc. (London) 73, 244 (1959), and L. Brewer and S. Trajmar, J. Chem. Phys. 35, 1585 (1962). Vibrational and rotational analyses were not performed. Assuming that the observed spectra correspond to the transition $A^2\Pi \leftarrow X^2\Sigma$, we estimate the first excited state at 27000 cm⁻¹. The vibrational frequencies ν_1 and ν_3 are estimated from those of H₂O(g) and MgO(g). The ν_2 is tentatively estimated at 1000 cm⁻¹.

A linear structure is assumed by use of the prediction of A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953), for "HAg" molecules with less than 11 valence electrons (MgOH has 9 valence electrons). Confirmation of this prediction is scanty for molecules having "A" as the most electronegative element; however, recent microwave evidence [R. L. Kuczkowski, D. R. Lide, Jr., and L. C. Krishner, J. Chem. Phys. 44, 3131 (1966)] for the linearity of KOH and CaOH confirms the prediction for these molecules having 8 valence electrons. The O-H bond distance is assumed to be the same as that of H₂O(g) and the Mg-O bond distance is estimated from that of MgO(g).

HMG0

Magnesium Monohydroxide Unipositive Ion (MgOH⁺)

(Ideal Gas) GFW = 41.31882

T, °K	C _p	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	9.627	51.871	51.871	.000	143.000	140.335	-102.868
300	9.610	51.926	51.871	.017	143.002	140.318	-102.222
400	10.095	52.475	52.238	.975	143.140	139.404	-76.167
500	10.861	53.015	52.966	2.025	143.330	138.450	-60.516
600	11.398	53.046	53.139	3.139	143.545	137.452	-50.067
700	11.797	53.434	53.491	4.300	143.769	136.420	-42.592
800	12.115	53.831	53.861	5.496	143.985	135.354	-36.977
900	12.384	54.274	54.205	6.721	144.183	134.264	-32.604
1000	12.618	54.719	54.719	7.972	144.239	133.333	-29.140
1100	12.826	55.000	55.000	9.244	144.242	132.433	-26.312
1200	13.012	55.227	55.227	10.536	144.255	131.517	-23.953
1300	13.178	55.463	55.463	11.846	144.277	130.587	-21.954
1400	13.328	55.698	55.698	13.171	144.297	129.646	-20.314
1500	13.462	55.934	55.934	14.511	144.316	128.696	-18.940
1600	13.582	56.169	56.169	15.863	144.333	127.743	-17.808
1700	13.690	56.404	56.404	17.227	144.348	126.787	-16.810
1800	13.787	56.639	56.639	18.601	144.362	125.828	-15.937
1900	13.874	56.874	56.874	19.984	144.375	124.866	-15.163
2000	13.952	57.109	57.109	21.375	144.387	123.903	-14.479
2100	14.022	57.344	57.344	22.774	144.398	122.937	-13.876
2200	14.085	57.579	57.579	24.179	144.408	121.968	-13.359
2300	14.143	57.814	57.814	25.591	144.417	120.996	-12.925
2400	14.195	58.049	58.049	27.008	144.425	120.022	-12.568
2500	14.242	58.284	58.284	28.430	144.432	119.047	-12.281
2600	14.284	58.519	58.519	29.863	144.438	118.072	-12.054
2700	14.323	58.754	58.754	31.306	144.443	117.097	-11.881
2800	14.359	58.989	58.989	32.759	144.447	116.122	-11.754
2900	14.392	59.224	59.224	34.222	144.450	115.147	-11.668
3000	14.421	59.459	59.459	35.695	144.452	114.172	-11.611
3100	14.449	59.690	59.690	37.178	144.453	113.197	-11.584
3200	14.474	59.921	59.921	38.661	144.454	112.222	-11.584
3300	14.497	60.152	60.152	39.937	144.454	111.247	-11.608
3400	14.519	60.383	60.383	41.388	144.454	110.272	-11.651
3500	14.539	60.614	60.614	42.841	144.454	109.297	-11.714
3600	14.557	60.845	60.845	44.296	144.454	108.322	-11.797
3700	14.574	61.076	61.076	45.752	144.454	107.347	-11.899
3800	14.590	61.307	61.307	47.210	144.454	106.372	-12.019
3900	14.605	61.538	61.538	48.670	144.454	105.397	-12.154
4000	14.619	61.769	61.769	50.131	144.454	104.422	-12.304
4100	14.632	61.999	61.999	51.594	144.454	103.447	-12.469
4200	14.644	62.230	62.230	53.058	144.454	102.472	-12.649
4300	14.655	62.461	62.461	54.522	144.454	101.497	-12.844
4400	14.665	62.692	62.692	55.986	144.454	100.522	-13.054
4500	14.675	62.923	62.923	57.450	144.454	99.547	-13.279
4600	14.685	63.154	63.154	58.914	144.454	98.572	-13.519
4700	14.693	63.385	63.385	60.378	144.454	97.597	-13.774
4800	14.702	63.616	63.616	61.842	144.454	96.622	-14.044
4900	14.710	63.847	63.847	63.306	144.454	95.647	-14.329
5000	14.717	64.078	64.078	64.770	144.454	94.672	-14.634
5100	14.724	64.309	64.309	66.234	144.454	93.697	-14.959
5200	14.730	64.540	64.540	67.698	144.454	92.722	-15.304
5300	14.737	64.771	64.771	69.162	144.454	91.747	-15.669
5400	14.743	65.002	65.002	70.626	144.454	90.772	-16.054
5500	14.748	65.233	65.233	72.090	144.454	89.797	-16.459
5600	14.753	65.464	65.464	73.554	144.454	88.822	-16.884
5700	14.759	65.695	65.695	75.018	144.454	87.847	-17.329
5800	14.763	65.926	65.926	76.482	144.454	86.872	-17.794
5900	14.768	66.157	66.157	77.946	144.454	85.897	-18.279
6000	14.772	66.388	66.388	79.410	144.454	84.922	-18.784

June 30, 1968

MAGNESIUM MONOHYDROXIDE UNIPosITIVE ION (MgOH⁺) (IDEAL GAS)

Point Group [C_{∞v}]

S°_{298.15} = [51.9 ± 2] gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_i, cm⁻¹

[800] (1)

[900] (2)

[3500] (1)

O-H = [0.98] Å

Bond Distance: Mg-O = [1.8] Å

Bond Angle: Mg-O-H = [180°]

Rotational Constant: B₀ = [0.4755] cm⁻¹

Heat of Formation

The gaseous molecules NaOH, MgOH and AlOH have 8, 9 and 10 valence electrons, respectively. Due to the similarity in molecular structure, we assume that the ionization potential (IP) of MgOH is approximately the average of IP(NaOH) and IP(AlOH). Adopting IP = 9 and 7.5 eV for NaOH (1) and AlOH (2), respectively, we obtain IP(MgOH) = 8.5 eV. Based on this value and ΔH°_f(MgOH, g) = -52 ± 20 kcal/mol we derive ΔH°_f(MgOH⁺, g) = 143 ± 40 kcal/mol which is tentatively adopted. The estimated value IP(MgOH) is close to IP(MgF) = 7.8 ± 0.3 eV (1), where MF and MgOH are isoelectronic molecules, and thus confirms the value within its uncertainty.

Heat Capacity and Entropy

Walsh (3) predicted that ABH molecules (H = hydrogen atom) containing 10 or less valence electrons will be linear in their ground state. Since MgOH⁺ molecule has 8 valence electrons, we assume it to be linear. The vibrational frequencies are estimated by comparison with those for NaOH(g) and MgOH(g). The O-H bond distance is assumed to be the same as that in H₂O(g). The Mg-O bond distance is estimated (4). The moment of inertia is 5.874 × 10⁻³⁹ g cm². The ground state quantum weight is assumed to be the same as that of NaOH(g). The enthalpy at 0°K is -2.24 kcal/mol.

References

1. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
2. See JANAF ALOH⁺(g) table (Dec. 31, 1967) for details.
3. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
4. L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).

GFW = 41.31882

ΔH°_f = [144 ± 40] kcal/mol

ΔH°_f = [143 ± 40] kcal/mol

σ = 1

HMgO⁺

HMgO⁺

Mol. Wt. = 15.0167

(IDEAL GAS)

IMIDOZEN (NH)

MOL. WT. = 15.0167

Ground State Configuration $3 \sum^-$
 $S_{298.15}^\circ = 43.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = 81.0 \pm 2.5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 298.15 = 81.0 \pm 2.5 \text{ kcal. mole}^{-1}$

Electronic Level and Quantum Weight

$$\frac{\sum_i g_i}{0} \text{ cm.}^{-1} \frac{g_i}{3}$$

$\omega_e = 3315 \text{ cm.}^{-1}$
 $\omega_e x_e = 94.7 \text{ cm.}^{-1}$
 $\omega_e = 16.6684 \text{ cm.}^{-1}$
 $\alpha_e = 0.646 \text{ cm.}^{-1}$
 $\sigma = 1$
 $r_e = 1.038 \text{ \AA}$

Heat of Formation.

The value, $\Delta H_f^\circ 298 (\text{NH}, g) = 81.0 \pm 2.5 \text{ kcal. mole}^{-1}$, was calculated from the selected dissociation energy, $D_0 = 83 \pm 2 \text{ kcal. mole}^{-1}$, based on the following investigations. J. L. Franklin, V. H. Dibel, R. M. Reese and M. Krause, J. Am. Chem. Soc. 80, 298 (1958) and R. I. Reed and W. Snedden, J. Chem. Soc. 4132 (1959) have determined the dissociation energy of $\text{NH}(g)$ by electron impact as $83 \pm 2 \text{ kcal. mole}^{-1}$ and $85.3 \pm 6 \text{ kcal. mole}^{-1}$, respectively. A. L. Companion and F. O. Ellison, J. Chem. Phys. 32, 1132 (1960), and P. C. H. Jordan and H. C. Lonquet-Higgins, Mol. Phys. 5, 121 (1962) have calculated theoretically the dissociation energy by a semi-empirical method and obtained $83.3 \text{ kcal. mole}^{-1}$ and $81.2 \text{ kcal. mole}^{-1}$, respectively. These results are in good agreement. G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., D. Van Nostrand Company, New York, 1950, has estimated the dissociation energy $D_0(\text{NH}, g) = 3.8 \text{ e.v.}$ ($87.6 \text{ kcal. mole}^{-1}$) based on the average of two earlier theoretical calculations by R. S. Mulliken, ($D_0 = 4.2 \text{ e.v.}$), Rev. Mod. Phys. 4, 1 (1932) and O. King ($D_0 = 3.4 \text{ e.v.}$), J. Chem. Phys. 5, 378 (1938). A. G. Gaydon, "Dissociation Energies", 2nd Ed. Chapman & Hall Ltd, London, 1953, favored O. Glockler's estimation $D_0 = 86.3 \text{ kcal. mole}^{-1}$ which was based upon the comparison of force constants and D values of related hydrides (i.e. CH, OH and PH).

Heat Capacity & Entropy.

The rotational constants B_e and α_e were obtained from R. N. Dixon, Can. J. Phys. 37, 1171 (1959). The vibrational constants ω_e and $\omega_e x_e$ were calculated from Dixon's data: $B_e = 16.6684 \text{ cm.}^{-1}$, $D_e = 16.85 \times 10^{-4} \text{ cm.}^{-1}$ and $\omega_e = 3125.6 \text{ cm.}^{-1}$ by the relation $D_e = 4 B_e^2 / \omega_e^2$ and $\omega_e = \omega_e - 2 \omega_e x_e$.

D. E. Milligen and M. E. Jacox, J. Chem. Phys. 41, 2838 (1964) have observed from the spectrum of NH the vibrational fundamental $\omega = 3135 \pm 2 \text{ cm.}^{-1}$ in Ar and N_2 matrices. K. Rosengren and O. C. Flamentel, J. Chem. Phys. 43, 507 (1965) also reported $\omega = 3122.2 \pm 0.6 \text{ cm.}^{-1}$ in N_2 matrix and $\omega = 3131.6 \pm 0.4 \text{ cm.}^{-1}$ in Ar matrix.

Nitroxyl Hydride (HNO)

(Ideal Gas) Mol. Wt. = 31.016

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.065	43.927	24.498	24.498	24.498	INFINITE
200	7.065	59.902	24.215	24.215	24.215	24.018
298	8.279	52.729	23.800	23.800	23.800	19.688
300	8.287	52.781	23.796	23.796	23.796	19.580
400	8.788	55.230	23.598	23.598	23.598	15.263
500	9.342	57.751	23.438	23.438	23.438	12.693
600	9.869	59.091	23.315	23.315	23.315	10.990
700	10.345	60.559	23.222	23.222	23.222	9.779
800	10.766	61.968	23.155	23.155	23.155	8.874
900	11.134	63.258	23.107	23.107	23.107	8.172
1000	11.454	64.448	23.078	23.078	23.078	7.612
1100	11.731	65.553	23.061	23.061	23.061	7.153
1200	11.970	66.584	23.055	23.055	23.055	6.772
1300	12.177	67.551	23.056	23.056	23.056	6.449
1400	12.356	68.460	23.064	23.064	23.064	6.172
1500	12.511	69.318	23.074	23.074	23.074	5.932
1600	12.646	70.130	23.087	23.087	23.087	5.722
1700	12.764	70.900	23.101	23.101	23.101	5.536
1800	12.867	71.633	23.116	23.116	23.116	5.371
1900	12.958	72.331	23.130	23.130	23.130	5.223
2000	13.038	72.998	23.143	23.143	23.143	5.090
2100	13.108	73.635	23.155	23.155	23.155	4.970
2200	13.171	74.247	23.164	23.164	23.164	4.860
2300	13.227	74.834	23.172	23.172	23.172	4.760
2400	13.277	75.398	23.179	23.179	23.179	4.668
2500	13.322	75.940	23.186	23.186	23.186	4.584
2600	13.363	76.464	23.192	23.192	23.192	4.506
2700	13.399	76.969	23.197	23.197	23.197	4.434
2800	13.432	77.457	23.203	23.203	23.203	4.367
2900	13.463	77.929	23.208	23.208	23.208	4.305
3000	13.490	78.385	23.215	23.215	23.215	4.246
3100	13.515	78.828	23.220	23.220	23.220	4.192
3200	13.538	79.258	23.225	23.225	23.225	4.141
3300	13.559	79.675	23.228	23.228	23.228	4.093
3400	13.578	80.080	23.230	23.230	23.230	4.048
3500	13.596	80.473	23.234	23.234	23.234	4.006
3600	13.612	80.857	23.237	23.237	23.237	3.966
3700	13.628	81.230	23.240	23.240	23.240	3.928
3800	13.642	81.594	23.243	23.243	23.243	3.893
3900	13.655	81.948	23.245	23.245	23.245	3.859
4000	13.667	82.294	23.247	23.247	23.247	3.827
4100	13.678	82.632	23.249	23.249	23.249	3.796
4200	13.689	82.961	23.251	23.251	23.251	3.766
4300	13.699	83.283	23.253	23.253	23.253	3.736
4400	13.708	83.599	23.255	23.255	23.255	3.706
4500	13.717	83.907	23.257	23.257	23.257	3.676
4600	13.725	84.208	23.259	23.259	23.259	3.646
4700	13.732	84.503	23.261	23.261	23.261	3.616
4800	13.739	84.793	23.263	23.263	23.263	3.586
4900	13.746	85.076	23.265	23.265	23.265	3.556
5000	13.752	85.354	23.267	23.267	23.267	3.526
5100	13.758	85.626	23.269	23.269	23.269	3.496
5200	13.764	85.893	23.271	23.271	23.271	3.466
5300	13.770	86.156	23.273	23.273	23.273	3.436
5400	13.775	86.413	23.275	23.275	23.275	3.406
5500	13.779	86.666	23.277	23.277	23.277	3.376
5600	13.784	86.914	23.279	23.279	23.279	3.346
5700	13.788	87.158	23.281	23.281	23.281	3.316
5800	13.792	87.398	23.283	23.283	23.283	3.286
5900	13.796	87.634	23.285	23.285	23.285	3.256
6000	13.800	87.866	23.287	23.287	23.287	3.226

March 31, 1963

NITROXYL HYDRIDE (HNO)

(IDEAL GAS)

MOL. WT. = 31.016

Point Group C_sΔH°_f 0 = 24.5 kcal. mole⁻¹S°_{298.15} = 52.729 cal. deg.⁻¹ mole⁻¹

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹

2854.17 (1)

1570 (1)

1110 (1)

Bond Distance: H-N = 1.020 ± 0.02 Å N=O = 1.239 ± 0.005 Å

Bond Angle: H-N-O = 114° 25' ± 2°

Product of the Moments of Inertia: I_AI_BI_C = 5.939 X 10⁻¹¹⁸ g.³ cm.⁶

Heat of Formation

ΔH°_f 298.15 for HNO(g) was calculated from D(H-NO) = 48.6 kcal. mole⁻¹ at 0°K. reported by M. J. Y. Clement and D. A. Ramsay, Can. J. Phys. 39, 205 (1961).

Heat Capacity and Entropy

Vibrational frequencies were assigned by J. L. Bancroft, J. M. Hollis and D. A. Ramsay, Can. J. Phys. 40, 322 (1962) and H. Brown and G. Pimental, J. Chem. Phys. 29, 883 (1958). Bond distances and bond angles were taken from J. L. Bancroft, J. M. Hollis, and D. A. Ramsay, loc. cit. The molecular constants given by F. W. Dalby, Can. J. Phys. 35, 1336 (1958) were: r(N=O) = 1.216 Å, r(N-H) = 1.0628 Å, and X_{HNO} = 108.5°. The three principal moments of inertia are: 1.262 X 10⁻⁴⁰, 2.1067 X 10⁻³⁹, and 2.2330 X 10⁻³⁹ g. cm.²

HNO

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	INFINITE	2.635	-16.852	-16.852	INFINITE
100	8.027	49.729	68.125	1.840	-17.492	-15.187	33.190
200	9.238	55.595	60.527	-0.966	-17.971	-12.693	13.870
298	10.840	59.586	59.586	-0.000	-18.340	-10.020	7.344
300	10.869	59.653	59.586	-0.20	-18.346	-9.968	7.261
400	12.275	62.979	60.030	1.180	-18.593	-9.698	3.898
500	13.412	65.845	60.913	2.666	-18.738	-9.252	1.858
600	14.318	68.374	61.950	3.854	-18.811	-8.767	0.690
700	15.044	70.637	63.032	5.324	-18.855	-8.250	0.480
800	15.637	72.686	64.113	6.859	-18.822	-7.700	0.289
900	16.131	74.557	65.171	8.448	-18.783	-7.135	0.115
1000	16.548	76.279	66.197	10.082	-18.721	-6.567	0.000
1100	16.905	77.873	67.187	11.765	-18.644	-6.000	0.000
1200	17.213	79.358	68.032	13.492	-18.553	-5.433	0.000
1300	17.480	80.746	68.757	15.197	-18.453	-4.867	0.000
1400	17.712	82.050	69.339	16.956	-18.345	-4.300	0.000
1500	17.915	83.279	70.787	18.738	-18.231	-3.733	0.000
1600	18.093	84.442	71.605	20.539	-18.115	-3.167	0.000
1700	18.245	85.544	72.755	22.355	-17.997	-2.600	0.000
1800	18.389	86.590	73.853	24.188	-17.876	-2.033	0.000
1900	18.511	87.588	74.886	26.033	-17.754	-1.467	0.000
2000	18.620	88.540	75.895	27.890	-17.634	-0.900	0.000
2100	18.717	89.451	76.881	29.757	-17.515	-0.333	0.000
2200	18.802	90.321	77.849	31.637	-17.397	0.233	0.000
2300	18.882	91.162	78.789	33.531	-17.285	0.800	0.000
2400	18.952	91.967	79.713	35.439	-17.174	1.367	0.000
2500	19.015	92.742	79.713	37.368	-17.069	1.933	0.000
2600	19.073	93.489	78.407	39.212	-16.965	2.500	0.000
2700	19.122	94.205	77.035	41.077	-16.860	3.067	0.000
2800	19.172	94.806	75.635	42.952	-16.754	3.633	0.000
2900	19.215	95.379	80.077	44.846	-16.648	4.200	0.000
3000	19.254	95.931	80.605	46.880	-16.544	4.767	0.000
3100	19.290	96.463	81.119	48.907	-16.441	5.333	0.000
3200	19.323	96.976	81.621	50.927	-16.339	5.900	0.000
3300	19.353	97.476	82.111	52.941	-16.238	6.467	0.000
3400	19.381	97.964	82.588	54.960	-16.138	7.033	0.000
3500	19.407	98.442	83.055	56.977	-16.038	7.600	0.000
3600	19.431	98.919	83.512	58.989	-15.938	8.167	0.000
3700	19.453	99.386	83.958	60.996	-15.838	8.733	0.000
3800	19.473	100.810	84.395	62.999	-15.738	9.300	0.000
3900	19.493	101.316	84.822	64.998	-15.638	9.867	0.000
4000	19.510	101.810	85.241	66.978	-15.538	10.433	0.000
4100	19.527	102.292	85.651	68.930	-15.438	11.000	0.000
4200	19.542	102.761	86.057	70.877	-15.338	11.567	0.000
4300	19.557	103.223	86.458	72.819	-15.238	12.133	0.000
4400	19.570	103.673	86.853	74.758	-15.138	12.700	0.000
4500	19.583	104.113	87.212	76.693	-15.038	13.267	0.000
4600	19.595	104.543	87.584	78.612	-14.938	13.833	0.000
4700	19.607	104.976	87.950	80.527	-14.838	14.400	0.000
4800	19.617	105.405	88.311	82.438	-14.738	14.967	0.000
4900	19.627	105.782	88.661	84.345	-14.638	15.533	0.000
5000	19.636	106.179	89.007	86.248	-14.538	16.100	0.000
5100	19.645	106.568	89.348	88.148	-14.438	16.667	0.000
5200	19.653	106.949	89.683	90.045	-14.338	17.233	0.000
5300	19.660	107.323	90.016	91.938	-14.238	17.800	0.000
5400	19.669	107.691	90.346	93.827	-14.138	18.367	0.000
5500	19.676	108.052	90.665	95.712	-14.038	18.933	0.000
5600	19.683	108.407	90.969	97.595	-13.938	19.500	0.000
5700	19.689	108.755	91.278	99.477	-13.838	20.067	0.000
5800	19.695	109.100	91.582	101.358	-13.738	20.633	0.000
5900	19.701	109.435	91.882	103.235	-13.638	21.200	0.000
6000	19.707	109.766	92.177	105.112	-13.538	21.767	0.000

NITROUS ACID, CIS-(HNO₂)

(IDEAL GAS)

MOL. WT. = 47.016

Point Group C_{2v}
 $\Delta H_f^0 = -16.85 \pm 0.32$ kcal. mole⁻¹
 $\Delta H_f^{298.15} = -18.34 \pm 0.32$ kcal. mole⁻¹
 $\Delta H_f^{298.15} = -18.34 \pm 0.32$ kcal. mole⁻¹
Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
3462 (1)	855 (1)
1639 (1)	525 (1)
1350 (1)	638 (1)

Bond Distances: O-N = 1.20 Å N-O = 1.46 Å O-H = 0.98 Å

Bond Angle: O-N-O = 114° N-O-H = 103°

Product of the Moments of Inertia: I_AI_BI_C = 5.50704 X 10⁻¹¹⁶ g.³ cm.⁶

Heat of Formation

P. O. Ashmore and B. J. Tyler, J. Chem. Soc. 1017 (1961) reported $\Delta H_f^{298.15} = -9.06 \pm 0.32$ kcal. mole⁻¹ for the reaction: NO(g) + NO₂(g) + H₂O(g) → 2HNO₂(g), yielding $\Delta H_f^{298.15} = -18.57 \pm 0.20$ kcal. mole⁻¹ for HNO₂(g). L. H. Jones, R. M. Badger and G. E. Moore, J. Chem. Phys., 19, 1599 (1951) estimated the difference in energy of cis- and trans-HNO₂(g) to be 506 ± 250 cal. mole⁻¹. Hence the value of $\Delta H_f^{298.15}$ for cis-HNO₂(g) was calculated.

The heat of reaction and the equilibrium constants for the formation of HNO₂(g) have been calculated by M. M. Karvanev and O. A. Skvortsov, Russ. J. Phys. Chem. 36, 566 (1962). The value of $\Delta H_f^{298.15}$ reported is -18.6 kcal. mole⁻¹. However, based on the heat of formation of liquid HNO₂, P. O. Ashmore and B. P. Levitt, Trans. Faraday Soc., 53, 945 (1957) give $\Delta H_f^0 = -13.7$ kcal. mole⁻¹. The corresponding value reported by W. A. Rösser and H. Wise, J. Chem. Phys., 26, 571 (1957) is -20.0 kcal. mole⁻¹, based on the experimental data of L. O. Wayne and D. M. Yost, J. Chem. Phys., 19, 41 (1951), and the entropy of the equilibrium mixture of the trans- and cis-HNO₂(g) calculated by L. H. Jones, R. M. Badger and G. E. Moore, loc. cit.

Heat Capacity and Entropy

Vibrational frequencies, bond distances, and bond angles were obtained from L. Dor and P. Tarte, Bull. Soc. Roy. Sci., LG. 478 (1951) and L. H. Jones, R. M. Badger and G. E. Moore, loc. cit. The three principal moments of inertia are: 1.0271 X 10⁻³⁹, 6.8242 X 10⁻³⁹, and 7.8520 X 10⁻³⁹ g.² cm.²

T, °K.	C _p ^o	—cal. mole ⁻¹ deg. ⁻¹ —	—(F°-H ₂₉₈ °)/T—	—kcal. mole ⁻¹ —	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.000	INFINITE	-2.451	-17.349	-17.349	INFINITE	
100	8.027	49.610	68.177	-1.856	-15.522	9.290	
200	9.328	55.504	68.177	-1.808	-15.522	9.290	
298	11.000	59.546	59.546	-0.999	-18.484	14.410	7.702
300	11.029	59.614	59.546	-0.920	-18.640	10.508	
400	13.243	65.886	60.891	2.497	-19.207	-4.771	7.017
500	14.614	68.435	61.891	3.897	-19.269	-6.711	6.711
600	15.110	70.712	63.034	5.374	-19.284	-8.333	6.333
700	15.677	72.767	64.124	6.915	-19.266	-9.705	5.905
800	16.305	74.600	65.150	8.507	-19.224	-10.877	5.477
900	16.982	76.235	66.124	10.147	-19.161	-11.889	5.049
1000	17.700	77.669	67.048	11.831	-19.085	-12.859	4.619
1100	18.458	78.909	67.918	13.559	-18.996	-13.789	4.189
1200	19.255	80.000	68.742	15.329	-18.906	-14.689	3.759
1300	20.090	80.969	69.518	17.142	-18.817	-15.559	3.329
1400	20.962	81.818	70.242	19.000	-18.728	-16.409	2.899
1500	21.870	82.557	70.932	20.898	-18.639	-17.239	2.469
1600	22.812	83.217	71.582	20.835	-18.569	-18.049	2.039
1700	23.787	83.817	72.202	20.835	-18.482	-18.839	1.609
1800	24.795	84.366	72.792	20.835	-18.387	-19.609	1.179
1900	25.835	84.866	73.352	20.835	-18.287	-20.359	0.749
2000	26.905	85.326	73.882	20.835	-18.182	-21.089	0.319
2100	28.005	85.748	74.382	20.835	-18.072	-21.799	-0.119
2200	29.135	86.132	74.852	20.835	-17.957	-22.489	-0.549
2300	30.295	86.478	75.292	20.835	-17.837	-23.159	-0.979
2400	31.485	86.788	75.702	20.835	-17.712	-23.809	-1.409
2500	32.705	87.062	76.082	20.835	-17.582	-24.439	-1.839
2600	33.955	87.302	76.432	20.835	-17.447	-25.049	-2.269
2700	35.235	87.508	76.752	20.835	-17.307	-25.639	-2.699
2800	36.545	87.682	77.042	20.835	-17.162	-26.209	-3.129
2900	37.885	87.822	77.302	20.835	-17.012	-26.759	-3.559
3000	39.255	87.928	77.532	20.835	-16.857	-27.289	-3.989
3100	40.655	87.998	77.732	20.835	-16.697	-27.799	-4.419
3200	42.085	88.038	77.902	20.835	-16.532	-28.289	-4.849
3300	43.545	88.048	78.042	20.835	-16.362	-28.759	-5.279
3400	45.035	88.028	78.152	20.835	-16.187	-29.209	-5.709
3500	46.555	87.968	78.232	20.835	-16.007	-29.639	-6.139
3600	48.105	87.868	78.282	20.835	-15.822	-30.049	-6.569
3700	49.685	87.728	78.302	20.835	-15.632	-30.439	-6.999
3800	51.295	87.548	78.292	20.835	-15.437	-30.809	-7.429
3900	52.935	87.328	78.252	20.835	-15.237	-31.159	-7.859
4000	54.605	86.968	78.182	20.835	-15.032	-31.489	-8.289
4100	56.305	86.468	78.082	20.835	-14.822	-31.799	-8.719
4200	58.035	85.828	77.952	20.835	-14.607	-32.089	-9.149
4300	59.795	85.058	77.782	20.835	-14.387	-32.359	-9.579
4400	61.585	84.158	77.582	20.835	-14.162	-32.609	-10.009
4500	63.405	83.128	77.352	20.835	-13.932	-32.839	-10.439
4600	65.255	81.968	77.082	20.835	-13.697	-33.049	-10.869
4700	67.135	80.678	76.782	20.835	-13.457	-33.239	-11.299
4800	69.045	79.258	76.452	20.835	-13.212	-33.409	-11.729
4900	70.985	77.708	76.082	20.835	-12.962	-33.559	-12.159
5000	72.955	76.028	75.682	20.835	-12.707	-33.689	-12.589
5100	74.955	74.218	75.252	20.835	-12.447	-33.799	-13.019
5200	76.985	72.278	74.782	20.835	-12.182	-33.889	-13.449
5300	79.045	70.218	74.282	20.835	-11.912	-33.959	-13.879
5400	81.135	68.038	73.752	20.835	-11.637	-34.009	-14.309
5500	83.255	65.728	73.182	20.835	-11.357	-34.039	-14.739
5600	85.405	63.288	72.582	20.835	-11.072	-34.049	-15.169
5700	87.585	60.728	71.952	20.835	-10.782	-34.039	-15.599
5800	89.795	58.048	71.282	20.835	-10.487	-34.009	-16.029
5900	92.035	55.248	70.582	20.835	-10.187	-33.959	-16.459
6000	94.305	52.328	69.852	20.835	-9.882	-33.889	-16.889

June 30, 1963

Point Group C_s

S_{298.15} = 59.545 cal. deg.⁻¹ mole⁻¹

ΔH_f^o = -17.37 ± 0.32 kcal. mole⁻¹

ΔH_f^o = -18.84 ± 0.32 kcal. mole⁻¹

Round State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω _v , cm. ⁻¹	ω _v , cm. ⁻¹
3590 (1)	794 (1)
1896 (1)	598 (1)
1260 (1)	543 (1)

Bond Distances: O-N = 1.20 Å N-O = 1.46 Å O-H = 0.98 Å

Bond Angle: O-N-O = 118° N-O-H = 105°

Product of the Moments of Inertia: I_AI_BI_C = 4.91847 × 10⁻¹¹⁶ g.³ cm.⁶

σ⁻ = 1

Heat of Formation.

P. O. Ashmore and B. J. Tyler, J. Chem. Soc. 1017 (1961) reported ΔH_f^o 298.15 = -9.06 ± 0.32 kcal. mole⁻¹ for the reaction: NO(g) + NO₂(g) + H₂O(g) = 2HNO₂(g), yielding ΔH_f^o 298.15 = -18.57 ± 0.20 kcal. mole⁻¹ for HNO₂(g). L. H. Jones, R. M. Badger and O. E. Moore, J. Chem. Phys., 19, 1599 (1951) estimated the difference in energy of cis- and trans- HNO₂(g) to be 506 ± 250 cal. mole⁻¹. Hence the value of ΔH_f^o 298.15 for trans-HNO₂(g) was calculated.

The heat of reaction and the equilibrium constants for the formation of HNO₂(g) have been calculated by M. Kervaeve and G. A. Skvortsov, Russ. J. Phys. Chem. 35, 566 (1962). The value of ΔH_f^o 298.15 reported is -18.8 kcal. mole⁻¹. However, based on the heat of formation of liquid HNO₂, P. O. Ashmore and B. F. Levitt, Trans. Faraday Soc., 53, 945 (1957) give ΔH_f^o = -13.7 kcal. mole⁻¹. The corresponding value reported by W. A. Rosser and H. Wise, J. Chem. Phys., 25, 571 (1957) is -20.0 kcal. mole⁻¹, based on the experimental data of L. G. Wayne and D. M. Yost, J. Chem. Phys. 19, 41 (1951), and the entropy of the equilibrium mixture of the trans- and cis-HNO₂(g) calculated by L. H. Jones, R. M. Badger and O. E. Moore, loc. cit.

Heat Capacity and Entropy.

Vibrational frequencies, bond distances, and bond angles were taken from L. H. Jones, R. M. Badger, and O. E. Moore, loc. cit. The values of vibrational frequencies were in good agreement to those reported by L. Dor and P. Tarte, Bull. Soc. Roy. Sci., 478 (1951). The three principal moments of inertia are: 7.860 × 10⁻⁴⁰, 7.5268 × 10⁻³⁹, and 8.3129 × 10⁻³⁹ g. cm.²

Nitric Acid (HNO₃)

(Ideal Gas) Mol. Wt. = 63.016

T, °K.	C _p ^o	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	Log K _p
0	0.000	INFINITE	-	2.615	-29.755	INFINITE
100	8.107	53.003	73.187	-2.018	-26.766	58.342
200	10.110	59.129	64.745	-1.123	-31.527	24.603
298	12.748	63.663	57.000	-0.103	-36.100	12.966
300	12.795	63.742	56.963	-0.24	-36.109	12.821
400	15.103	67.500	46.104	1.423	-32.472	12.704
500	16.930	71.325	35.269	3.028	-26.664	12.664
600	18.348	74.543	26.551	4.795	-22.736	12.743
700	19.450	77.278	19.875	6.678	-18.906	12.816
800	20.325	80.114	14.267	8.678	-15.268	12.880
900	21.031	82.950	10.747	10.747	-12.830	12.937
1000	21.613	85.797	8.197	12.880	-10.594	13.000
1100	22.098	88.680	6.218	15.066	-8.460	13.068
1200	22.508	91.601	4.607	17.297	-6.423	13.140
1300	22.858	94.551	3.247	19.578	-4.483	13.215
1400	23.159	97.542	2.167	21.897	-2.640	13.292
1500	23.419	100.569	1.319	24.266	-0.894	13.370
1600	23.646	103.634	0.748	26.680	0.854	13.448
1700	23.841	106.740	0.437	29.140	2.594	13.525
1800	24.017	109.878	0.278	31.640	4.324	13.600
1900	24.170	113.048	0.167	34.170	6.044	13.672
2000	24.306	116.250	0.092	36.720	7.754	13.742
2100	24.426	119.484	0.051	39.290	9.454	13.810
2200	24.530	122.750	0.032	41.880	11.144	13.875
2300	24.630	126.040	0.020	44.490	12.824	13.938
2400	24.716	129.350	0.012	47.120	14.494	13.998
2500	24.793	132.680	0.006	49.770	16.154	14.055
2600	24.863	136.030	0.003	52.440	17.804	14.108
2700	24.926	139.400	0.001	55.130	19.444	14.158
2800	24.984	142.780	0.000	57.840	21.074	14.205
2900	25.037	146.180	0.000	60.570	22.694	14.248
3000	25.085	149.600	0.000	63.320	24.304	14.288
3100	25.129	153.040	0.000	66.090	25.904	14.325
3200	25.169	156.500	0.000	68.880	27.494	14.358
3300	25.206	160.000	0.000	71.690	29.074	14.388
3400	25.240	163.520	0.000	74.520	30.644	14.415
3500	25.271	167.060	0.000	77.370	32.204	14.439
3600	25.300	170.620	0.000	80.240	33.754	14.460
3700	25.326	174.200	0.000	83.130	35.294	14.478
3800	25.351	177.800	0.000	86.040	36.824	14.493
3900	25.375	181.420	0.000	88.970	38.344	14.506
4000	25.397	185.060	0.000	91.920	39.854	14.517
4100	25.417	188.720	0.000	94.890	41.354	14.526
4200	25.435	192.400	0.000	97.880	42.844	14.533
4300	25.452	196.100	0.000	100.890	44.324	14.538
4400	25.469	199.820	0.000	103.920	45.794	14.542
4500	25.485	203.560	0.000	106.970	47.254	14.545
4600	25.499	207.320	0.000	109.940	48.704	14.548
4700	25.512	211.100	0.000	112.930	50.144	14.550
4800	25.523	214.900	0.000	115.940	51.574	14.552
4900	25.538	218.720	0.000	118.970	53.004	14.554
5000	25.549	222.560	0.000	121.920	54.424	14.556
5100	25.560	226.420	0.000	124.890	55.834	14.558
5200	25.569	230.300	0.000	127.880	57.234	14.559
5300	25.578	234.200	0.000	130.890	58.624	14.560
5400	25.586	238.120	0.000	133.920	60.004	14.561
5500	25.597	242.060	0.000	136.970	61.374	14.562
5600	25.605	246.020	0.000	140.040	62.734	14.563
5700	25.613	250.000	0.000	143.130	64.084	14.564
5800	25.623	254.000	0.000	146.240	65.424	14.565
5900	25.628	258.030	0.000	149.270	66.754	14.566
6000	25.634	262.090	0.000	152.320	68.074	14.567

June 30, 1962

NITRIC ACID (HNO₃)

(IDEAL GAS)

MOL. WT. = 63.016

Point Group C_{3v}
 $\Delta H_f^o = -29.76 \pm 0.10$ kcal. mole⁻¹
 $\Delta H_f^o = 63.663$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^o = -32.10 \pm 0.10$ kcal. mole⁻¹
Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
1320 (1)	765 (1)
896 (1)	3580 (1)
680 (1)	1335 (1)
1710 (1)	465 (1)
583 (1)	

Bond Distance: O-N = 1.206 ± 0.005 Å N-O = 1.405 ± 0.005 Å O-H = $[0.96] \text{ Å}$ Bond Angle: O-N-O = $130^\circ \pm 20'$ N-O-H = $102^\circ \pm 30'$ $\sigma = 1$ Product of the Moments of Inertia: $I_A I_B I_C = 6.08612 \times 10^{-115} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

ΔH_f^o 298.15 was taken from National Bureau of Standards Report 7437, January 1, 1962. Equilibria involving HNO₃ were measured by E. J. Jones, J. Am. Chem. Soc. 55, 2274 (1933), G. Peck, J. Am. Chem. Soc. 76, 5858 (1954) and H. E. Abel, H. Schmid and M. Stein-Wien, Z. Elektrochem. 56, 692 (1950), yielding $\Delta H_f^o = -32.06$, -32.02 , and -32.09 kcal. mole⁻¹, respectively. O. Becker and W. A. Roth, Z. Elektrochem. 40, 836 (1934) and J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882-1886, measured the heat of neutralization of HNO₃(aq.) with NH₃, combining these values with the data for NH₄NO₃ yields $\Delta H_f^o = -32.27$ and -32.07 kcal. M. Berthelot, "Sur la Force des Matieres Explosives," 3rd. ed., Paris, 1883, measured the heat of reaction of N₂O₄(g) and Cl₂(g), obtaining $\Delta H_f^o = -32.10$ kcal. mole⁻¹. The value of ΔH_f^o 298.15 reported by W. R. Forsythe and W. P. Cissaque, J. Am. Chem. Soc. 64, 48 (1942) was -31.994 kcal. mole⁻¹. The value adopted is the weighted average of these six values.

Heat Capacity and Entropy.

Vibrational frequencies were obtained from A. Palm and M. Kilpatrick, J. Chem. Phys. 23, 1562 (1955). Bond distances and bond angles were taken from D. J. Millen and J. R. Morton, J. Chem. Soc., 1523 (1960). The basic parameters of HNO₃(g) reported by P. A. Akshin, L. V. Vilkov and V. Y. Rosolovskii, Zhur. Strukt. Khim. 1, 1 (1960) were: $r(\text{N-O}) = 1.22 \pm 0.01$ Å; $r(\text{N-O}) = 1.40 \pm 0.01$ Å and $\angle \text{O-N-O} = 135^\circ \pm 2.5^\circ$. Forsythe and Cissaque, loc. cit. have calculated the absolute entropy of pure nitric acid (g) from calorimetric data. The value obtained was $S_{298.15}^o = 63.62$ cal. deg.⁻¹ mole⁻¹. The entropy of nitric acid vapor at 298.1°K. has also been computed by H. Cohn, C. K. Ingold, and H. G. Poole, J. Chem. Soc. 4272 (1952) to be 63.70 cal. deg.⁻¹ mole⁻¹. The three principal moments of inertia are: 6.4299×10^{-39} , 7.0314×10^{-39} , and $1.3461 \times 10^{-38} \text{ g. cm.}^2$.

HNO₃

Sodium Hydride (NaH)

(Crystal) Mol. Wt. = 23.999

SODIUM HYDRIDE (NaH)

(CRYSTAL)

MOL. WT. = 23.999

HNa

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	∞	INFINITE	-1.496	-12.433	-12.433	INFINITE
100	4.182	15.913	-1.315	-12.952	-11.439	25.000
200	6.763	11.203	-0.760	-13.481	-9.484	19.680
298	8.698	9.584	∞	-13.490	-8.023	16.880
300	8.732	9.564	∞	-13.492	-7.988	5.819
400	10.150	12.343	∞	-14.233	-6.086	3.325
500	11.270	14.734	2.040	-14.250	-4.045	1.766
600	12.120	16.868	3.212	-14.149	-2.011	∞
700	12.840	18.792	4.461	-13.957	-0.003	∞
800	13.400	20.545	5.775	-13.691	1.973	∞
900	13.850	22.150	7.138	-13.374	3.913	∞
1000	14.200	23.628	8.541	-13.020	5.815	1.271
1100	14.500	24.996	9.977	-12.643	7.679	1.526
1200	14.740	26.269	11.439	-12.248	9.507	1.815
1300	14.920	27.456	12.923	-11.873	11.373	2.108
1400	15.063	28.567	14.422	-11.516	13.248	2.400
1500	15.160	29.610	15.934	-11.166	15.116	2.676

$$\Delta H_f^0 = -12.43 \pm 0.02 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^0 = -13.49 \pm 0.02 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 9.564 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_d = [700]^{\circ}\text{K.}$$

Heat of Formation.

ΔH_f^0 298.15 was obtained from S. R. Gunn and L. G. Green, *J. Am. Chem. Soc.* **80**, 4762 (1958). The value of ΔH_f^0 298.15 reported by C. E. Messer, L. G. Fasolino and C. E. Thalmeier, *J. Am. Chem. Soc.* **77**, 4524 (1955) was -13.60 $\pm$ 0.27 kcal. mole⁻¹ which is in excellent agreement with the value given by S. R. Gunn and L. G. Green, loc. cit. The results of the previous investigations were also reviewed by C. E. Messer, et al., loc. cit.

Heat Capacity and Entropy.

C_p below 350°K were measured by E. F. Westrum, et al., University of Michigan, Ann Arbor, Michigan, private communication, May 19, 1960. C_p above 350°K were estimated by comparison with those for LiH(c). C_p 59.94 $\sim$ 91.84°K., were also measured by E. V. Sayre and J. J. Heaver, *J. Chem. Phys.* **19**, 584 (1950). S° at 100°, 200°, and 298.15° were taken from E. F. Westrum, et al., loc. cit., using $S_{10}^\circ(\text{extrap.}) = 0.008 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Temperature of Decomposition.

T_d was estimated from the value of ΔF_f^0 in the table. The value of T_d given by D. M. Banas, J. J. McSharry and E. A. Sullivan, *J. Am. Chem. Soc.* **77**, 2007 (1955) was 940°K. It was assumed that NaH would behave similarly to LiH and that decomposition pressure would be purity dependent, and this would produce apparently high T_d 's.

March 31, 1963

HNa

Sodium Hydride (NaH)

(Ideal Gas) Mol. Wt. = 23.999

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	6.81	37.330	1.386	30.166	30.166	30.166	INFINITE
200	7.241	37.330	1.386	30.166	30.166	30.166	INFINITE
298	7.241	44.000	1.386	30.166	30.166	30.166	INFINITE
300	7.246	45.001	1.386	30.166	30.166	30.166	INFINITE
400	7.569	47.176	1.386	30.166	30.166	30.166	INFINITE
500	7.911	48.905	1.386	30.166	30.166	30.166	INFINITE
600	8.172	50.372	1.386	30.166	30.166	30.166	INFINITE
700	8.377	51.647	1.386	30.166	30.166	30.166	INFINITE
800	8.537	52.777	1.386	30.166	30.166	30.166	INFINITE
900	8.664	53.790	1.386	30.166	30.166	30.166	INFINITE
1000	8.767	54.708	1.386	30.166	30.166	30.166	INFINITE
1100	8.853	55.548	1.386	30.166	30.166	30.166	INFINITE
1200	8.926	56.321	1.386	30.166	30.166	30.166	INFINITE
1300	8.989	57.038	1.386	30.166	30.166	30.166	INFINITE
1400	9.044	57.707	1.386	30.166	30.166	30.166	INFINITE
1500	9.094	58.332	1.386	30.166	30.166	30.166	INFINITE
1600	9.139	58.921	1.386	30.166	30.166	30.166	INFINITE
1700	9.181	59.476	1.386	30.166	30.166	30.166	INFINITE
1800	9.220	60.002	1.386	30.166	30.166	30.166	INFINITE
1900	9.257	60.501	1.386	30.166	30.166	30.166	INFINITE
2000	9.292	60.977	1.386	30.166	30.166	30.166	INFINITE
2100	9.325	61.431	1.386	30.166	30.166	30.166	INFINITE
2200	9.357	61.866	1.386	30.166	30.166	30.166	INFINITE
2300	9.388	62.282	1.386	30.166	30.166	30.166	INFINITE
2400	9.418	62.683	1.386	30.166	30.166	30.166	INFINITE
2500	9.447	63.068	1.386	30.166	30.166	30.166	INFINITE
2600	9.475	63.439	1.386	30.166	30.166	30.166	INFINITE
2700	9.503	63.797	1.386	30.166	30.166	30.166	INFINITE
2800	9.531	64.143	1.386	30.166	30.166	30.166	INFINITE
2900	9.558	64.478	1.386	30.166	30.166	30.166	INFINITE
3000	9.584	64.802	1.386	30.166	30.166	30.166	INFINITE
3100	9.610	65.117	1.386	30.166	30.166	30.166	INFINITE
3200	9.636	65.423	1.386	30.166	30.166	30.166	INFINITE
3300	9.662	65.719	1.386	30.166	30.166	30.166	INFINITE
3400	9.688	66.008	1.386	30.166	30.166	30.166	INFINITE
3500	9.713	66.290	1.386	30.166	30.166	30.166	INFINITE
3600	9.738	66.563	1.386	30.166	30.166	30.166	INFINITE
3700	9.763	66.831	1.386	30.166	30.166	30.166	INFINITE
3800	9.788	67.091	1.386	30.166	30.166	30.166	INFINITE
3900	9.813	67.346	1.386	30.166	30.166	30.166	INFINITE
4000	9.837	67.595	1.386	30.166	30.166	30.166	INFINITE
4100	9.862	67.838	1.386	30.166	30.166	30.166	INFINITE
4200	9.886	68.076	1.386	30.166	30.166	30.166	INFINITE
4300	9.910	68.309	1.386	30.166	30.166	30.166	INFINITE
4400	9.935	68.537	1.386	30.166	30.166	30.166	INFINITE
4500	9.959	68.760	1.386	30.166	30.166	30.166	INFINITE
4600	9.983	68.979	1.386	30.166	30.166	30.166	INFINITE
4700	10.007	69.194	1.386	30.166	30.166	30.166	INFINITE
4800	10.031	69.405	1.386	30.166	30.166	30.166	INFINITE
4900	10.055	69.612	1.386	30.166	30.166	30.166	INFINITE
5000	10.078	69.816	1.386	30.166	30.166	30.166	INFINITE
5100	10.102	70.016	1.386	30.166	30.166	30.166	INFINITE
5200	10.126	70.212	1.386	30.166	30.166	30.166	INFINITE
5300	10.150	70.405	1.386	30.166	30.166	30.166	INFINITE
5400	10.173	70.595	1.386	30.166	30.166	30.166	INFINITE
5500	10.197	70.782	1.386	30.166	30.166	30.166	INFINITE
5600	10.221	70.966	1.386	30.166	30.166	30.166	INFINITE
5700	10.244	71.147	1.386	30.166	30.166	30.166	INFINITE
5800	10.268	71.325	1.386	30.166	30.166	30.166	INFINITE
5900	10.291	71.501	1.386	30.166	30.166	30.166	INFINITE
6000	10.315	71.674	1.386	30.166	30.166	30.166	INFINITE

Dec. 31, 1960 Mar. 31, 1963

HNa

SODIUM HYDRIDE (NaH)

(IDEAL GAS)

MOL. WT. = 23.999

Ground State Configuration $1\sum^+ +$
 $S^0_{298.15} = 45.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^0_{f, 0} = 30.2 \pm 4.6 \text{ kcal. mole}^{-1}$
 $\Delta H^0_{f, 298.15} = 29.7 \pm 4.6 \text{ kcal. mole}^{-1}$

$\omega_e x_e = 19.72 \text{ cm.}^{-1}$
 $\omega_e = 4.3012 \text{ cm.}^{-1}$
 $B_e = 0.1353 \text{ cm.}^{-1}$
 $\sigma = 1$

Heat of Formation

$\Delta H^0_{f, 298.15}$ was calculated from $D^0_0 = 2.05 \pm 0.2 \text{ e.v.}$ reported by A. O. Deydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., 1953.

Heat Capacity and Entropy

All molecular and spectroscopic constants were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Inc., 1950.

HNa

SODIUM HYDROXIDE (NaOH)

(CRYSTAL)

MOL. WT. = 39.99717

Sodium Hydroxide (NaOH)

(Crystal)

Mol. Wt. = 39.99717

T. °K.	C _p ^a	S° ^b	-(S°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^c	ΔF _f ^d	Log K _f
0	∞.000	∞.000	INFINITE	2.506	-100.815	-100.815	INFINITE
100	6.691	3.713	26.257	2.254	-98.127	-98.127	214.456
200	11.850	10.176	16.655	1.802	-94.801	-94.801	103.265
298	14.228	13.450	13.450	∞.000	-90.867	-90.867	66.167
300	14.260	13.488	13.400	∞.026	-90.788	-90.788	66.147
400	15.520	19.772	15.976	1.518	-87.060	-87.060	47.567
500	17.963	23.461	17.109	3.176	-82.252	-82.252	36.380
600	20.560	29.710	18.418	6.655	-75.559	-75.559	28.970
700	20.560	32.879	20.435	8.711	-69.611	-69.611	23.780
800	20.560	35.624	22.166	10.767	-64.002	-64.002	19.003
900	20.560	38.046	23.798	12.823	-58.399	-58.399	16.007
1000	20.560	40.212	25.333	14.879	-52.805	-52.805	14.524
1100	20.560	42.172	26.776	16.935	-47.228	-47.228	12.587
1200	20.560	43.961	28.135	18.991	-41.903	-41.903	10.899
1300	20.560	45.606	29.416	21.047	-36.867	-36.867	9.224
1400	20.560	47.130	30.628	23.103	-32.134	-32.134	7.788
1500	20.560	48.549	31.776	25.159	-27.654	-27.654	6.569
1600	20.560	49.875	32.866	27.215	-23.422	-23.422	5.501
1700	20.560	51.122	33.904	29.271	-19.437	-19.437	4.564
1800	20.560	52.297	34.893	31.327	-15.681	-15.681	3.737
1900	20.560	53.409	35.839	33.383	-12.147	-12.147	3.001
2000	20.560	54.463	36.744	35.439	-8.822	-8.822	2.343

Dec. 31, 1950; Mar. 31, 1966

$\Delta H_f^{\circ} 0 = -100.82 \pm 0.1 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = -101.90 \pm 0.1 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} = 1.519 \text{ kcal. mole}^{-1}$
 $\Delta H_m^{\circ} = 1.519 \text{ kcal. mole}^{-1}$
 $\Delta H_g^{\circ} 298.15 (\text{to monomer}) = [51.5] \text{ kcal. mole}^{-1}$
 $\Delta H_g^{\circ} 298.15 (\text{to dimer}) = [49.0] \text{ kcal. mole}^{-1}$

Heat of Formation.

The standard enthalpy of formation, $\Delta H_f^{\circ} 298$ (NaOH, c) = $-101.90 \pm 0.1 \text{ kcal. mole}^{-1}$, was calculated from the heat of solution of sodium hydroxide (c) and the heat of sodium metal hydrolysis and the appropriate auxiliary data. N. A. Peshtetnikov¹ has measured the heat of solution NaOH(c) $\rightarrow$ NaOH(400 H₂O) as $-10.445 \pm 0.015 \text{ kcal. mole}^{-1}$ at 298.15°K. by solution calorimetry. Using the auxiliary heat of dilution reported by V. B. Parker², the selected heat of solution of sodium hydroxide (c) at infinite dilution is $-10.555 \text{ kcal. mole}^{-1}$. Also L. E. Murch and W. F. Glaque³ measured calorimetrically the heat of solution of solid samples of NaOH·nH₂O in the range from n = 0.1 to 1.0. When extrapolated to n = 0 and infinite dilution², this result yields the heat of solution of NaOH(c) at infinite dilution, $\Delta H_f^{\circ} 298 = -10.635 \text{ kcal. mole}^{-1}$, which is in good agreement with the value selected.

The heat of sodium metal hydrolysis, $\Delta H_f^{\circ} 298$, has been measured in the solution calorimeter by the following investigators. Na(c) + H₂O(l) $\rightarrow$ NaOH(nH₂O) + 1/2 H₂(g) $\Delta H_f^{\circ} 298$

Source	Number of Moles of H ₂ O	$\Delta H_f^{\circ} 298$ kcal. mole ⁻¹	$\Delta H_f^{\circ} 298$ kcal. mole ⁻¹	$\Delta H_f^{\circ} 298$ kcal. mole ⁻¹
Gunn et al. ³	1000	-44.047 ± 0.008	-112.446	-101.899
Messer et al. ⁴	CO	-44.215 ± 0.20	-112.530	-101.975
Ketchen et al. ⁵	CO	-44.054 ± 0.20	-112.369	-101.814

The values of $\Delta H_f^{\circ} 298$ (NaOH·nH₂O) were calculated from the heats of reaction $\Delta H_f^{\circ} 298$ using the $\Delta H_f^{\circ} 298$ (H₂O, l) = $-68.315 \text{ kcal. mole}^{-1}$.⁶ Combination of the selected heat of solution of NaOH(c) at infinite dilution with the heat of formation of NaOH(COOH₂) gives the heat of formation of NaOH(c) in the last column of the table. A weighted average of these three measurements has been taken for the selected heat of formation of sodium hydroxide (c).

The earlier investigations have been reviewed by F. R. Bichowsky and F. D. Rossini⁷, and C. E. Messer et al.⁴, and these earlier reported data are not adopted in the tabulation.

Heat Capacity and Entropy.

L. E. Murch and W. F. Glaque¹¹ have measured low temperature heat capacities of NaOH·0.04014 H₂O and NaOH·0.9776 H₂O from 15° to 320°K. and calculated the values of C_p for the pure phase of NaOH(c). T. B. Douglas and J. L. Dever⁹ have measured the enthalpy changes from 273° to 975°K. in the drop calorimeter and derived the heat capacities. The low temperature and the high temperature heat capacities were joined smoothly by Murch and Glaque, and the smooth values were adopted in the tabulation. Low temperature heat capacities from 60° to 300°K. have also been measured by J. C. R. Kelly and P. E. Snyder⁷, whose data are in good agreement with those reported by Murch and Glaque. M. M. Popov and D. M. Ginzburg¹⁰ have determined the heat capacities of NaOH(c) in the temperature range from 298° to 577°K. from the enthalpy measurements by drop calorimetry. The reported $H_{500}^{\circ} - H_{298}^{\circ} = 3.112 \text{ kcal. mole}^{-1}$ is in good agreement with the tabulated value.

Transition and Melting Data.

The adopted heat of transition and the transition temperature, and the adopted heat of melting and the melting point were obtained from Douglas and Dever,⁹ Popov and Ginzburg,¹⁰ reported the heat of transition $\Delta H_{tr}^{\circ} = 1.930 \text{ kcal. mole}^{-1}$ at 576.8°K. and the heat of melting $\Delta H_m^{\circ} = 1.629 \text{ kcal. mole}^{-1}$ at 595.16°K.

Heat of Sublimation.

See NaOH(g) table for details.

References

- N. A. Peshtetnikov, Zhur. Neorg. Khim. 5, 682 (1961).
- V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-NBS 2, April, 1965.
- S. R. Gunn and L. O. Green, J. Am. Chem. Soc. 80, 4782 (1958). S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking-Bomb Solution Calorimeters," UCL-7992, Oct. 1964.
- E. E. Ketchen and W. F. Glaque, J. Am. Chem. Soc. 77, 4524 (1955).
- E. E. Ketchen and W. F. Glaque, J. Am. Chem. Soc. 77, 4524 (1955).
- D. C. Wagner, M. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, NBS Tech. Note 270-1, Oct. 1965.
- J. C. R. Kelly and P. E. Snyder, J. Am. Chem. Soc. 73, 4114 (1951), ibid, 73, 5933 (1951).
- T. B. Douglas and J. L. Dever, J. Res. Nat'l. Bur. Std. 53, 81 (1954).
- M. M. Popov and F. D. Rossini, "The Thermochimistry of the Chemical Substances", Reinhold Publishing Corp., New York, 1955.
- M. M. Popov and O. M. Ginzburg, Zhur. Obshch. Khim. 26, 971 (1956). O. M. Ginzburg, ibid, 26, 968 (1956).
- L. E. Murch and W. F. Glaque, J. Phys. Chem. 66, 2052 (1962).

Sodium Hydroxide (NaOH)

Mol. wt. = 39.99717

HNaO

(Liquid) (Liquid) MOL. WT. = 39.99717

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100							
200							
298	20.990	17.727	17.727	0.000	- 99.998	- 89.659	65.722
300	20.988	17.857	17.727	0.039	- 99.984	- 89.595	65.270
400	20.946	23.615	18.549	2.168	- 97.850	- 85.400	62.900
500	20.881	28.611	23.611	2.168	- 95.317	- 81.850	60.200
600	20.570	32.275	21.821	6.272	- 98.702	- 79.579	28.987
700	20.430	35.435	23.547	8.322	- 98.098	- 76.441	23.866
800	20.290	38.154	25.207	10.358	- 97.509	- 73.387	20.049
900	20.150	40.236	26.780	12.388	- 96.946	- 70.487	17.047
1000	20.010	41.631	28.284	14.388	- 96.395	- 67.637	14.149
1100	19.870	42.552	29.659	16.382	- 95.879	- 64.823	12.839
1200	19.730	43.075	30.973	18.362	- 95.390	- 62.046	11.473
1300	19.590	43.321	32.212	20.328	- 94.930	- 59.302	9.515
1400	19.450	43.295	33.381	22.280	- 94.493	- 56.588	8.102
1500	19.310	43.032	34.487	24.216	- 94.079	- 53.903	6.805
1600	19.170	42.536	35.530	26.142	- 93.684	- 51.243	5.825
1700	19.030	41.832	36.531	28.052	- 93.309	- 48.694	4.894
1800	18.910	40.916	37.478	29.949	- 92.954	- 46.251	4.071
1900	18.795	39.816	38.381	31.788	- 92.619	- 43.911	3.358
2000	18.690	38.597	39.243	33.578	- 92.294	- 41.671	2.742
2100	18.595	37.270	40.067	35.322	- 91.979	- 39.530	2.090
2200	18.515	35.847	40.857	37.028	- 91.674	- 37.488	1.555
2300	18.447	34.331	41.615	38.700	- 91.379	- 35.546	1.068
2400	18.393	32.725	42.343	40.348	- 91.094	- 33.700	0.621
2500	18.346	31.043	43.043	41.975	- 90.819	- 31.954	0.217
2600	18.310	29.300	43.718	43.587	- 90.554	- 30.308	- 0.157
2700	18.287	27.500	44.369	45.177	- 90.299	- 28.762	- 0.503
2800	18.265	25.649	44.997	46.745	- 90.054	- 27.316	- 0.822
2900	18.250	23.750	45.600	48.290	- 89.819	- 25.970	- 1.126
3000	18.238	21.800	46.193	49.815	- 89.594	- 24.724	- 1.416

$$S_{298.15}^{\circ} = 17.727 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = -99.998 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 1.519 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{\circ}(\text{to monomer}) = 37.9 \text{ kcal. mole}^{-1}$$

$$T_m = 592.25^{\circ}\text{K.}$$

$$T_b(\text{monomeric gas}) = 1662.7^{\circ}\text{K.}$$

Heat of Formation.

The heat of formation of NaOH(l) at 298°K. was obtained from that of the crystal by adding ΔH_m° and the difference between $H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

The selected heat capacities in the temperature range from 592.3° to 1000°K. were obtained from the enthalpy measurements of sodium hydroxide (l) in the drop calorimeter by T. B. Douglas and J. L. Dever¹. The heat capacities below the melting point and above 1000°K. were extrapolated from the selected heat capacity curve.

Douglas and Dever¹ have also compared their heat capacity values with those from W. D. Powers and G. C. Blalock² who have applied the same drop method to determine the heat capacities of NaOH(l). Both results are in reasonable agreement. M. M. Popov and G. M. Ginzburg³ applying the same technique obtained different values of heat capacity. The smoothed enthalpy data reported by Ginzburg⁴ are 200 to 500 cal. mole⁻¹ smaller than the tabulated values at the temperature range from 700° to 1000°K.

The entropy ($S_{298}^{\circ} = 17.65 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See NaOH(c) table for details.

Vaporization Data.

The boiling point 1662.7°K. was calculated as the temperature at which the free energies of formation (ΔF_f°) for both NaOH(l) and NaOH(g) are equal. The difference in the heats of formation (ΔH_f°) of NaOH(l) and NaOH(g) at the boiling point is the heat of vaporization. If $\text{Na}_2\text{(OH)}_2\text{(g)}$ is also considered as a minor component in the vapor mixture (approximately 6% of total vapor pressure at the boiling point) the calculated boiling point is 1653°K. (see NaOH(g) table for details).

H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), have studied the vapor pressures of liquid NaOH and reported the boiling point as 1661°K.

Reference:

- 1 T. B. Douglas and J. L. Dever, J. Res. Nat'l. Bur. Std. 53, 81 (1954).
- 2 W. D. Powers and G. C. Blalock, "Enthalpies and Specific Heats of Alkali and Alkaline Earth Hydroxides at High Temperatures", ORNL-1653, Oak Ridge Nat'l. Lab. Jan. 1954.
- 3 M. M. Popov and G. M. Ginzburg, Zhur. Obshchei Khim. 26, 971 (1956).
- 4 G. M. Ginzburg, Ibid. 26, 968 (1956).

HNaO

Sodium Hydroxide (NaOH)

(Ideal Gas) Mol. Wt. = 39.99717

SODIUM HYDROXIDE (NaOH)

(IDEAL GAS)

MOL. WT. = 39.99717

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.095	46.936	2.550	-49.359	-49.359	INFINITE
200	8.889	52.790	1.752	-49.618	-50.447	110.252
298	9.486	56.456	∞	-50.400	-51.135	55.878
300	9.496	56.515	∞	-50.407	-51.615	37.602
400	9.986	59.316	5.92	-51.479	-51.804	28.359
500	10.391	61.589	2.012	-51.916	-51.958	22.711
600	10.722	63.516	3.058	-52.308	-52.098	18.915
700	10.996	65.188	4.154	-52.668	-52.468	16.184
800	11.235	66.672	5.009	-53.003	-52.803	14.123
900	11.449	68.008	6.400	-53.322	-53.121	12.509
1000	11.646	69.224	8.169	-53.629	-53.429	11.210
1100	11.827	70.343	10.297	-53.926	-53.726	10.142
1200	11.995	71.376	12.612	-54.214	-54.014	9.163
1300	12.149	72.345	15.128	-54.497	-54.297	8.077
1400	12.290	73.251	17.840	-54.774	-54.574	7.166
1500	12.418	74.103	20.748	-55.047	-54.847	6.337
1600	12.535	74.909	23.853	-55.316	-55.116	5.639
1700	12.642	75.672	27.162	-55.581	-55.381	5.063
1800	12.738	76.397	30.672	-55.842	-55.642	4.607
1900	12.825	77.088	34.388	-56.100	-55.900	4.251
2000	12.904	77.748	38.310	-56.355	-56.155	3.984
2100	12.976	78.380	42.448	-56.607	-56.407	3.793
2200	13.041	78.990	46.802	-56.856	-56.656	3.624
2300	13.100	79.566	51.372	-57.102	-56.902	3.474
2400	13.154	80.124	56.160	-57.345	-57.145	3.341
2500	13.203	80.662	61.168	-57.585	-57.385	3.221
2600	13.247	81.181	66.406	-57.821	-57.621	3.111
2700	13.288	81.682	71.874	-58.054	-57.854	3.009
2800	13.325	82.166	77.572	-58.284	-58.084	2.914
2900	13.360	82.634	83.500	-58.511	-58.311	2.826
3000	13.391	83.087	89.658	-58.735	-58.535	2.744
3100	13.420	83.527	96.046	-58.956	-58.756	2.667
3200	13.447	83.953	102.664	-59.174	-58.974	2.594
3300	13.472	84.368	109.512	-59.389	-59.189	2.525
3400	13.494	84.770	116.590	-59.599	-59.399	2.460
3500	13.516	85.162	123.900	-59.806	-59.606	2.399
3600	13.535	85.543	131.442	-59.999	-59.799	2.342
3700	13.554	85.914	139.218	-60.189	-59.989	2.289
3800	13.571	86.275	147.230	-60.375	-60.175	2.239
3900	13.586	86.628	155.478	-60.558	-60.358	2.192
4000	13.601	86.972	163.962	-60.737	-60.537	2.148
4100	13.615	87.308	172.682	-60.912	-60.712	2.107
4200	13.628	87.637	181.638	-61.083	-60.883	2.068
4300	13.640	87.957	190.830	-61.250	-61.050	2.031
4400	13.651	88.271	200.258	-61.413	-61.213	1.996
4500	13.662	88.578	209.924	-61.572	-61.372	1.963
4600	13.672	88.878	219.828	-61.727	-61.527	1.931
4700	13.682	89.173	229.970	-61.878	-61.678	1.899
4800	13.691	89.461	240.350	-62.025	-61.825	1.869
4900	13.699	89.743	250.968	-62.168	-61.968	1.840
5000	13.707	90.020	261.824	-62.307	-62.107	1.812
5100	13.715	90.291	272.918	-62.442	-62.242	1.785
5200	13.722	90.558	284.250	-62.573	-62.373	1.759
5300	13.728	90.819	295.820	-62.700	-62.500	1.734
5400	13.735	91.076	307.630	-62.823	-62.623	1.709
5500	13.741	91.328	319.680	-62.942	-62.742	1.685
5600	13.747	91.576	331.980	-63.058	-62.858	1.661
5700	13.752	91.819	344.530	-63.170	-62.970	1.638
5800	13.757	92.058	357.330	-63.278	-63.078	1.615
5900	13.762	92.293	370.380	-63.382	-63.182	1.592
6000	13.767	92.525	383.680	-63.482	-63.282	1.570

Dec. 31, 1960; Mar. 31, 1966

Point Group C_{2v}
 $S_{298.15} = [56.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = 1

 $\Delta H_f^0 = -49.4 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 298.15 = -50.4 \pm 5 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
437 (1)	[1300](1)
	[3700](1)

Bond Distance: Na-O = [1.97] Å

Bond Angle: Na-O-H = [110°]

Product of the Moments of Inertia: $I_A I_B I_C = [5.3082] \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

σ = 1

Heat of Formation.

R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. **29**, 454 (1958), have found in their mass-spectrometric studies that the NaOH(l) vaporizes mainly as gaseous dimer in the temperature range from 575° to 723°K. They have also calculated by the slope method the heat of dimerization, $\Delta H_{298}^0 = -54 \pm 5 \text{ kcal. mole}^{-1}$, for $2\text{NaOH(g)} = \text{Na}_2\text{(OH)}_2\text{(g)}$ and the heat of sublimation, $\Delta H_{298}^0 = 46.3 \pm 3 \text{ kcal. mole}^{-1}$, for $\text{NaOH(c)} = \text{NaOH(g)}$. The second law values were determined using ion intensity ratios, however, a third law calculation using a single data point converted by the authors to absolute pressure (J. Phys. Chem. **62**, 488 (1958)) yields $\Delta H_{298}^0 = -51.6 \text{ kcal. mole}^{-1}$, ΔH_{298}^0 (to monomer) = $-49.5 \text{ kcal. mole}^{-1}$ and ΔH_{298}^0 (to dimer) = $-41.1 \text{ kcal. mole}^{-1}$, which are in agreement within the limit of uncertainty. Later, Porter and Schoonmaker, J. Chem. Phys. **31**, 830 (1959), found the activity of molten alkali hydroxide had been reduced in the presence of MgO in their sample container, and the uncertainty in the heat of sublimation might be $\pm 5 \text{ kcal. mole}^{-1}$, but the heat of dimerization should not be seriously affected because it was calculated from alcohols of both species. In order to have good agreement between the calculated total pressure of monomer and dimer of sodium hydroxide (g) and the observed vapor pressures by H. von Wartenberg and P. Albrecht, Z. Elektrochem. **27**, 182 (1921), the heat of dimerization and the heat of sublimation have been so chosen as $\Delta H_{298}^0 = -54 \text{ kcal. mole}^{-1}$ and $\Delta H_{298}^0 = 46.3 \text{ kcal. mole}^{-1}$ and the boiling point is 1653°K . which is in good agreement with $1661 \pm 20^\circ\text{K}$. reported by Wartenberg and Albrecht, loc. cit. The heats of formation were calculated from the selected heat of dimerization and heat of sublimation as ΔH_{298}^0 (NaOH, g) = $-50.4 \text{ kcal. mole}^{-1}$ and ΔH_{298}^0 (Na₂(OH)₂, g) = $-154.8 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The bent molecular configuration with the bond angle of 110° was proposed by S. H. Bauer, R. M. Diner and P. F. Porter, J. Chem. Phys. **23**, 931 (1958). The bond distance O-H was estimated from that in H₂O(g). The bond distance Na-O was estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-F(g) to the bond distance Na-F(g) (1.92595 Å) which has been accurately measured by R. K. Bauer and H. Lew, Can. J. Phys. **41**, 1461 (1963). The Na-O stretching frequency was obtained from L. H. Spinar and J. L. Margrave, Spectrochim. Acta **12**, 244 (1956), in the infrared spectroscopic studies. The O-H stretching and the bending frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rigid convergence to a constant as a heavier atom is attached. The three principal moments of inertia are $I_A = [0.1252] \times 10^{-59}$, $I_B = [6.449] \times 10^{-59}$ and $I_C = [6.5742] \times 10^{-59} \text{ g. cm.}^2$.

Hydroxyl (OH)

(Ideal Gas) Mol. wt. = 17.0074

HYDROXYL (OH)

(IDEAL GAS)

MOL. WT. = 17.0074

T, K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	2.162	9.289	9.289	INFINITE
100	7.798	35.726	50.398	1.467	9.001	19.672	9.001
200	7.356	40.985	44.541	.711	9.393	8.671	9.475
298	7.167	43.880	43.880	.000	9.432	8.307	9.689
300	7.165	43.925	43.881	.043	9.432	8.209	9.686
400	7.087	45.971	42.881	.725	9.432	7.920	9.682
500	7.055	47.551	44.687	1.432	9.434	7.540	9.679
600	7.057	48.837	45.275	2.137	9.411	7.163	9.609
700	7.090	49.927	45.653	2.845	9.379	6.791	9.512
800	7.130	50.852	45.942	3.553	9.338	6.428	9.402
900	7.173	51.721	46.172	4.275	9.298	6.062	9.275
1000	7.232	52.491	47.488	5.003	9.250	5.706	9.127
1100	7.339	53.195	47.975	5.742	9.206	5.353	8.964
1200	7.549	53.847	48.437	6.491	9.164	5.005	8.794
1300	7.769	54.425	48.867	7.248	9.124	4.661	8.619
1400	7.966	54.929	49.260	8.005	9.086	4.320	8.440
1500	8.147	55.366	49.626	8.769	9.050	3.980	8.258
1600	8.303	55.733	50.079	9.536	9.014	3.642	8.072
1700	8.435	56.063	50.447	10.307	8.980	3.307	7.882
1800	8.547	56.365	50.739	11.077	8.947	2.975	7.687
1900	8.641	56.635	51.000	11.846	8.915	2.646	7.487
2000	8.718	56.871	51.236	12.614	8.881	2.313	7.282
2100	8.779	57.086	51.447	13.381	8.849	1.988	7.072
2200	8.815	57.286	51.637	14.148	8.815	1.662	6.857
2300	8.836	57.465	51.806	14.914	8.782	1.336	6.637
2400	8.844	57.626	51.956	15.679	8.749	1.010	6.412
2500	8.857	57.773	52.094	16.443	8.711	.680	6.182
2600	8.872	57.910	52.214	17.209	8.675	.352	5.947
2700	8.885	58.036	52.317	17.974	8.637	.024	5.707
2800	8.896	58.153	52.406	18.738	8.597	-.308	5.462
2900	8.906	58.262	52.482	19.499	8.555	-.633	5.212
3000	8.914	58.355	52.548	20.255	8.511	-.959	4.957
3100	8.914	58.444	52.603	21.011	8.472	-1.288	4.702
3200	8.914	58.528	52.648	21.766	8.427	-1.619	4.447
3300	8.914	58.607	52.684	22.521	8.383	-1.957	4.192
3400	8.905	58.682	52.712	23.276	8.333	-2.297	3.937
3500	8.893	58.721	52.738	24.030	8.283	-2.646	3.682
3600	8.879	58.773	52.754	24.784	8.232	-2.991	3.427
3700	8.864	58.818	52.760	25.538	8.179	-3.342	3.172
3800	8.848	58.858	52.758	26.292	8.129	-3.697	2.917
3900	8.831	58.893	52.746	27.046	8.069	-4.050	2.662
4000	8.813	58.922	52.724	27.800	8.011	-4.403	2.407
4100	8.794	58.945	52.692	28.554	7.952	-4.756	2.152
4200	8.774	58.962	52.650	29.308	7.892	-5.109	1.897
4300	8.753	58.974	52.600	30.062	7.830	-5.462	1.642
4400	8.731	58.980	52.542	30.816	7.760	-5.815	1.387
4500	8.708	58.984	52.478	31.570	7.690	-6.168	1.132
4600	8.684	58.984	52.408	32.324	7.619	-6.521	.877
4700	8.659	58.979	52.333	33.078	7.548	-6.874	.622
4800	8.633	58.969	52.253	33.832	7.477	-7.227	.367
4900	8.606	58.953	52.168	34.586	7.406	-7.580	.112
5000	8.578	58.932	52.078	35.340	7.335	-7.933	-.143
5100	8.549	58.905	51.983	36.094	7.264	-8.286	-.398
5200	8.519	58.872	51.883	36.848	7.193	-8.639	-.653
5300	8.488	58.834	51.778	37.602	7.122	-8.992	-.908
5400	8.456	58.791	51.668	38.356	7.051	-9.345	-.113
5500	8.423	58.744	51.553	39.110	6.980	-9.698	-.368
5600	8.389	58.693	51.433	39.864	6.909	-10.051	-.623
5700	8.354	58.638	51.308	40.618	6.838	-10.404	-.878
5800	8.318	58.579	51.178	41.372	6.767	-10.757	-.113
5900	8.281	58.516	51.043	42.126	6.696	-11.110	-.368
6000	8.243	58.449	50.903	42.880	6.625	-11.463	-.623

Dec. 31, 1960; Mar. 31, 1966

Ground State Configuration 2π

$S_{298.15}^0 = 43.880 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^0 = 9.290 \pm 0.3 \text{ kcal. mole}^{-1}$

$\Delta H_f^0_{298.15} = 9.432 \pm 0.3 \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$\epsilon_i, \text{ cm.}^{-1}$	$\frac{g_i}{2}$
0	2
139.7	2

$\omega_e x_e = 82.81 \text{ cm.}^{-1}$

$\omega_e = 3755.21 \text{ cm.}^{-1}$

$\sigma = 1$

$r_e = 0.9706 \text{ \AA}$

$\alpha_e = 0.714 \text{ cm.}^{-1}$

Heat of Formation.

P. Orty, Trans. Acad. Sci. 408 (1959) has summarized the determinations of the heat of formation of OH and concludes that the short extrapolation by Barrow, Arkiv. Fysik, 11, 281 (1956) of the $E(\sum^+)$ to $A(\sum^+)$ system gives the most reliable result. The value of $D_0 = 101.33 \text{ kcal. mole}^{-1}$ was adopted and leads to a heat of formation of $9.432 \text{ kcal. mole}^{-1}$. A recent determination of the dissociation energy from measurements of the concentration of the radicals in water oxygen mixtures by A. P. Furman and A. V. Frost, Vestn. Mosk. Univ., Ser. II Khim. 15, 25 (1961) gives $\Delta H_f^0(\text{OH}) = 102.8 \pm 0.8 \text{ kcal. mole}^{-1}$ in good agreement with the adopted value. Also V. A. Medvedev, V. V. Korobov and V. P. Baluz, Zhur. Fiz. Khim. 33, 58 (1959) reported a heat of dissociation of $102.2 \pm 1 \text{ kcal. mole}^{-1}$ from dissociation of water in a spherical bomb.

Heat Capacity and Entropy.

The molecular constants were all given by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. New York, 1950. This calculation gives values in excellent agreement with L. Haar, A. S. Friedman and C. W. Beckett, National Bureau of Standards Monograph No. 20, May 1961. The agreement with the higher order correction calculations of H. L. Johnston, J. Belzer and L. Savedoff, TR 316-5, Ohio State University, available as ATU 139 967, is good between 298 and 4000°K. This earlier work uses different constants and also a different value of the ground state splitting constant, but at 6000°K. the entropy difference is still less than 0.25%.

Hydroxyl Unipositive Ion (OH⁺)

(Ideal Gas) Mol. Wt. = 17.0068

HO⁺

T, °K.	C _p ^o	S ^o - (F ^o -H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H ^o - H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0							
100	6.969	43.657	43.657	-0.000	314.800	312.254	-228.888
200							
298	6.969	43.657	43.657	-0.013	314.809	312.238	-227.465
300	6.969	43.700	43.657	0.13	314.809	312.238	-227.465
400	6.982	45.707	43.631	7.10	315.301	311.306	-170.090
500	7.020	47.268	44.448	4.448	315.783	310.252	-135.611
600	7.095	48.554	45.028	2.115	309.101	309.101	-112.590
700	7.204	49.655	45.612	2.830	316.728	307.871	-96.122
800	7.337	50.626	46.179	3.557	317.200	306.573	-83.752
900	7.480	51.498	46.723	4.298	317.675	305.217	-74.117
1000	7.625	52.294	47.241	5.053	318.155	303.807	-66.397
1100	7.765	53.027	47.734	5.823	318.639	302.349	-60.071
1200	7.897	53.709	48.204	6.606	319.128	300.847	-54.792
1300	8.019	54.345	48.652	7.402	319.619	299.304	-50.317
1400	8.131	54.944	49.080	8.209	320.115	297.722	-46.476
1500	8.233	55.508	49.490	9.028	320.612	296.106	-43.143
1600	8.326	56.043	49.883	9.856	321.109	294.454	-40.321
1700	8.410	56.550	50.260	10.692	321.608	292.775	-37.639
1800	8.487	57.033	50.623	11.537	322.106	291.063	-35.340
1900	8.557	57.494	50.973	12.390	322.605	289.326	-33.280
2000	8.621	57.934	51.310	13.249	323.104	287.562	-31.423
2100	8.680	58.356	51.636	14.114	323.601	285.772	-29.741
2200	8.734	58.761	51.950	14.984	324.097	283.959	-28.209
2300	8.785	59.151	52.255	15.860	324.591	282.121	-26.808
2400	8.831	59.526	52.550	16.741	325.085	280.266	-25.527
2500	8.875	59.887	52.837	17.626	325.575	278.387	-24.337
2600	8.915	60.236	53.114	18.516	326.066	276.491	-23.241
2700	8.954	60.573	53.384	19.409	326.554	274.576	-22.225
2800	8.990	60.899	53.647	20.307	327.040	272.642	-21.281
2900	9.024	61.216	53.903	21.207	327.524	270.690	-20.400
3000	9.056	61.522	54.152	22.111	328.006	268.720	-19.576
3100	9.087	61.819	54.394	23.019	328.488	266.738	-18.805
3200	9.116	62.108	54.631	23.929	328.967	264.740	-18.081
3300	9.144	62.389	54.862	24.842	329.445	262.725	-17.400
3400	9.171	62.663	55.087	25.758	329.920	260.694	-16.757
3500	9.197	62.929	55.307	26.676	330.394	258.652	-16.151
3600	9.223	63.188	55.523	27.597	330.866	256.598	-15.578
3700	9.247	63.441	55.733	28.521	331.336	254.526	-15.034
3800	9.270	63.688	55.939	29.446	331.805	252.446	-14.519
3900	9.293	63.929	56.141	30.375	332.273	250.351	-14.029
4000	9.315	64.165	56.339	31.305	332.737	248.241	-13.563
4100	9.337	64.395	56.532	32.238	333.201	246.123	-13.120
4200	9.358	64.621	56.722	33.172	333.664	243.994	-12.696
4300	9.379	64.841	56.909	34.109	334.125	241.856	-12.292
4400	9.399	65.057	57.091	35.048	334.585	239.703	-11.906
4500	9.419	65.268	57.271	35.989	335.042	237.541	-11.537
4600	9.438	65.476	57.447	36.932	335.500	235.370	-11.183
4700	9.457	65.679	57.620	37.877	335.956	233.188	-10.843
4800	9.476	65.878	57.790	38.823	336.412	230.997	-10.518
4900	9.494	66.074	57.957	39.772	336.866	228.794	-10.205
5000	9.513	66.266	58.121	40.722	337.319	226.584	-9.904
5100	9.530	66.454	58.283	41.674	337.771	224.367	-9.615
5200	9.548	66.639	58.442	42.628	338.223	222.140	-9.336
5300	9.566	66.821	58.598	43.584	338.674	219.906	-9.068
5400	9.583	67.000	58.752	44.541	339.124	217.656	-8.809
5500	9.600	67.176	58.904	45.500	339.574	215.406	-8.559
5600	9.617	67.350	59.053	46.461	340.021	213.134	-8.318
5700	9.634	67.520	59.200	47.424	340.470	210.872	-8.085
5800	9.650	67.688	59.345	48.388	340.918	208.591	-7.860
5900	9.667	67.853	59.488	49.354	341.365	206.305	-7.642
6000	9.683	68.015	59.628	50.321	341.812	204.019	-7.431

Mar. 31, 1966

HO⁺HYDROXYL UNIPOSITIVE ION (OH⁺) (IDEAL GAS) MOL. WT. = 17.0068

Ground State Configuration $3 \sum^-$ $\Delta H_f^o = 313.3 \pm 2.5$ kcal. mole⁻¹
 $S_{298.15}^o = 43.657$ cal. deg.⁻¹ mole⁻¹ $\Delta H_f^o = 314.0 \pm 2.5$ kcal. mole⁻¹
 $S_{298.15}^o = 314.0 \pm 2.5$ kcal. mole⁻¹

Electronic Levels and Multiplicities

$$\frac{g_i}{\epsilon_i, \text{ cm.}^{-1}}$$

0

3

$$\omega_e x_e = \{74\}$$

$$\sigma = 1$$

$$\alpha_e = 0.732 \text{ cm.}^{-1}$$

$$r_e = 1.0289 \text{ \AA}$$

$$\omega_e = \{2955\} \text{ cm.}^{-1}$$

$$B_e = 16.795 \text{ cm.}^{-1}$$

Heat of Formation.

The ionization potential of hydroxyl has been determined by M. M. Mann, A. Hustrulid and J. T. Tate, Phys. Rev. 58, 340 (1940) from electron impact data on water vapor, as 13.6 e.v. S. N. Foner and R. L. Hudson, J. Chem. Phys. 25, 602 (1956) have measured the appearance potential of OH⁺ from OH as 13.18 ± 0.1 e.v. (303.96 kcal.). This value was the one adopted to obtain the heat of formation of OH⁺(g) from that of OH(g) at 0°K.

Heat Capacity and Entropy.

The molecular constants, with the exception of $\omega_e x_e$, were all given by O. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. New York, 1950. The value of $\omega_e x_e$ was estimated by analogy with OH(g) and other diatomic hydrides.

The value of H_{298}^o at 0°K. is -2.06 kcal. mole⁻¹.

Hydroxyl Uninegative Ion (OH⁻)

(Ideal Gas) Mol. Wt. = 17.0079

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg ⁻¹	-(H ^o -H ₂₉₈)/T	cal. mole ⁻¹	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0									
100	6.965	41.229	41.229	-0.000	-34.400	-33.248	24.371		
200	6.965	41.272	41.229	-0.13	-34.400	-33.248	24.216		
300	6.969	43.276	41.502	-0.710	-34.912	-32.776	17.008		
400	6.978	44.832	42.018	-1.407	-35.427	-32.182	14.067		
500	7.002	46.106	42.596	-2.106	-35.952	-31.484	11.468		
600	7.047	47.188	43.177	-2.808	-36.486	-30.606	8.584		
700	7.116	48.133	43.739	-3.516	-37.027	-29.833	8.150		
800	7.204	48.977	44.275	-4.232	-37.571	-29.062	7.018		
900	7.306	49.741	44.784	-4.957	-38.115	-28.298	6.099		
1000	7.415	50.442	45.267	-5.693	-38.659	-27.543	5.337		
1100	7.527	51.092	45.725	-6.440	-39.200	-26.796	4.693		
1200	7.638	51.699	46.162	-7.190	-39.738	-26.053	4.140		
1300	7.746	52.269	46.578	-7.948	-40.275	-25.311	3.659		
1400	7.848	52.807	46.975	-8.714	-40.810	-24.570	3.237		
1500	7.944	53.317	47.356	-9.537	-41.345	-23.828	2.864		
1600	8.034	53.801	47.721	-10.336	-41.878	-23.084	2.520		
1700	8.118	54.263	48.072	-11.144	-42.409	-22.341	2.228		
1800	8.196	54.704	48.409	-11.960	-42.941	-21.598	1.956		
1900	8.267	55.126	48.734	-12.783	-43.472	-20.855	1.707		
2000	8.334	55.531	49.049	-13.613	-44.004	-20.112	1.479		
2100	8.396	55.920	49.352	-14.449	-44.536	-19.369	1.270		
2200	8.453	56.294	49.646	-15.292	-45.067	-18.626	1.076		
2300	8.506	56.655	49.930	-16.140	-45.601	-17.883	0.897		
2400	8.556	57.004	50.206	-16.993	-46.136	-17.140	0.730		
2500	8.602	57.340	50.473	-17.851	-46.671	-16.397	0.574		
2600	8.645	57.666	50.735	-18.713	-47.208	-15.654	0.428		
2700	8.685	57.981	50.988	-19.580	-47.747	-14.911	0.291		
2800	8.723	58.286	51.234	-20.450	-48.285	-14.168	0.161		
2900	8.758	58.582	51.474	-21.324	-48.827	-13.425	0.039		
3000	8.792	58.870	51.708	-22.202	-49.369	-12.682	0.076		
3100	8.823	59.150	51.936	-23.082	-49.913	-11.939	0.185		
3200	8.853	59.422	52.159	-23.966	-50.459	-11.196	0.280		
3300	8.881	59.686	52.377	-24.853	-51.005	-10.453	0.368		
3400	8.908	59.944	52.589	-25.742	-51.554	-9.710	0.482		
3500	8.934	60.196	52.797	-26.635	-52.104	-8.967	0.572		
3600	8.958	60.441	52.999	-27.529	-52.657	-8.224	0.658		
3700	8.982	60.680	53.199	-28.426	-53.211	-7.481	0.740		
3800	9.004	60.913	53.394	-29.326	-53.766	-6.738	0.819		
3900	9.026	61.142	53.585	-30.227	-54.323	-6.000	0.895		
4000	9.047	61.365	53.772	-31.131	-54.882	-5.257	0.968		
4100	9.067	61.583	53.955	-32.036	-55.442	-4.514	1.038		
4200	9.086	61.797	54.135	-32.944	-56.004	-3.771	1.105		
4300	9.105	62.006	54.312	-33.854	-56.567	-3.028	1.170		
4400	9.123	62.211	54.485	-34.765	-57.132	-2.285	1.233		
4500	9.141	62.411	54.655	-35.678	-57.697	-1.542	1.294		
4600	9.158	62.608	54.822	-36.593	-58.265	-0.799	1.352		
4700	9.174	62.801	54.987	-37.510	-58.834	-0.056	1.409		
4800	9.190	62.990	55.148	-38.428	-59.404	0.687	1.464		
4900	9.206	63.176	55.307	-39.348	-59.974	1.430	1.517		
5000	9.222	63.359	55.463	-40.269	-60.546	2.194	1.569		
5100	9.237	63.538	55.616	-41.192	-61.120	2.957	1.619		
5200	9.251	63.714	55.767	-42.116	-61.694	3.720	1.667		
5300	9.266	63.887	55.916	-43.042	-62.269	4.483	1.715		
5400	9.280	64.057	56.063	-43.970	-62.845	5.246	1.761		
5500	9.294	64.224	56.207	-44.898	-63.422	6.009	1.806		
5600	9.307	64.389	56.349	-45.828	-64.000	6.772	1.849		
5700	9.321	64.551	56.489	-46.760	-64.579	7.535	1.892		
5800	9.334	64.711	56.627	-47.692	-65.159	8.298	1.933		
5900	9.347	64.868	56.763	-48.626	-65.739	9.061	1.973		
6000									

Mar. 31, 1966

HO⁻

HYDROXYL UNINEGATIVE ION (OH⁻) (IDEAL GAS) MOL. WT. = 17.0079

Ground State Configuration 1Σ⁺
 $\Delta H_f^o = -32.9 \pm 1.0$ kcal. mole⁻¹
 $\Delta H_f^o(298.15) = -34.4 \pm 1.0$ kcal. mole⁻¹

Electronic Levels and Multiplicities

$\frac{\epsilon_1, \text{cm}^{-1}}{0}$ $\frac{g_1}{1}$

$\omega_e = 3735 \pm 560$ cm⁻¹
 $\omega_e x_e = [74.7] \text{ cm}^{-1}$
 $B_e = 18.87$ cm⁻¹
 $\sigma = 1$
 $r_e = 1.834 \text{ Å}$
 $\alpha_e = [0.65] \text{ cm}^{-1}$

Heat of Formation

L. M. Branscomb, Joint Institute for Laboratory Astrophysics Report No. 62, Feb. 1st, 1966 has deduced an electron affinity of OH of 1.83 ± 0.04 e.v. (42.2 ± 0.9 kcal.) from the photodetachment spectrum of OH⁻(g). The vibrational state was deduced to be the ground state since no other absorption sequences could be detected by a thorough search. F. M. Page, Faraday Soc. Discussions 13, 87 (1955) has reviewed the methods and results of earlier determinations of the electron affinity of OH(g) and concludes that it is 65 ± 1 kcal. However he does state that it is not generally known whether the flame systems chiefly investigated are in thermodynamic equilibrium. In a later paper F. M. Page and T. M. Sugden, Trans. Faraday Soc. 53, 1092 (1957) conclude that much higher concentrations of radicals are obtained in flames than predicted thermodynamically. However for certain systems at lower temperatures they estimate only a factor of 3 increase in concentration and thus calculate the electron affinity as 61 kcal. mole⁻¹. The value reported by Branscomb, loc. cit. is adopted here.

Heat Capacity and Entropy

Branscomb loc. cit. has used his photodetachment spectra to obtain values of ω_e , B_e and r_e for OH⁻(g) which are remarkably similar to those for OH(g). The values of $\omega_e x_e$ and α_e were estimated by comparison with OH(g) and other hydrides. The ground state configuration was assumed to be that of HF(g) with which it is isoelectronic. The value of H_m-H_{298} at 0°K. is -2.057 kcal. mole⁻¹.

HO⁻

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	Log K _p
0	7.940	∞	∞	2.390	5.497	INFINITE
100	7.940	45.618	1.574	5.497	6.209	15.566
200	8.003	51.135	5.5132	7.799	5.214	7.742
298	8.338	54.383	0.000	5.000	8.049	5.900
300	8.347	54.434	0.015	4.986	8.067	5.877
400	8.507	54.914	0.077	4.883	8.083	5.859
500	8.679	55.360	0.166	4.787	8.099	5.848
600	8.860	55.784	0.271	4.698	8.116	5.839
700	9.045	56.190	0.391	4.616	8.134	5.830
800	9.233	56.578	0.525	4.540	8.151	5.822
900	9.424	56.948	0.673	4.470	8.167	5.815
1000	9.618	57.300	0.834	4.406	8.182	5.809
1100	9.814	57.634	1.007	4.347	8.197	5.803
1200	10.012	57.950	1.191	4.292	8.211	5.797
1300	10.212	58.248	1.385	4.241	8.225	5.791
1400	10.414	58.528	1.588	4.193	8.238	5.785
1500	10.618	58.790	1.799	4.148	8.250	5.779
1600	10.824	59.034	2.017	4.106	8.261	5.773
1700	11.031	59.261	2.242	4.066	8.271	5.767
1800	11.240	59.471	2.474	4.028	8.281	5.761
1900	11.450	59.664	2.713	3.992	8.290	5.755
2000	11.661	59.841	2.958	3.959	8.299	5.749
2100	11.872	60.000	3.209	3.927	8.307	5.743
2200	12.084	60.142	3.465	3.896	8.315	5.737
2300	12.296	60.268	3.726	3.866	8.323	5.731
2400	12.508	60.378	3.991	3.836	8.330	5.725
2500	12.720	60.474	4.260	3.806	8.337	5.719
2600	12.932	60.556	4.533	3.776	8.343	5.713
2700	13.144	60.624	4.810	3.746	8.349	5.707
2800	13.356	60.678	5.091	3.716	8.354	5.701
2900	13.568	60.719	5.375	3.686	8.359	5.695
3000	13.780	60.747	5.662	3.656	8.363	5.689
3100	13.992	60.762	5.951	3.626	8.367	5.683
3200	14.204	60.764	6.242	3.596	8.370	5.677
3300	14.416	60.753	6.534	3.566	8.373	5.671
3400	14.628	60.730	6.827	3.536	8.375	5.665
3500	14.840	60.694	7.121	3.506	8.377	5.659
3600	15.052	60.646	7.416	3.476	8.378	5.653
3700	15.264	60.586	7.712	3.446	8.378	5.647
3800	15.476	60.514	8.009	3.416	8.377	5.641
3900	15.688	60.430	8.307	3.386	8.375	5.635
4000	15.900	60.334	8.605	3.356	8.372	5.629
4100	16.112	60.226	8.903	3.326	8.368	5.623
4200	16.324	60.107	9.201	3.296	8.363	5.617
4300	16.536	60.000	9.500	3.266	8.357	5.611
4400	16.748	59.884	9.800	3.236	8.350	5.605
4500	16.960	59.758	10.100	3.206	8.343	5.599
4600	17.172	59.622	10.400	3.176	8.336	5.593
4700	17.384	59.476	10.700	3.146	8.328	5.587
4800	17.596	59.320	11.000	3.116	8.320	5.581
4900	17.808	59.154	11.300	3.086	8.312	5.575
5000	18.020	58.978	11.600	3.056	8.303	5.569
5100	18.232	58.792	11.900	3.026	8.295	5.563
5200	18.444	58.596	12.200	2.996	8.286	5.557
5300	18.656	58.390	12.500	2.966	8.277	5.551
5400	18.868	58.174	12.800	2.936	8.268	5.545
5500	19.080	57.948	13.100	2.906	8.258	5.539
5600	19.292	57.712	13.400	2.876	8.249	5.533
5700	19.504	57.466	13.700	2.846	8.239	5.527
5800	19.716	57.210	14.000	2.816	8.229	5.521
5900	19.928	56.954	14.300	2.786	8.219	5.515
6000	20.140	56.698	14.600	2.756	8.209	5.509

Mar. 31, 1964

HYDROPEROXYL (HO₂)

(IDEAL GAS)

MOL. WT. = 33.008

Point Group C₁
ΔH_f° O = 6 ± 2 kcal. mole⁻¹
ΔH_f° 298.15 = 54.383 cal. deg.⁻¹ mole⁻¹
ΔH_f° 298.15 = 5 ± 2 kcal. mole⁻¹
Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	g _i
1389.4	(1)
1101	(1)
3414	(1)

Bond length: H-O = [0.958] Å
Bond angle: HOO = [120°]
Product of the Moments of Inertia: I_AI_BI_C = [0.6424] X 10⁻¹¹⁷ g.³ cm.⁶
σ = 1

Heat of Formation.

S. N. Foner and R. L. Hudson, J. Chem. Phys. 36, 2681 (1962) have determined the ionization potential of HO₂ and the appearance potential of HO₂⁺ from H₂O₂. Using the ΔH_f° of H₂O₂(g) determined by P. A. Giguere and I. D. Liu, J. Am. Chem. Soc. 77, 6477 (1955), they calculate ΔH_f° O HO₂ = 5.7 ± 2 kcal. mole⁻¹.

Heat Capacity and Entropy.

The point group must be C₁ as the two oxygen atoms have been shown to be non-equivalent, from the increased number of infra-red bands obtained when using O₁₆ enriched with 28% of O₁₈, by D. E. Milligen and M. E. Jacox, J. Chem. Phys. 39, 2027 (1963). They also reported the three frequencies given above in the infra-red spectrum of the matrix isolated HO₂ radical. The bond lengths were taken equal to those estimated by M. E. Boyd, J. Chem. Phys. 37, 1317 (1962), the angle was that recommended by Milligen and Jacox, loc. cit. Boyd's conclusion that the lowest energy configuration should be an isosceles triangle could not be accepted in view of the nonequivalence of the oxygen atoms. The electronic ground state was taken as 2A" as predicted by A. D. Walsh, J. Chem. Soc. London, 2288 (1953).

Phosphorus Monohydride (PH)
(Ideal Gas) GFW = 31.98177

T, °K	C _p ^o	S ^o	-(G°-H°)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	log K _p
0	0.000	0.000	INFINITE	- 2.047	60.407	60.407	INFINITE
100	6.959	39.295	53.092	- 1.380	60.624	60.624	- 126.897
200	6.962	44.120	47.538	- .688	60.700	60.700	- 60.595
298	6.970	46.900	46.900	0.000	60.600	60.600	- 38.772
300	6.970	46.944	46.901	.013	60.597	60.597	- 38.498
400	7.008	48.953	47.174	.711	60.416	60.294	- 27.476
500	7.100	50.525	47.693	1.416	60.200	60.200	- 20.885
600	7.242	51.832	48.277	2.133	59.966	60.319	- 16.507
700	7.411	52.863	48.867	2.866	59.706	60.506	- 13.393
800	7.596	53.693	49.456	3.596	59.412	60.650	- 10.910
900	7.756	54.365	49.996	4.383	59.004	60.725	- 8.832
1000	7.914	55.691	50.528	5.166	58.489	60.749	- 7.485
1100	8.057	56.452	51.029	5.965	57.876	60.711	- 6.711
1200	8.186	57.156	51.511	6.777	57.166	60.605	- 6.065
1300	8.307	57.803	51.971	7.599	56.373	60.431	- 5.551
1400	8.419	58.399	52.411	8.432	55.506	60.191	- 5.151
1500	8.519	58.923	52.832	9.285	54.576	60.000	- 4.845
1600	8.615	59.376	53.237	10.142	53.584	60.000	- 4.589
1700	8.706	60.101	53.625	11.004	52.543	60.000	- 4.389
1800	8.792	60.798	53.996	11.871	51.464	60.000	- 4.242
1900	8.874	61.078	54.359	12.767	50.351	60.000	- 4.146
2000	8.954	61.536	54.707	13.658	49.204	60.000	- 4.091
2100	9.030	61.974	55.042	14.537	48.024	60.000	- 4.084
2200	9.104	62.396	55.464	15.404	46.814	60.000	- 4.124
2300	9.174	62.803	55.871	16.259	45.584	60.000	- 4.204
2400	9.243	63.196	56.264	17.104	44.334	60.000	- 4.324
2500	9.308	63.573	56.642	18.224	43.064	60.000	- 4.484
2600	9.372	63.939	56.970	19.160	41.774	60.000	- 4.684
2700	9.432	64.294	57.244	20.101	40.464	60.000	- 4.924
2800	9.487	64.641	57.461	21.047	39.134	60.000	- 5.204
2900	9.547	64.972	57.611	21.999	37.784	60.000	- 5.524
3000	9.600	65.297	57.685	22.956	36.414	60.000	- 5.884
3100	9.651	65.612	57.697	23.919	34.924	60.000	- 6.284
3200	9.701	65.920	57.643	24.886	33.314	60.000	- 6.724
3300	9.749	66.219	57.511	25.859	31.584	60.000	- 7.204
3400	9.793	66.510	57.311	26.834	29.734	60.000	- 7.724
3500	9.836	66.795	57.047	27.817	27.764	60.000	- 8.284
3600	9.877	67.073	56.722	28.803	25.684	60.000	- 8.884
3700	9.917	67.344	56.347	29.793	23.494	60.000	- 9.524
3800	9.957	67.608	55.921	30.784	21.194	60.000	- 10.204
3900	9.997	67.868	55.446	31.774	18.784	60.000	- 10.924
4000	10.027	68.121	54.925	32.785	16.264	60.000	- 11.684
4100	10.062	68.369	54.359	33.789	13.644	60.000	- 12.484
4200	10.095	68.612	53.751	34.787	10.924	60.000	- 13.324
4300	10.128	68.850	53.096	35.779	8.104	60.000	- 14.204
4400	10.158	69.083	52.401	36.762	5.184	60.000	- 15.124
4500	10.188	69.312	51.659	37.839	2.164	60.000	- 16.084
4600	10.217	69.536	50.886	38.860	- .856	60.000	- 17.084
4700	10.246	69.756	50.083	39.824	- 3.876	60.000	- 18.124
4800	10.274	69.971	49.246	40.731	- 6.896	60.000	- 19.204
4900	10.302	70.184	48.374	41.574	- 9.916	60.000	- 20.324
5000	10.329	70.393	47.469	42.349	- 12.936	60.000	- 21.484
5100	10.356	70.597	46.539	43.064	- 15.956	60.000	- 22.684
5200	10.383	70.799	45.584	43.717	- 18.976	60.000	- 23.924
5300	10.410	70.997	44.604	44.304	- 21.996	60.000	- 25.204
5400	10.435	71.192	43.596	44.824	- 24.916	60.000	- 26.524
5500	10.461	71.383	42.626	45.274	- 27.836	60.000	- 27.884
5600	10.487	71.572	41.624	45.654	- 30.756	60.000	- 29.284
5700	10.513	71.758	40.584	45.964	- 33.676	60.000	- 30.724
5800	10.538	71.941	39.504	46.204	- 36.596	60.000	- 32.204
5900	10.564	72.121	38.374	46.374	- 39.516	60.000	- 33.724
6000	10.589	72.299	37.194	46.484	- 42.436	60.000	- 35.284

Dec. 31, 1960; Sept. 30, 1962; June 30, 1967

PHOSPHORUS MONOHYDRIDE (PH) (IDEAL GAS)

Ground State Configuration 3s² 3p² ΔH_f^o = 60.4 ± 8 kcal/mol
S_{298.15} = 46.9 gibbs/mol ΔH_{f,298.15} = 60.6 ± 8 kcal/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i	E _i , cm ⁻¹	g _i
0	3	29560	6
[7650]	2	[38110]	2
[15150]	1	[57490]	1

ω_e = 2380 cm⁻¹ ω_ex_e = [55] cm⁻¹ σ = 1
B_e = 8.412 cm⁻¹ α_e = [0.28] cm⁻¹ r_e = 1.43 Å

Heat of Formation

Jordan (1) estimated the dissociation energy (D₀) of PH(g) as 70.44 kcal/mol using a semiempirical theoretical method. The corresponding value for the heat of formation (ΔH_{f,298.15}) is 60.6 ± 8 kcal/mol.

Heat Capacity and Entropy

Jordan (1) predicted five electronic levels (X²Σ, A²Σ, B²Σ, D²Σ, E²Σ) based on the reported value (2) of 29560 cm⁻¹ for the C²D level (this level is designated A₁ by Herzberg (2)). Several qualitative spectroscopic investigations of PH(g) have been reported and are in general accord with the predictions of Jordan (1). Ishaq and Pearsa (3) reported the values of the rotational constant B_e and the fundamental vibrational frequency ω_e. The value of ω_e is calculated from the Morse potential function. The bond distance is calculated from B_e. The value of the anharmonic vibrational term ω_ex_e is estimated from the relation ω_ex_e = ω_e²/(4D₀ + 2ω_e).

References

1. P. C. Jordan, J. Chem. Phys., **41**, 1442 (1964).
2. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
3. M. Ishaq and R. W. B. Pearsa, Proc. Roy. Soc. (London) **A123**, 265 (1919), and R. W. B. Pearsa, *ibid.*, **A123**, 328 (1919).

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 208.22

Lead Monohydride (PbH) (Ideal Gas)

T, °K	C _p	S°	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	4.000	INFINITE	2.074	57.032	57.032	INFINITE	
100	4.000	56.940	1.383	56.940	56.940	-119.122	
200	6.970	56.970	1.383	56.970	56.970	-119.122	
298	7.045	52.737	1.383	56.940	56.940	-36.866	
300	7.048	52.780	0.013	56.445	49.955	-36.391	
400	7.244	54.833	53.015	56.135	47.835	-26.135	
500	7.501	56.476	1.464	55.874	45.786	-20.012	
600	7.755	57.867	54.155	55.597	43.706	-15.952	
700	7.980	59.079	54.774	54.163	42.041	-13.125	
800	8.170	60.158	55.381	53.897	40.328	-11.016	
900	8.328	61.129	55.966	53.652	38.647	-9.384	
1000	8.461	62.014	56.527	53.427	36.992	-8.084	
1100	8.574	62.826	57.064	53.216	35.358	-7.025	
1200	8.672	63.576	57.575	53.021	33.744	-6.165	
1300	8.761	64.274	58.064	52.834	32.145	-5.504	
1400	8.843	64.926	58.531	52.652	30.560	-4.770	
1500	8.921	65.539	58.978	52.474	28.990	-4.224	
1600	8.997	66.117	59.407	52.294	27.439	-3.766	
1700	9.072	66.665	59.818	52.115	25.882	-3.327	
1800	9.146	67.185	60.213	51.933	24.342	-2.955	
1900	9.220	67.682	60.593	51.751	22.814	-2.624	
2000	9.294	68.157	60.959	51.566	21.296	-2.327	
2100	9.368	68.612	61.313	8.929	21.340	-2.221	
2200	9.441	69.049	61.655	16.269	21.932	-2.176	
2300	9.513	69.471	61.985	17.217	22.530	-2.141	
2400	9.583	69.877	62.306	18.171	23.135	-2.107	
2500	9.652	70.270	62.616	19.133	23.741	-2.074	
2600	9.720	70.650	62.918	20.102	24.358	-2.047	
2700	9.785	71.018	63.211	21.077	24.980	-2.022	
2800	9.848	71.375	63.497	22.059	25.608	-1.999	
2900	9.908	71.721	63.774	23.047	26.247	-1.978	
3000	9.966	72.058	64.045	24.040	26.891	-1.959	
3100	10.021	72.386	64.309	25.040	27.543	-1.942	
3200	10.074	72.705	64.566	26.044	28.203	-1.926	
3300	10.124	73.016	64.817	27.054	28.873	-1.912	
3400	10.171	73.319	65.063	28.069	29.550	-1.899	
3500	10.215	73.614	65.303	29.088	30.235	-1.888	
3600	10.257	73.902	65.538	30.112	30.930	-1.878	
3700	10.296	74.184	65.768	31.140	31.632	-1.868	
3800	10.333	74.459	65.993	32.171	32.343	-1.860	
3900	10.368	74.728	66.213	33.206	33.060	-1.853	
4000	10.400	74.991	66.430	34.245	33.783	-1.846	
4100	10.430	75.248	66.642	35.286	34.517	-1.840	
4200	10.459	75.500	66.850	36.331	35.259	-1.835	
4300	10.485	75.746	67.054	37.378	36.004	-1.830	
4400	10.510	75.987	67.254	38.428	36.761	-1.826	
4500	10.533	76.224	67.451	39.480	37.520	-1.822	
4600	10.555	76.456	67.644	40.534	38.281	-1.819	
4700	10.575	76.683	67.834	41.591	39.043	-1.816	
4800	10.594	76.906	68.020	42.649	39.808	-1.814	
4900	10.612	77.124	68.204	43.709	40.632	-1.812	
5000	10.629	77.339	68.385	44.772	41.473	-1.811	
5100	10.644	77.549	68.562	45.835	42.323	-1.809	
5200	10.659	77.756	68.737	46.900	43.077	-1.808	
5300	10.673	77.959	68.909	47.967	43.839	-1.808	
5400	10.687	78.159	69.079	49.035	44.651	-1.807	
5500	10.699	78.355	69.245	50.104	45.468	-1.807	
5600	10.711	78.548	69.410	51.175	46.292	-1.807	
5700	10.723	78.738	69.572	52.247	47.118	-1.807	
5800	10.734	78.924	69.731	53.319	47.954	-1.807	
5900	10.744	79.108	69.889	54.393	48.789	-1.807	
6000	10.754	79.289	70.044	55.468	49.627	-1.808	

June 30, 1982

Heat of Formation. ΔH_f° 298.15 was calculated from the dissociation energy of PbH(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration and spectroscopic data were obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950). Electronic levels and multiplicity were estimated by comparison with those for PbF(g).

Mol. Wt. = 208.22

 ΔH_f° 298.15 = 56.5 ± 4.6 kcal. mole⁻¹ S° 298.15 = 52.737 cal. deg⁻¹ mole⁻¹Ground State Configuration $2\pi_{1/2}^2$

Electronic Levels and Multiplicities

$$\frac{\epsilon, \text{ cm}^{-1}}{[\infty]} = \frac{g_1}{2}$$

$$\omega_e = 1564.1 \text{ cm}^{-1} \quad \omega_e x_e = 29.75 \text{ cm}^{-1}$$

$$B_e = 4.971 \text{ cm}^{-1} \quad \alpha_e = 0.144 \text{ cm}^{-1}$$

$$D^\circ = 1$$

Ground State Configuration 2_{II}

$\Delta H_{fO}^{\circ} = 34.4 \pm 4 \text{ kcal/mol}$

$\Delta H_{298.15}^{\circ} = 46.73 \text{ gibbs/mol}$

$\Delta H_{298.15}^{\circ} = 34.6 \pm 4 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	2	58636	2
376.9	2	[63850]	4
30662.4	2	75000	18

Heat of Formation

Mackle (1) estimated ΔH_{298}° of SH(g) as 34.6 ± 4 kcal/mol, this value being an average of three independent determinations.

He obtained these three values by the following methods: (A) He calculated ΔH_{298}° of SH(g) as 34.9 ± 4.5 kcal/mol from ΔH_{298}° of thiobenzyl alcohol (g), ΔH_{298}° of the benzyl radical, and the heat of dissociation (D_0°) of thiobenzyl alcohol reported by Senon and Darwent (2). (B) A value of 35.2 ± 4.5 kcal/mol was calculated from ΔH_{298}° of $\text{C}_2\text{H}_5\text{SH(g)}$ and ΔH_{298}° of $\text{C}_2\text{H}_5\text{SH(g)}$ reported by Franklin and Lumpkin (3). (C) He calculated that ΔH_{298}° of $\text{SH}^\bullet + \text{H}^\bullet$ and $\text{SH}^\bullet + \text{SH}^\bullet$ reported by Palmer and Lossing (4). The adopted value of 34.5 ± 4 kcal/mol compares well with a value of 34.9 kcal/mol obtained from a linear Birge-Sponer extrapolation of the potential function.

Heat Capacity and Entropy

The high resolution spectra of SH(g) have been studied by Ramsay (5) and Johns and Ramsay (6) in the near UV and by Morrow (7) in the vacuum UV. The energy levels of the doublet ground state and of the first excited state ($^2\Sigma$) were reported by Ramsay (6). Six of the seven higher excited levels ($4^3\Sigma$, $5^3\Sigma$, $6^3\Sigma$, $7^3\Sigma$, $8^3\Sigma$, $9^3\Sigma$) were reported by Morrow (7), the last five of which are shown as an average of 75000 cm⁻¹. The remaining electronic level ($1^3\Sigma$) is estimated by analogy with the electronic levels of SD(g) reported by Morrow (7).

Ramsay (3) reported the following rotational and vibrational constants: $B_0 = 9.461 \text{ cm}^{-1}$, $\omega_e = 2702 \text{ cm}^{-1}$, and $\omega_e x_e = 0.01 \text{ cm}^{-1}$. The value of a_e is calculated from the Morse potential function. The rotational constant B_e is calculated from $B_e = B_0 + a_e/2$. The bond distance is calculated from B_e .

References

- H. Mackle, *Tetrahedron* **32**, 1159 (1963).
A. H. Schon and B. de B. Darwent, *J. Amer. Chem. Soc.* **77**, 5282 (1955).
J. L. Franklin and H. E. Lurpink, *J. Amer. Chem. Soc.* **74**, 1023 (1952).
T. F. Palmer and J. P. Lossing, *J. Amer. Chem. Soc.* **84**, 4661 (1961).
D. A. Ramsay, *J. Chem. Phys.* **20**, 1920 (1952).
J. W. C. Johns and D. A. Ramsay, *Can. J. Phys.* **37**, 210 (1961).
B. A. Morrow, *Can. J. Phys.* **44**, 2947 (1966).

Zirconium Hydride (ZrH)

(Ideal Gas) Mol. wt. = 92.228

NOL. WT. = 92.228

(IDEAL GAS)

ZIRCONIUM HYDRIDE (ZrH)

T, °K.	C _p ^o	S ^o - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞.000	INFINITE	-	2.077	123.652	123.652	INFINITE
100	6.962	44.006	57.848	1.386	123.751	120.907	-26.423
200	6.978	48.935	52.282	-0.689	123.624	118.008	-129.046
298	7.006	51.638	51.638	-0.000	123.400	115.432	-84.610
300	7.009	51.682	51.638	-0.13	123.396	115.283	-84.053
400	7.348	53.756	51.919	1.735	123.135	112.750	-61.601
500	7.632	55.426	52.459	1.484	122.864	110.186	-48.160
600	7.891	56.841	53.074	2.260	122.586	107.676	-39.219
700	8.126	58.067	53.611	3.061	122.301	105.218	-32.647
800	8.286	59.169	54.100	3.781	122.000	102.789	-26.379
900	8.427	60.153	54.513	4.476	121.774	100.389	-21.425
1000	8.543	61.048	55.483	5.565	121.510	98.038	-19.014
1100	8.639	61.866	56.026	6.424	121.236	95.704	-17.018
1200	8.717	62.617	56.459	7.122	120.959	93.443	-15.408
1300	8.787	63.322	56.810	7.698	120.679	91.249	-14.022
1400	8.845	63.976	57.012	8.049	119.451	89.059	-12.660
1500	8.896	64.588	57.963	9.436	119.167	86.898	-11.577
1600	8.942	65.163	58.306	10.428	118.875	84.757	-10.623
1700	8.983	65.707	58.810	11.725	118.575	82.634	-9.773
1800	9.016	66.221	59.169	12.765	118.269	80.541	-9.022
1900	9.053	66.710	59.489	13.528	117.952	78.461	-8.345
2000	9.084	67.175	59.957	14.435	117.628	76.368	-7.734
2100	9.113	67.619	60.312	15.345	117.296	74.313	-7.196
2200	9.140	68.045	60.653	16.256	116.952	72.449	-6.773
2300	9.165	68.453	60.978	17.168	116.600	70.671	-6.332
2400	9.191	68.841	61.303	18.091	116.242	68.971	-5.866
2500	9.214	69.216	61.612	19.011	115.985	67.348	-5.494
2600	9.237	69.578	61.911	19.934	115.728	65.760	-5.150
2700	9.259	69.927	62.202	20.861	115.469	64.266	-4.837
2800	9.279	70.267	62.482	21.796	115.209	62.819	-4.537
2900	9.300	70.590	62.758	22.734	114.949	61.419	-4.262
3000	9.320	70.906	63.024	23.665	114.688	59.952	-4.005
3100	9.339	71.212	63.283	24.578	114.427	58.516	-3.766
3200	9.357	71.510	63.533	25.483	114.166	57.145	-3.545
3300	9.377	71.797	63.782	26.389	113.905	55.846	-3.332
3400	9.396	72.077	64.022	27.289	113.644	54.619	-3.134
3500	9.414	72.350	64.256	28.189	113.376	53.417	-2.948
3600	9.432	72.615	64.484	29.071	113.101	52.246	-2.773
3700	9.449	72.874	64.708	29.948	112.826	51.145	-2.608
3800	9.464	73.127	64.928	30.821	112.551	50.109	-2.453
3900	9.484	73.372	65.139	31.691	112.276	49.134	-2.303
4000	9.501	73.613	65.348	32.558	112.001	48.213	-2.163
4100	9.518	73.847	65.552	33.424	111.726	47.346	-2.029
4200	9.535	74.077	65.753	34.292	111.451	46.534	-1.903
4300	9.552	74.302	65.950	35.157	111.176	45.776	-1.786
4400	9.568	74.521	66.141	36.022	110.901	45.076	-1.668
4500	9.585	74.736	66.330	36.887	110.626	44.437	-1.558
4600	9.601	74.947	66.515	37.750	110.351	43.802	-1.454
4700	9.617	75.154	66.697	38.612	110.076	43.274	-1.354
4800	9.632	75.357	66.877	39.474	109.801	42.746	-1.260
4900	9.650	75.555	67.050	40.336	109.526	42.218	-1.174
5000	9.666	75.751	67.222	41.197	109.251	41.690	-1.090
5100	9.682	75.942	67.391	42.059	108.976	41.162	-1.008
5200	9.697	76.130	67.557	42.921	108.701	40.634	-0.928
5300	9.713	76.316	67.721	43.783	108.426	40.106	-0.848
5400	9.730	76.497	67.882	44.645	108.151	39.578	-0.768
5500	9.745	76.676	68.040	45.507	107.876	39.050	-0.688
5600	9.761	76.851	68.196	46.369	107.601	38.522	-0.608
5700	9.777	77.024	68.349	47.231	107.326	37.994	-0.528
5800	9.793	77.194	68.500	48.093	107.051	37.466	-0.448
5900	9.808	77.362	68.649	48.955	106.776	36.938	-0.368
6000	9.824	77.527	68.796	49.817	106.501	36.410	-0.288

June 30, 1963

Ground State Configuration [2Π]

ΔH_f^o 0 = [123.7] kcal. mole⁻¹

S_{298.15} = [51.638] cal. deg.⁻¹ mole⁻¹

ΔH_f^o 298.15 = [123.4] kcal. mole⁻¹

Electronic Levels and Multiplicities

E ₁ , cm. ⁻¹	E ₁
0	[4]

ω_e x_e = [19] cm.⁻¹

δ_e = 1

ω_e = [5.1] cm.⁻¹

r_e = [1.821] Å

Heat of Formation.

ΔH_f^o 0 was estimated as 123.7 kcal. mole⁻¹ by J. S. Oordon, Astroystema International, Livingston, New Jersey, private communication, January 10, 1963. ΔH_f^o 298.15 was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Oordon, loc. cit. r_e was calculated from the relationship r_e = (16.858778/μB_e)^{1/2} Å.

T, °K	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(H° - H° ₂₉₈)/T	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100	6.892	31.251	31.251	0.000	0.000	0.000	0.000	0.000
200	6.892	31.250	31.250	0.000	0.000	0.000	0.000	0.000
298	6.892	31.250	31.250	0.000	0.000	0.000	0.000	0.000
300	6.894	31.251	31.251	0.013	0.000	0.000	0.000	0.000
400	6.895	31.247	31.247	0.007	0.000	0.000	0.000	0.000
500	6.893	31.246	31.246	0.000	0.000	0.000	0.000	0.000
600	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
700	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
800	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
900	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
1000	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
1100	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
1200	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
1300	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
1400	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
1500	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
1600	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
1700	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
1800	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
1900	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
2000	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
2100	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
2200	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
2300	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
2400	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
2500	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
2600	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
2700	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
2800	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
2900	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
3000	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
3100	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
3200	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
3300	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
3400	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
3500	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
3600	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
3700	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
3800	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
3900	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
4000	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
4100	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
4200	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
4300	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
4400	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
4500	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
4600	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
4700	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
4800	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
4900	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
5000	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
5100	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
5200	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
5300	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
5400	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
5500	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
5600	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
5700	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
5800	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
5900	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000
6000	6.894	31.246	31.246	0.000	0.000	0.000	0.000	0.000

March 31, 1961

$D_0^0 = 105.286 \pm 0.15$ kcal. mole⁻¹
 $\Delta H_f^0 = 299.15 = 0$
 $S_0^0 = 31.21 \pm 0.01$ cal. deg⁻¹ mole⁻¹
 Ground State Configuration $1 \sum_g^+$

$\omega_e = 4405.3$ cm⁻¹
 $\omega_e x_e = 125.325$ cm⁻¹
 $D_e = 0.04644$ cm⁻¹
 $\alpha_e = 0.7417$ Å⁻¹
 $r_e = 0.7417$ Å
 $\phi = 2$

Heat Capacities and Entropy

H. W. Woolley, R. B. Scott and P. G. Brickwedde, J. Research Nat. Bur. Standards 41, 379 (1946), calculated the thermodynamic functions by a method of direct summation for normal H₂ (75% ortho and 25% para) using spectroscopic constants derived from an analysis of U. V. band spectra. These constants are more preferable for use in a summation method than those obtained by G. Herzberg, Can. J. Res. A29, 144 (1950) from the measured quadrupole transitions in the ground state which accurately describe the lower vibrational levels only. In any case the difference in the functions resulting from the two sets of data are less than 0.3%.

Since the entropies of Woolley et al. contain a contribution from nuclear spin, a correction of -Rln4 was applied. However, the entropy due to the mixing of ortho and para hydrogen which is a consequence of nuclear spin is included in the total entropy since this results in correct equilibrium constants based upon third law calculations. Differences in the values of R and C_p were found to have a negligible effect upon the functions.

Similar calculations with a different method of estimating the higher rotational levels by H. L. Johnston, L. G. Savedorff, and J. Belzer, Technical Report No. 2, Project R.P-316, Ohio State Univ. (1949), result in functions that are 0.5% lower above 5000°K.

For details concerning the dissociation energy see the monatomic hydrogen sheet.



MOL. WT. = 112.21874

Potassium Hydroxide, Dimeric ($\text{K}_2\text{O}_2\text{H}_2$)
(Ideal Gas) Mol. Wt. = 112.21874

POTASSIUM HYDROXIDE, DIMERIC ($\text{K}_2\text{O}_2\text{H}_2$) (IDEAL GAS)

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	13.000	0.000	INFINITE	INFINITE	4.415	-154.317	-154.317	INFINITE
100	17.684	40.000	80.082	1.827	-156.952	-150.679	-150.679	164.656
200	19.465	78.366	80.000	0.000	-157.387	-147.620	-147.620	108.208
300	19.496	78.487	80.336	0.036	-157.403	-147.559	-147.559	107.497
400	21.073	84.315	79.150	2.066	-159.406	-143.932	-143.932	78.641
500	22.452	89.170	80.682	4.244	-160.144	-139.975	-139.975	61.183
600	23.578	93.366	82.454	6.548	-160.747	-135.881	-135.881	49.495
700	24.488	97.072	84.283	8.952	-161.255	-131.695	-131.695	41.117
800	25.239	100.392	86.092	11.440	-161.695	-127.444	-127.444	34.816
900	25.879	103.403	87.851	13.997	-162.088	-123.137	-123.137	29.902
1000	26.455	106.159	89.546	16.613	-162.459	-118.750	-118.750	25.962
1100	26.925	108.702	91.173	19.281	-162.800	-112.358	-112.358	22.323
1200	27.362	111.063	92.733	21.996	-163.110	-104.336	-104.336	19.002
1300	27.751	113.269	94.222	24.752	-163.390	-96.333	-96.333	16.195
1400	28.100	115.339	95.664	27.545	-163.640	-88.338	-88.338	13.790
1500	28.412	117.288	97.041	30.371	-163.869	-80.356	-80.356	11.708
1600	28.692	119.131	98.365	33.226	-164.068	-72.391	-72.391	9.888
1700	28.943	120.878	99.638	36.108	-164.238	-64.439	-64.439	8.284
1800	29.168	122.539	100.865	39.014	-164.380	-56.499	-56.499	6.860
1900	29.370	124.122	102.047	41.941	-164.496	-48.573	-48.573	5.587
2000	29.552	125.633	103.189	44.887	-164.588	-40.656	-40.656	4.443
2100	29.716	127.079	104.293	47.851	-164.659	-32.751	-32.751	3.408
2200	29.864	128.464	105.360	50.830	-164.708	-24.856	-24.856	2.469
2300	29.998	129.795	106.394	53.823	-164.736	-16.976	-16.976	1.613
2400	30.119	131.074	107.396	56.829	-164.745	-9.099	-9.099	0.829
2500	30.230	132.306	108.367	59.847	-164.748	-1.241	-1.241	0.108
2600	30.330	133.494	109.311	62.875	-164.748	6.622	6.622	0.557
2700	30.422	134.640	110.228	65.912	-164.748	14.467	14.467	1.171
2800	30.505	135.748	111.120	68.959	-164.748	22.308	22.308	1.741
2900	30.582	136.820	111.988	72.013	-164.748	30.151	30.151	2.272
3000	30.652	137.858	112.833	75.075	-164.748	37.978	37.978	2.762
3100	30.717	138.864	113.656	78.143	-164.748	45.808	45.808	3.229
3200	30.776	139.840	114.459	81.218	-164.748	53.634	53.634	3.663
3300	30.831	140.788	115.243	84.298	-164.748	61.451	61.451	4.070
3400	30.881	141.709	116.008	87.384	-164.748	69.269	69.269	4.453
3500	30.928	142.605	116.745	90.474	-164.748	77.088	77.088	4.814
3600	30.972	143.477	117.485	93.569	-164.748	84.912	84.912	5.155
3700	31.012	144.326	118.199	96.669	-164.748	92.731	92.731	5.477
3800	31.050	145.154	118.898	99.772	-164.748	100.553	100.553	5.783
3900	31.085	145.961	119.581	102.879	-164.748	108.377	108.377	6.073
4000	31.117	146.748	120.251	105.989	-164.748	116.202	116.202	6.350
4100	31.148	147.517	120.906	109.102	-164.748	124.049	124.049	6.612
4200	31.176	148.268	121.549	112.218	-164.748	131.894	131.894	6.863
4300	31.203	149.002	122.179	115.337	-164.748	139.749	139.749	7.103
4400	31.228	149.719	122.797	118.459	-164.748	147.610	147.610	7.332
4500	31.252	150.421	123.403	121.583	-164.748	155.489	155.489	7.552
4600	31.274	151.108	124.008	124.709	-164.748	163.380	163.380	7.762
4700	31.295	151.781	124.582	127.838	-164.748	171.284	171.284	7.960
4800	31.314	152.440	125.155	130.968	-164.748	179.208	179.208	8.160
4900	31.333	153.086	125.719	134.094	-164.748	187.142	187.142	8.347
5000	31.350	153.719	126.272	137.234	-164.748	195.095	195.095	8.528
5100	31.367	154.340	126.817	140.370	-164.748	203.050	203.050	8.703
5200	31.382	154.950	127.352	143.508	-164.748	211.084	211.084	8.872
5300	31.397	155.547	127.878	146.647	-164.748	219.126	219.126	9.036
5400	31.411	156.134	128.396	149.787	-164.748	227.175	227.175	9.194
5500	31.424	156.711	128.906	152.929	-164.748	235.264	235.264	9.349
5600	31.437	157.277	129.407	156.072	-164.748	243.385	243.385	9.499
5700	31.449	157.834	129.901	159.216	-164.748	251.536	251.536	9.644
5800	31.460	158.381	130.387	162.362	-164.748	259.727	259.727	9.787
5900	31.471	158.919	130.866	165.508	-164.748	267.957	267.957	9.926
6000	31.482	159.448	131.338	168.656	-164.748	276.226	276.226	10.062

June 30, 1962; Mar. 31, 1966

Point Group C_{2h}
 $S^{\circ}_{298.15} = [78.4] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies	ω , cm. ⁻¹	ω , cm. ⁻¹
$\Delta H^{\circ}_f 0 = -154.3 \pm 5 \text{ kcal. mole}^{-1}$	[273](1)	[3700](1)
$\Delta H^{\circ}_f 298.15 = -157.4 \pm 5 \text{ kcal. mole}^{-1}$	[150](1)	[3700](1)
	[235](1)	[1250](1)
	[150](1)	[1250](1)
	[255](1)	[1250](1)
	[250](1)	[1250](1)

Bond Distance: K-O = $[2.43] \text{ \AA}$ O-H = $[0.96] \text{ \AA}$
 Bond Angle: K-O-K = $[90^{\circ}]$ K-O-H = $[110^{\circ}]$
 Products of the Moments of Inertia: $I^{\text{H}_2\text{O}}_{\text{B}} = [3.7587] \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$
 $\sigma = 2$

Heat of Formation.
 See KOH(g) table for details.

Heat Capacity and Entropy.

S. H. Bauer, R. H. Diner and R. F. Porter, J. Chem. Phys. **29**, 991 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. **31**, 830 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances $0.2 \text{ \AA}$ larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. **33**, 533 (1960), have also postulated a model for $\text{Li}_2(\text{OH})_2(\text{g})$ which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the bond angle O-Li-O = 100° . The last one was adopted for the molecular configuration of $\text{K}_2(\text{OH})_2$, but the bond angle O-K-O was modified to 90° (i.e. a square planar configuration for potassium and oxygen atoms). The bond angle K-O-H in $\text{K}_2(\text{OH})_2(\text{g})$ was assumed to be 110° . The bond distance K-O in $\text{K}_2(\text{OH})_2(\text{g})$ was estimated 10% longer than that in KOH(g). The bond distance O-H was estimated to be the same in $\text{H}_2\text{O}(\text{g})$. The three principal moments of inertia are $I_A = [17.5202] \times 10^{-39}$, $I_B = [38.5534] \times 10^{-39}$ and $I_C = [55.6452] \times 10^{-39} \text{ g. cm.}^2$

The first six selected vibrational frequencies were taken to be equal to those for $\text{K}_2\text{P}_2(\text{g})$ (see $\text{K}_2\text{P}_2(\text{g})$ table), and the rest were O-H stretching and bending frequencies which have been suggested by Berkowitz et al., loc. cit.



Lithium Hydroxide, Dimeric (Li₂O₂H₂)
(Ideal Gas) Mol. Wt. = 47.89274

LITHIUM HYDROXIDE, DIMERIC (Li₂O₂H₂) (IDEAL GAS) MOL. WT. = 47.89274

T, °K	C _p	cal. mole ⁻¹ deg ⁻¹	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	∞	∞	∞	∞	∞	∞	∞	∞
100	9.116	50.762	77.218	-2.646	-178.587	-178.587	-178.587	INFINITE
200	12.682	64.563	100.430	-2.646	-178.587	-178.587	-178.587	988.173
298	16.882	64.563	129.631	-2.646	-178.587	-178.587	-178.587	126.534
300	16.935	64.668	130.000	-2.646	-178.587	-178.587	-178.587	125.715
400	19.420	68.895	155.259	-1.854	-182.274	-169.477	-169.477	92.598
500	21.319	74.443	166.651	-3.896	-184.498	-166.041	-166.041	72.576
600	22.761	78.463	169.291	6.103	-185.172	-162.283	-162.283	59.111
700	23.873	82.059	70.006	8.437	-185.718	-158.424	-158.424	49.462
800	24.762	85.307	71.719	10.870	-186.173	-154.495	-154.495	42.206
900	25.497	88.267	73.395	13.384	-186.567	-150.510	-150.510	36.549
1000	26.123	90.986	75.020	15.966	-186.910	-146.484	-146.484	32.014
1100	26.666	93.402	76.588	18.606	-187.211	-142.426	-142.426	28.298
1200	27.143	95.843	78.096	21.297	-187.478	-138.344	-138.344	25.196
1300	27.565	98.033	79.546	24.033	-187.715	-134.241	-134.241	22.568
1400	27.939	100.090	80.941	26.809	-187.927	-130.119	-130.119	20.312
1500	28.271	102.029	82.283	29.619	-188.120	-125.982	-125.982	18.356
1600	28.568	103.863	83.575	32.462	-188.294	-121.834	-121.834	16.642
1700	28.833	105.603	84.820	35.332	-188.447	-117.682	-117.682	14.787
1800	29.069	107.258	86.021	38.227	-188.582	-113.528	-113.528	12.940
1900	29.282	108.835	87.180	41.145	-188.698	-109.372	-109.372	11.290
2000	29.472	110.342	88.301	44.083	-188.797	-105.215	-105.215	9.807
2100	29.644	111.785	89.385	47.039	-188.878	-101.058	-101.058	8.466
2200	29.798	113.167	90.435	50.011	-188.942	-96.901	-96.901	7.247
2300	29.938	114.495	91.452	52.998	-188.991	-92.744	-92.744	6.136
2400	30.064	115.772	92.439	55.998	-189.026	-88.587	-88.587	5.118
2500	30.178	117.001	93.397	59.010	-189.048	-84.430	-84.430	4.182
2600	30.283	118.187	94.328	62.033	-189.058	-80.273	-80.273	3.319
2700	30.378	119.332	95.233	65.066	-189.058	-76.116	-76.116	2.521
2800	30.464	120.438	96.114	68.109	-189.048	-71.959	-71.959	1.781
2900	30.544	121.509	96.971	71.159	-189.026	-67.802	-67.802	1.091
3000	30.616	122.545	97.806	74.217	-188.991	-63.645	-63.645	0.449
3100	30.683	123.550	98.621	77.282	-188.942	-59.488	-59.488	-
3200	30.745	124.525	99.415	80.354	-188.878	-55.331	-55.331	-1.152
3300	30.801	125.472	100.190	83.431	-188.797	-51.174	-51.174	-1.715
3400	30.854	126.393	100.947	86.514	-188.698	-47.017	-47.017	-2.243
3500	30.902	127.288	101.687	89.602	-188.582	-42.860	-42.860	-2.740
3600	30.947	128.159	102.411	92.694	-188.447	-38.703	-38.703	-3.209
3700	30.989	129.007	103.118	95.791	-188.294	-34.546	-34.546	-3.651
3800	31.028	129.834	103.810	98.892	-188.120	-30.389	-30.389	-4.061
3900	31.064	130.641	104.488	101.996	-187.927	-26.232	-26.232	-4.446
4000	31.097	131.428	105.152	105.104	-187.715	-22.075	-22.075	-4.817
4100	31.129	132.196	105.802	108.216	-187.478	-17.918	-17.918	-5.177
4200	31.158	132.946	106.439	111.330	-187.211	-13.761	-13.761	-5.531
4300	31.186	133.680	107.064	114.447	-186.910	-9.604	-9.604	-5.881
4400	31.212	134.397	107.677	117.567	-186.567	-5.447	-5.447	-6.231
4500	31.236	135.099	108.279	120.690	-186.173	-1.290	-1.290	-6.581
4600	31.259	135.786	108.869	123.814	-185.718	2.867	2.867	-6.931
4700	31.280	136.458	109.449	126.941	-185.172	6.999	6.999	-7.281
4800	31.300	137.117	110.019	130.070	-184.498	11.132	11.132	-7.631
4900	31.319	137.762	110.579	133.201	-183.715	15.265	15.265	-7.981
5000	31.337	138.395	111.129	136.334	-182.826	19.398	19.398	-8.331
5100	31.354	139.016	111.669	139.469	-181.834	23.531	23.531	-8.681
5200	31.370	139.625	112.201	142.605	-180.744	27.664	27.664	-9.031
5300	31.386	140.223	112.724	145.743	-179.558	31.797	31.797	-9.381
5400	31.400	140.810	113.239	148.882	-178.277	35.930	35.930	-9.731
5500	31.414	141.386	113.750	152.023	-176.902	40.063	40.063	-10.081
5600	31.427	141.952	114.254	155.165	-175.433	44.196	44.196	-10.431
5700	31.439	142.508	114.735	158.308	-173.977	48.329	48.329	-10.781
5800	31.451	143.055	115.219	161.453	-172.531	52.462	52.462	-11.131
5900	31.462	143.595	115.695	164.598	-171.094	56.595	56.595	-11.481
6000	31.473	144.122	116.166	167.745	-169.667	60.728	60.728	-11.831

Dec. 31, 1960; Mar. 31, 1966

Point Group C_{2h}
S_{298.15} = [64.6] cal. deg⁻¹ mole⁻¹
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω _v , cm ⁻¹	ω _v , cm ⁻¹	ω _v , cm ⁻¹
[465](1)	[3700](1)	[3700](1)
[305](1)	[3700](1)	[3700](1)
[407](1)	[1250](1)	[1250](1)
[385](1)	[1250](1)	[1250](1)
[640](1)	[1250](1)	[1250](1)
[460](1)	[1250](1)	[1250](1)

Bond Distances: Li-O = [1.76] Å O-H = [0.96] Å

Bond Angle: Li-O-Li = [90]° Li-O-H = [110]°

Product of the Moments of Inertia: I_AI_BI_C = [4.56956] X 10⁻¹¹⁵ g.³ cm.⁶

σ = 2

Heat of Formation.

J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. **35**, 533 (1960), have studied the Li₂O(c)-H₂O(g) equilibrium by the mass-spectrometric method. Using the reported equilibrium constants in the temperature range from 1100° to 1450°K. the heat of reaction Li₂OH₂(g) → 2LiOH(g) at 298° has been calculated by the second law and the third law methods as 63.2 and 63.7 kcal. mole⁻¹, respectively. (The third law drift is 0.5 ± 1.5 e.u.) Combination of the third law value (ΔH_f⁰ 298 = 63.7 kcal. mole⁻¹) with the heat of formation of lithium hydroxide (g) (ΔH_f⁰ 298 = -58.8 kcal. mole⁻¹) gives the heat of formation of dimeric lithium hydroxide (g) (ΔH_f⁰ 298 = -181.4 kcal. mole⁻¹) which has been adopted in the tabulation.

J. B. Berkowitz-Mattuck and A. Buchler, J. Phys. Chem. **67**, 1386 (1963), have also studied the Li₂O(c)-H₂O(g) equilibrium by the transpiration method, and reported two equilibrium constants (K₁₀₉₅° = 0.105 and K₁₁₄₅° = 0.357) for the reaction Li₂O(c) + H₂O(g) → Li₂OH₂(g). Using the third law method, the heat of reaction has been calculated from the equilibrium constants as 12.7 kcal. mole⁻¹ at 298.15°K. The heat of formation of Li₂OH₂(g) can be derived as ΔH_f⁰ 298 = -188.2 ± 3.5 kcal. mole⁻¹ which is different from the adopted value of Berkowitz, Meschi and Chupka, loc. cit. Berkowitz-Mattuck and Buchler attempted to explain the difference by inferring that the solid-gas equilibrium was not properly established in the measurement of Berkowitz, Meschi and Chupka, however, the absence of drift in the third law analysis does not support this conclusion.

Heat Capacity and Entropy.

S. H. Bauer, R. M. Diner and R. P. Porter, J. Chem. Phys. **29**, 991 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. P. Porter, J. Chem. Phys. **31**, 830 (1959), have suggested a square planer model without hydrogen bonding with alkali-oxygen bond distances 0.2 Å larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. **33**, 533 (1960), have also postulated a model for Li₂OH₂(g) which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the bond angle O-Li-O = 100°. The last one was adopted for the molecular configuration of Li₂OH₂(g), but the bond angle O-Li-O was modified to 90° (i.e. a square planar configuration for lithium and oxygen atoms). This bond angle Li-O-H in Li₂OH₂(g) was assumed to be 110°. The bond distance Li-O in Li₂OH₂(g) was estimated 10% longer than that in LiOH(g). The bond distance O-H was estimated to be the same in H₂O(g). The three principal moments of inertia are: I_A = [9.445] X 10⁻³⁹, I_B = [3.789] X 10⁻³⁹ and I_C = [12.803] X 10⁻³⁹ g. cm.²

The first six selected vibrational frequencies were taken to be equal to those for Li₂P₂(g) (see Li₂P₂(g) table) and the rest were O-H stretching and bending frequencies.

H₂Li₂O₂



Magnesium Dihydride (MgH₂)

(Crystal) Mol. Wt. = 26.336

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	0.000	INFINITE	-1.270	-16.250	-	INFINITE
100	3.053	1.520	1.155	-1.163	-17.056	-14.553	31.782
200	6.043	4.630	8.120	-0.698	-17.756	-11.871	12.072
298	8.450	7.431	7.431	0.000	-18.200	-8.781	6.436
300	8.487	7.483	7.431	0.016	-18.208	-8.723	6.354
400	10.350	10.456	7.767	0.060	-18.208	-8.723	5.066
500	12.350	12.456	8.090	0.067	-18.206	-8.706	3.200
600	13.200	14.965	9.405	3.336	-18.906	1.123	0.409
700	14.230	17.080	10.352	4.710	-18.927	4.465	1.394
800	15.080	18.038	11.317	6.177	-18.891	7.804	2.132
900	15.750	18.854	12.217	7.621	-18.851	11.143	2.732
1000	16.250	20.524	13.220	9.321	-20.657	14.653	3.200
1100	16.637	24.109	14.140	10.966	-20.740	18.186	3.613
1200	16.910	25.569	15.032	12.644	-20.623	21.719	3.955
1300	17.151	26.932	15.996	14.347	-20.517	25.283	4.244
1400	17.360	28.411	16.730	16.073	-20.408	28.846	4.484
1500	17.508	29.413	17.536	17.816	-20.309	32.490	4.691
1600	17.620	30.547	18.314	19.573	-49.827	40.605	5.546
1700	17.708	31.618	19.065	21.339	-49.345	46.245	5.945
1800	17.800	32.632	19.761	23.114	-48.864	51.853	6.205
1900	17.868	33.597	20.493	24.899	-48.381	57.448	6.468
2000	18.000	34.518	21.171	26.694	-47.898	62.992	6.688

MAGNESIUM DIHYDRIDE (MgH₂) (CRYSTAL)

MOL. WT. = 26.336

ΔH_f^o 0 = -16.3 ± 2.2 kcal. mole⁻¹
 ΔH_f^o 298.15 = -18.2 ± 2.2 kcal. mole⁻¹
 S_{298.15}^o = 7.43 ± 0.20 cal. deg.⁻¹ mole⁻¹
 T_d = [560]°K.

Heat of Formation.

The heat of hydrolysis of MgH₂(c) was measured by O. C. Sinke and D. R. Stull, Thermal Laboratory, The Dow Chemical Company, private communication, July, 1956. The value of ΔH_f^o 298.15 was calculated to be -19.1 ± 2 kcal. mole⁻¹. From the decomposition pressure measurements for MgH₂(c) reported by P. H. Ellinger, et al., J. Am. Chem. Soc. 77, 2647 (1955) and J. F. Stampfer, Jr., C. E. Holley, Jr. and J. F. Suttle, J. Am. Chem. Soc. 82, 3504 (1960), the values of ΔH_f^o 298.15 for MgH₂(c) were found to be -17.9 ± 1.0 and -17.7 kcal. mole⁻¹, respectively. The value used was the average of these three.

Heat Capacity and Entropy.

The low temperature heat capacities (25-300°K.) was measured by O. C. Sinke and D. L. Hildenbrand, Thermal Laboratory, The Dow Chemical Company, private communication, February 1958. Above 300°K. the C_p values were estimated by comparison with those for MgF₂(c). S_{298.15} was obtained from O. C. Sinke and D. L. Hildenbrand, loc. cit., using S₂₅^o (extrap.) = 0.037 cal. deg.⁻¹ mole⁻¹.

Temperatures of Decomposition.

T_d was estimated from the value of ΔF_f^o in the table.



Magnesium Dihydroxide (Mg(OH)₂)

(Crystal)

GF_W = 58.32674

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^b	ΔG ^c	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	5.167	2.320	27.933	2.561	-216.431	-216.431	1.000
200	13.592	8.670	16.652	1.586	-219.873	-213.300	0.66.166
298	18.437	15.100	15.100	0.000	-220.769	-206.449	225.597
300	18.500	15.214	15.100	-0.38	-221.003	-199.122	145.060
400	21.300	20.939	15.862	2.031	-221.025	-191.420	104.806
500	23.400	25.924	17.387	4.269	-220.859	-184.534	60.660
600	25.300	30.492	18.076	6.506	-220.166	-177.227	41.110
700	27.000	34.644	18.774	8.744	-219.533	-170.21	24.110
800	28.400	38.400	19.474	12.101	-218.900	-163.014	44.534
900	30.200	41.561	20.174	15.041	-218.264	-155.969	37.879
1000	31.900	44.826	20.874	18.141	-220.264	-148.957	32.533

Dec. 31, 1960; Dec. 31, 1966; Mar. 31, 1967

MAGNESIUM DIHYDROXIDE (Mg(OH)₂)

(CRYSTAL)

OPW = 58.32674

ΔH _f ^o = -218.43 ± 0.5 kcal/mol	ΔH _f ^o = -218.43 ± 0.5 kcal/mol
ΔH _f ^o = -218.43 ± 0.5 kcal/mol	ΔH _f ^o = -218.43 ± 0.5 kcal/mol
ΔH _f ^o = -218.43 ± 0.5 kcal/mol	ΔH _f ^o = -218.43 ± 0.5 kcal/mol
ΔH _f ^o = -218.43 ± 0.5 kcal/mol	ΔH _f ^o = -218.43 ± 0.5 kcal/mol
ΔH _f ^o = -218.43 ± 0.5 kcal/mol	ΔH _f ^o = -218.43 ± 0.5 kcal/mol
ΔH _f ^o = -218.43 ± 0.5 kcal/mol	ΔH _f ^o = -218.43 ± 0.5 kcal/mol
ΔH _f ^o = -218.43 ± 0.5 kcal/mol	ΔH _f ^o = -218.43 ± 0.5 kcal/mol
ΔH _f ^o = -218.43 ± 0.5 kcal/mol	ΔH _f ^o = -218.43 ± 0.5 kcal/mol
ΔH _f ^o = -218.43 ± 0.5 kcal/mol	ΔH _f ^o = -218.43 ± 0.5 kcal/mol
ΔH _f ^o = -218.43 ± 0.5 kcal/mol	ΔH _f ^o = -218.43 ± 0.5 kcal/mol

Heat of Formation

The adopted value is an average of -221.10 and -220.85 kcal/mol obtained from ΔH_f^o = 9.08 and 8.84 kcal/mol for the dehydration reaction Mg(OH)₂(c) = MgO(c) + H₂O(l). The two values correspond to naturally occurring brucite and to synthetic Mg(OH)₂ prepared from MgO by hydration at 177°C under a steam pressure of about 9 atm. The enthalpies of reaction are derived from studies of Taylor and Wells on the heats of solution of various samples of Mg(OH)₂ and MgO in aqueous HCl. These studies show that the heat of dehydration is quite dependent on the nature of the MgO sample; e.g., values for synthetic Mg(OH)₂ vary monotonically from 9.79 to 8.84 kcal/mol for MgO ignited at temperatures from 450 to 1425°C, respectively. The authors ascribe this difference primarily to increase in particle size at the higher ignition temperatures. We have adopted the results at 1425°C, since they are reasonably consistent with the high temperature samples on which the JANAF heat of formation for MgO is based. The uncertainty is estimated as ± 0.5 kcal/mol.

Shomate and Huffman have confirmed the heat of solution of MgO (ignited at 1000°C) within about 0.3 kcal. Their value may be combined with the heat of solution for synthetic Mg(OH)₂, determined under similar conditions by Torgeson and Sahana, to obtain ΔH_f^o = 8.85 kcal/mol for the dehydration reaction. At the other extreme, the heat of solution data of Olauque and Archibald lead to ΔH_f^o = 9.74 kcal/mol; however, this value corresponds to MgO ignited at 350°C. The MgO sample was microcrystalline and had significant excess Cp, as suggested by Olauque and Archibald and later confirmed by data of T. H. K. Barron et al., Proc. Roy. Soc. (London) A250, 70 (1959). Olauque and Archibald intentionally used the microcrystalline form which would be similar to the product in their decomposition pressure measurements (190 and 212°C). Thus, it is not surprising that third law analysis of their decomposition pressures yields essentially the same heat of formation as their solution data (see summary below). Decomposition data at higher pressures have been reported by W. S. Pyfe, Am. J. Sci. 256, 729 (1958); D. M. Roy and R. Roy, ibid. 255, 573 (1957); O. C. Kennedy, ibid. 254, 567 (1956); O. M. Zhabrova and B. M. Kadenatzi, J. Gen. Chem. USSR (Eng. Transl.) 23, 1129 (1954); and L. O. Berg and I. S. Rassonskaya, Dokl. Akad. Nauk SSSR 81, 855 (1951). These data do not significantly affect the heat of formation, however, because of uncertainties in the attainment of equilibrium and in reduction to standard state values.

Source	Mg(OH) ₂ Sample	Temp. of MgO Formation, °C	Heat of Dehydration ΔH _f ^o 298.15 (kcal/mol)	ΔH _f ^o 298.15
1. Taylor & Wells (1938)	Brucite	1425	9.08	-221.10
	Synthetic	1425	8.84	-220.86
	Synthetic	1000	9.18	-221.20
	Synthetic	450	9.79	-221.81
2. Torgeson (1948) - Shomate (1943)	Synthetic	1000	8.85	-220.87
3. Olauque & Archibald (1937)	Synthetic*	350	9.74	-221.74
	Kp data	190, 212	20.13**	-221.62

*Prepared by reaction of KOH with MgCl₂(aq) at 210°C, rather than by hydration of MgO.

**For Mg(OH)₂(c) = MgO(c) + H₂O(g) rather than Mg(OH)₂(c) = MgO(c) + H₂O(l).

References

1. K. Taylor and L. S. Wells, J. Res. Natl. Bur. Std. 21, 133 (1938).
2. D. R. Torgeson and Th. G. Sahana, J. Am. Chem. Soc. 70, 2156 (1948); C. H. Shomate and E. H. Huffman, ibid. 65, 1625 (1943).
3. W. F. Olauque and R. C. Archibald, J. Am. Chem. Soc. 59, 561 (1937).

Heat Capacity and Entropy

Low temperature heat capacities are from the data (22-321°K) of Olauque and Archibald, loc. cit., who used a synthetic, microcrystalline sample prepared by reaction of KOH with aqueous MgCl₂ at 210°C. The entropy is derived from the heat capacities using S₂₉₈^o = 0.027 eu. Above 321°K the heat capacities are extrapolated graphically. Enthalpy data (393-667°K) reported by P. N. Lashchenko and D. I. Kompanski, Zh. Prikl. Khim. 9, 628 (1935), were stated to be based on a calorimeter temperature close to room temperature. Within this uncertainty and the experimental scatter of about ± 5%, the enthalpy data are consistent with the selected values.

Temperature of Decomposition

T_d is calculated as the temperature at which ΔG_r^o = 0 for Mg(OH)₂(c) = MgO(c) + H₂O(g).



Magnesium Dihydroxide (Mg(OH)₂)
(Ideal Gas) GFW = 58.32674

T, °K	C _p ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	0.000	INFINITE	-	3.551	-134.556	-134.556	INFINITE
100	10.764	51.319	177.704	2.639	-135.251	-135.251	291.932
200	13.455	59.653	66.758	1.421	-135.894	-135.894	143.992
298	15.403	65.408	45.408	0.000	-136.300	-129.556	94.967
300	15.435	65.503	45.503	0.029	-136.308	-129.515	94.351
400	17.859	74.063	37.258	3.402	-137.026	-124.770	54.537
500	18.067	74.063	37.258	3.402	-137.026	-124.770	54.537
600	14.962	77.439	64.680	5.295	-137.297	-122.294	44.545
700	19.694	80.418	70.148	7.189	-137.536	-119.772	37.394
800	20.320	83.090	71.602	9.191	-137.763	-117.221	32.023
900	20.858	85.316	73.915	11.352	-137.981	-114.550	28.485
1000	21.358	87.740	76.916	13.798	-138.183	-111.750	24.885
1100	21.790	89.796	75.687	15.520	-140.552	-108.992	21.655
1200	22.176	91.709	76.944	17.119	-140.762	-105.113	19.326
1300	22.519	93.498	78.149	18.454	-140.961	-103.217	17.352
1400	22.818	95.116	79.316	19.558	-141.151	-101.303	15.642
1500	23.095	95.742	80.417	20.518	-141.331	-99.369	13.798
1600	23.336	96.261	81.486	21.349	-141.501	-97.429	12.239
1700	23.549	96.682	82.515	22.084	-141.661	-95.489	10.863
1800	23.739	97.034	83.507	22.734	-141.811	-93.549	9.642
1900	23.908	97.331	84.463	23.301	-141.951	-91.609	8.569
2000	24.060	97.582	85.389	23.798	-142.081	-89.669	7.569
2100	24.195	104.729	86.290	24.229	-142.201	-87.729	6.683
2200	24.317	105.858	87.145	24.601	-142.311	-85.789	5.877
2300	24.426	106.941	87.982	24.916	-142.411	-83.849	5.143
2400	24.523	107.983	88.819	25.179	-142.501	-81.909	4.470
2500	24.614	108.988	89.582	25.390	-142.591	-79.969	3.853
2600	24.698	109.953	90.347	25.559	-142.671	-78.029	3.282
2700	24.768	110.886	91.090	25.692	-142.751	-76.089	2.755
2800	24.834	111.788	91.813	25.799	-142.821	-74.149	2.266
2900	24.895	112.660	92.517	25.885	-142.891	-72.209	1.831
3000	24.951	113.505	93.203	25.951	-142.961	-70.269	1.437
3100	25.002	114.324	93.871	26.000	-143.021	-68.329	1.080
3200	25.049	115.119	94.523	26.038	-143.071	-66.389	0.761
3300	25.092	115.890	95.159	26.068	-143.121	-64.449	0.477
3400	25.131	116.641	95.779	26.090	-143.161	-62.509	0.230
3500	25.168	117.369	96.386	26.108	-143.191	-60.569	0.020
3600	25.202	118.079	96.979	26.122	-143.211	-58.629	-0.147
3700	25.234	118.770	97.558	26.132	-143.231	-56.689	-0.314
3800	25.263	119.443	98.125	26.140	-143.251	-54.749	-0.481
3900	25.290	120.098	98.682	26.146	-143.261	-52.809	-0.648
4000	25.315	120.740	99.224	26.150	-143.271	-50.869	-0.815
4100	25.339	121.365	99.756	26.152	-143.281	-48.929	-0.982
4200	25.361	121.976	100.278	26.153	-143.291	-46.989	-1.149
4300	25.382	122.573	100.790	26.154	-143.301	-45.049	-1.316
4400	25.401	123.158	101.292	26.155	-143.311	-43.109	-1.483
4500	25.419	123.728	101.784	26.156	-143.321	-41.169	-1.650
4600	25.436	124.287	102.267	26.157	-143.331	-39.229	-1.817
4700	25.452	124.834	102.741	26.158	-143.341	-37.289	-1.984
4800	25.467	125.370	103.207	26.159	-143.351	-35.349	-2.151
4900	25.481	125.891	103.663	26.160	-143.361	-33.409	-2.318
5000	25.495	126.410	104.115	26.161	-143.371	-31.469	-2.485
5100	25.508	126.915	104.557	26.162	-143.381	-29.529	-2.652
5200	25.520	127.411	104.992	26.163	-143.391	-27.589	-2.819
5300	25.531	127.897	105.419	26.164	-143.401	-25.649	-2.986
5400	25.542	127.977	105.836	26.165	-143.411	-23.709	-3.153
5500	25.552	128.043	106.254	26.166	-143.421	-21.769	-3.320
5600	25.562	128.104	106.663	26.167	-143.431	-19.829	-3.487
5700	25.571	128.159	107.063	26.168	-143.441	-17.889	-3.654
5800	25.580	130.201	107.458	26.169	-143.451	-15.949	-3.821
5900	25.589	130.201	107.853	26.170	-143.461	-14.009	-3.988
6000	25.596	131.068	108.230	26.171	-143.471	-12.069	-4.155

June 30, 1967



MAGNESIUM DIHYDROXIDE [Mg(OH)₂]

(IDEAL GAS)

GFW = 58.32674

Point Group [C_{2h}]

ΔH_f^o = [-134.6 ± 3] kcal/mol

S_{298.15} = [65.4] gibbs/mol

ΔH_f^o = [-135.3 ± 3] kcal/mol

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
[3200](1)	[600](1)	[1400](1)
[1200](1)	[240](1)	[360](1)
[700](1)	[3300](1)	[100](1)

Bond Distances: Mg-O = [1.80] Å

O-H = [1.07] Å

Bond Angles: Mg-O-H = [105°]

O-Mg-O = [180°]

Product of the Moments of Inertia: I_AI_BI_C = [95.6929] x 10⁻¹¹⁷ g cm

σ = [2]

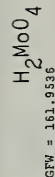
Heat of Formation

Vapor densities of magnesium-bearing species over magnesium oxide were determined, using the transpiration method, by C. A. Alexander, J. S. Ogden and A. Levy, J. Chem. Phys. **32**, 3057 (1963). The MgO reacted with water vapor present in the carrier gas to form a gaseous product, presumably Mg(OH)₂. The authors eliminated MgOH and other species requiring the formation of gaseous oxygen as a likely product by holding constant the partial pressure of water but varying the ratio of oxygen and argon in the carrier gas. Experiments with different partial pressures of water indicated that each mole of water produced an equivalent number of moles of product in the vapor. This eliminates [Mg(OH)₂]₂ as a possible product, but not, for example, (MgO)₂H₂O. Species of the latter type are quite unlikely with magnesium, so the reaction is considered to be MgO(c) + H₂O(g) = Mg(OH)₂(g). Equilibrium data (1853-2020°K) given graphically by Alexander et al. yield ΔH_f^o = 67.6 ± 1.9 kcal/mol by second law analysis and ΔH_f^o = 65.2 kcal/mol with a drift of -1.5 ± 1 eu by third law analysis.

Heat Capacity and Entropy

The infrared spectra of Mg(OH)₂(c) were observed in the region 365-3700 cm⁻¹ by C. Cabannes-Ott, Ann. Chim. (Paris) **5**, 903-60 (1960). The vibrational frequencies of the gas are estimated by comparison with those for Mg(OH)₂(c), H₂O(g), H₂O₂(g), MgO(g) and MgF₂(g), and are adjusted to give reasonable agreement between the second and third law heats of reaction. The bond distances are estimated by comparison with those of MgF₂(g), MgO(g) and H₂O(g). The O-Mg-O angle is assumed to be 180°, while the Mg-O-H angle is assumed to be the same as that in H₂O(g). The three principal moments of inertia are I_A = 2.713 x 10⁻⁴⁰, I_B = 18.6455 x 10⁻³⁹ and I_C = 18.9168 x 10⁻³⁹ g cm².





(IDEAL GAS)

MOLYBDIC ACID (H_2MoO_4)

Point Group $\{C_{2v}\}$

$S_{298.15}^\circ = [89.97 \pm 2.0] \text{ gibbs/mol}$

Ground State Quantum Weight = [1]

$\Delta H_f^\circ = -201.6 \pm 1.0 \text{ kcal/mol}$

$\Delta H_f^\circ_{298.15} = -203.4 \pm 1.0 \text{ kcal/mol}$

Molybdic Acid
(Ideal Gas)

GFW = 161.9535

T, °K	Cp°	gibbs/mol S°	-(Cp°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔCp°	Lag Kp
0	.000	INFINITE	INFINITE	5.326	-201.436	-201.436	INFINITE
100	16.000	42.750	104.590	4.158	-202.582	-202.582	432.637
200	24.560	77.750	184.160	2.816	-203.400	-203.400	117.932
298	28.893	84.870	215.581	.000	-203.400	-186.170	
300	28.951	85.124	84.971	.046	-203.404	-186.076	137.013
400	27.562	92.684	85.983	2.680	-182.950	99.959	77.727
500	26.440	99.050	87.977	5.537	-203.396	-177.625	
600	30.781	104.342	90.291	8.551	-203.223	-172.726	62.915
700	31.769	109.367	92.678	11.682	-202.993	-167.660	52.346
800	32.578	113.665	95.038	14.902	-202.727	-162.633	44.929
900	33.216	117.340	97.326	18.192	-202.435	-157.636	38.279
1000	33.743	121.066	99.527	21.541	-202.124	-152.675	33.367
1100	34.168	124.305	101.634	24.936	-201.805	-147.786	29.350
1200	34.566	127.297	103.650	28.377	-201.482	-142.916	26.016
1300	34.892	130.077	105.577	31.850	-201.168	-137.972	23.195
1400	35.173	132.673	107.421	35.353	-200.865	-133.123	20.781
1500	35.418	135.108	109.186	38.893	-200.580	-128.292	18.692
1600	35.633	137.401	110.879	42.436	-200.317	-123.493	16.867
1700	35.821	139.567	112.503	46.000	-200.074	-118.697	15.258
1800	35.987	141.619	115.064	49.599	-199.862	-113.907	13.830
1900	36.133	143.569	115.566	53.206	-199.676	-109.136	12.553
2000	36.264	145.426	117.013	56.826	-199.522	-104.378	11.406
2100	36.380	147.198	118.409	60.458	-199.400	-99.623	10.366
2200	36.483	148.893	119.756	64.101	-199.317	-94.874	9.425
2300	36.576	150.517	121.058	67.754	-199.270	-90.129	8.564
2400	36.660	152.073	122.318	71.416	-199.269	-85.377	7.775
2500	36.735	153.575	123.539	75.086	-199.329	-80.640	7.050
2600	36.803	155.031	124.722	78.763	-199.453	-75.904	6.379
2700	36.865	156.405	125.870	82.446	-199.657	-71.130	5.758
2800	36.921	157.747	126.984	86.136	-199.947	-66.365	5.180
2900	36.972	159.044	128.068	89.830	-200.327	-61.564	4.640
3000	37.019	160.298	129.121	93.530	-200.704	-56.752	4.120
3100	37.062	161.512	130.147	97.234	-201.085	-51.933	3.633
3200	37.101	162.690	131.145	100.942	-201.465	-47.115	3.177
3300	37.137	163.832	132.119	104.654	-201.845	-42.300	2.746
3400	37.171	164.941	133.068	108.370	-202.225	-37.486	2.344
3500	37.201	166.019	133.994	112.098	-202.602	-32.672	1.963
3600	37.230	167.068	134.898	115.810	-202.979	-27.859	1.602
3700	37.256	168.088	135.781	119.534	-203.354	-23.049	1.261
3800	37.281	169.082	136.645	123.261	-203.729	-18.240	.937
3900	37.303	170.050	137.489	126.990	-204.103	-13.431	.631
4000	37.324	170.995	138.315	130.721	-204.473	-8.620	.339
4100	37.344	171.917	139.123	134.455	-204.845	-3.810	.061
4200	37.363	172.817	139.915	138.190	-205.215	1.023	.204
4300	37.380	173.697	140.690	141.927	-205.582	5.815	.457
4400	37.396	174.556	141.450	145.667	-205.945	10.604	.699
4500	37.411	175.397	142.195	149.407	-206.302	15.393	.930
4600	37.425	176.219	142.926	153.148	-206.652	20.182	1.151
4700	37.439	177.024	143.643	156.890	-206.998	24.970	1.363
4800	37.451	177.812	144.347	160.636	-207.340	29.758	1.567
4900	37.463	178.585	145.037	164.387	-207.677	34.546	1.762
5000	37.474	179.342	145.716	168.139	-208.009	39.334	1.948
5100	37.485	180.084	146.383	171.892	-208.332	44.122	2.125
5200	37.495	180.812	147.038	175.646	-208.650	48.910	2.294
5300	37.504	181.526	147.682	179.396	-208.962	53.698	2.455
5400	37.513	182.227	148.315	183.147	-209.269	58.486	2.609
5500	37.522	182.916	148.938	186.896	-209.572	63.274	2.758
5600	37.530	183.592	149.551	190.631	-209.872	68.062	2.902
5700	37.538	184.256	150.154	194.384	-210.168	72.850	3.040
5800	37.545	184.909	150.747	198.139	-210.459	77.638	3.172
5900	37.552	185.551	151.332	201.893	-210.745	82.426	3.300
6000	37.558	186.182	151.907	205.644	-211.026	87.214	3.424

June 30, 1970

Vibrational Frequencies and Degeneracies

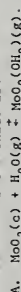
ω_1 , cm ⁻¹	ω_2 , cm ⁻¹	ω_3 , cm ⁻¹
[2000] (1)	[100] (1)	[800] (1)
[1900] (1)	[150] (1)	[200] (1)
[1000] (1)	[100] (1)	[950] (1)
[800] (1)	[360] (1)	[200] (1)
[700] (1)	[600] (1)	[250] (1)

Bond Distance: Mo-O = [1.83] Å O-H = [0.958] Å
 Bond Angle: O-Mo-O = [109.5°] H-O-Mo = [104.5°]
 HO-Mo-OH plane perpendicular to O-H-Mo plane $\sigma = [2]$

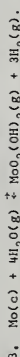
Product of the Moments of Inertia: $I_A I_B I_C = [1.5399 \times 10^{-113}] \text{ g cm}^6$

Heat of Formation

The enhanced volatility of metallic molybdenum and molybdenum trioxide in the presence of water vapor at high temperatures has been investigated by several workers (1, 2, 3) using transpiration techniques. Glemser and Haeseler (1) and Buitten (2) have shown that the major volatilization reaction of the oxide is:



For the reaction of metallic molybdenum with water vapor, Belton and Jordan (3) reported the existence of $\text{MoO}_3(\text{OH})_2(\text{g})$ according to the equilibrium:



Second and third law analyses of these equilibrium data are summarized below.

Investigator	Reaction	Range, °K	No. of Points	ΔH_{298}° (kcal/mol)	Drift	$\Delta H_f^\circ(\text{MoO}_3(\text{OH})_2)$ kcal/mol
Glemser and Haeseler (1)	A	873-983	Equation	38.2	31.9±0.3	-204.0 ± 0.5
Buitten (2)	A	673-773	Equation	30.0	32.2±0.3	-203.7 ± 0.5
Belton and Jordan (3)	B	1473-1773	Equation	30.1	28.6±0.1	-202.6 ± 0.3

* Third law values

The adopted value, $\Delta H_f^\circ(\text{MoO}_3(\text{OH})_2, \text{g}) = -203.4 \pm 1.0 \text{ kcal/mol}$, is an average of these three results.

Heat Capacity and Entropy

The assumed tetrahedral structure for $\text{MoO}_3(\text{OH})_2$ is from Jordan (4). The O-H bond length and H-O-Mo bond angle are assumed to be the same as for $\text{H}_2\text{O}(\text{g})$. The Mo-O bond length is from the compilation of Sutton (5) and assumed to be the same as for Ag_2MoO_4 . Individual moments of inertia are $I_A = 23.782 \times 10^{-39}$, $I_B = 25.415 \times 10^{-39}$, and $I_C = 25.478 \times 10^{-39} \text{ g cm}^2$.

The vibrational frequencies are estimated by comparison with those for $\text{H}_2\text{SO}_4(\text{g})$ (6, 7) and are adjusted to give $S^\circ(\text{MoO}_3(\text{OH})_2, \text{g}) = 137.4 \text{ gibbs/mol}$ at 1600°K. This entropy value is derived from a second law analysis of the equilibrium data for reaction B reported by Belton and Jordan (3).

References

1. V. O. Glemser and R. V. Haeseler, Z. Anorg. Allgem. Chem., **316**, 168 (1962).
2. J. Buitten, J. Catalysis, **10**, 188 (1968).
3. G. R. Belton and A. S. Jordan, J. Phys. Chem., **69**, 2085 (1965).
4. A. S. Jordan, Ph.D. Thesis, The University of Pennsylvania, 1965.
5. L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958).
6. P. A. Giguere and R. Savits, J. Amer. Chem. Soc., **85**, 287 (1963).
7. S. M. Chekalachal and F. L. Stafford, J. Amer. Chem. Soc., **88**, 723 (1966).



T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	— kcal. mole ⁻¹ —	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	∞	∞	∞	2.373	40.757	40.757	INFINITE
100	7.949	43.000	43.000	1.578	40.450	41.015	41.015	89.635
200	7.954	43.303	43.303	1.783	40.293	41.692	41.692	41.015
298	8.024	46.488	46.488	2.000	40.070	42.337	42.337	31.033
300	8.027	46.538	46.538	2.015	40.065	42.351	42.351	30.851
400	8.270	49.871	49.871	2.266	39.894	43.118	43.118	20.571
500	8.492	50.733	50.733	2.410	39.619	44.002	44.002	18.232
600	8.804	52.308	52.308	2.526	39.427	44.897	44.897	16.353
700	9.142	53.691	53.691	2.623	39.259	45.803	45.803	14.306
800	9.500	54.916	54.916	2.706	39.110	46.716	46.716	12.506
900	9.841	56.072	56.072	2.778	38.988	47.640	47.640	10.916
1000	10.180	57.127	57.127	2.840	38.884	48.573	48.573	9.474
1100	10.501	58.112	58.112	2.893	38.798	49.500	49.500	8.163
1200	10.799	59.039	59.039	2.939	38.729	50.425	50.425	6.974
1300	11.074	60.004	60.004	2.978	38.675	51.348	51.348	5.898
1400	11.316	60.944	60.944	3.012	38.635	52.267	52.267	4.932
1500	11.542	61.853	61.853	3.040	38.591	53.170	53.170	4.074
1600	11.743	62.744	62.744	3.063	38.559	54.071	54.071	3.316
1700	11.923	63.601	63.601	3.082	38.534	54.974	54.974	2.648
1800	12.084	64.428	64.428	3.098	38.517	55.878	55.878	2.062
1900	12.229	65.228	65.228	3.112	38.504	56.783	56.783	1.558
2000	12.359	66.005	66.005	3.124	38.492	57.688	57.688	1.124
2100	12.475	66.758	66.758	3.134	38.489	58.593	58.593	0.758
2200	12.580	67.486	67.486	3.142	38.486	59.498	59.498	0.450
2300	12.675	68.195	68.195	3.148	38.486	60.403	60.403	0.192
2400	12.761	68.881	68.881	3.152	38.486	61.308	61.308	-0.020
2500	12.838	69.548	69.548	3.155	38.486	62.213	62.213	-0.232
2600	12.908	70.195	70.195	3.157	38.486	63.118	63.118	-0.444
2700	12.972	70.823	70.823	3.158	38.486	64.023	64.023	-0.656
2800	13.031	71.435	71.435	3.159	38.486	64.928	64.928	-0.868
2900	13.081	72.032	72.032	3.159	38.486	65.833	65.833	-1.080
3000	13.133	72.615	72.615	3.159	38.486	66.738	66.738	-1.292
3100	13.177	73.185	73.185	3.159	38.486	67.643	67.643	-1.504
3200	13.218	73.742	73.742	3.159	38.486	68.548	68.548	-1.716
3300	13.256	74.286	74.286	3.159	38.486	69.453	69.453	-1.928
3400	13.291	74.818	74.818	3.159	38.486	70.358	70.358	-2.140
3500	13.323	75.338	75.338	3.159	38.486	71.263	71.263	-2.352
3600	13.353	75.847	75.847	3.159	38.486	72.168	72.168	-2.564
3700	13.381	76.345	76.345	3.159	38.486	73.073	73.073	-2.776
3800	13.407	76.832	76.832	3.159	38.486	73.978	73.978	-2.988
3900	13.431	77.308	77.308	3.159	38.486	74.883	74.883	-3.200
4000	13.453	77.773	77.773	3.159	38.486	75.788	75.788	-3.412
4100	13.474	78.228	78.228	3.159	38.486	76.693	76.693	-3.624
4200	13.493	78.673	78.673	3.159	38.486	77.598	77.598	-3.836
4300	13.511	79.108	79.108	3.159	38.486	78.503	78.503	-4.048
4400	13.526	79.533	79.533	3.159	38.486	79.408	79.408	-4.260
4500	13.545	79.948	79.948	3.159	38.486	80.313	80.313	-4.472
4600	13.560	80.353	80.353	3.159	38.486	81.218	81.218	-4.684
4700	13.574	80.748	80.748	3.159	38.486	82.123	82.123	-4.896
4800	13.587	81.133	81.133	3.159	38.486	83.028	83.028	-5.108
4900	13.599	81.508	81.508	3.159	38.486	83.933	83.933	-5.320
5000	13.612	81.873	81.873	3.159	38.486	84.838	84.838	-5.532
5100	13.623	82.228	82.228	3.159	38.486	85.743	85.743	-5.744
5200	13.633	82.573	82.573	3.159	38.486	86.648	86.648	-5.956
5300	13.643	82.908	82.908	3.159	38.486	87.553	87.553	-6.168
5400	13.653	83.233	83.233	3.159	38.486	88.458	88.458	-6.380
5500	13.662	83.548	83.548	3.159	38.486	89.363	89.363	-6.592
5600	13.670	83.853	83.853	3.159	38.486	90.268	90.268	-6.804
5700	13.678	84.148	84.148	3.159	38.486	91.173	91.173	-7.016
5800	13.686	84.433	84.433	3.159	38.486	92.078	92.078	-7.228
5900	13.694	84.708	84.708	3.159	38.486	92.983	92.983	-7.440
6000	13.701	84.973	84.973	3.159	38.486	93.888	93.888	-7.652

Dec. 31, 1960; Dec. 31, 1965

MOL. WT. = 16.02264

(IDEAL GAS)

AMIDOGEN (NH₂)

Point Group C_{2v}

ΔH_f⁰ 0 = 40.8 ± 3 kcal. mole⁻¹

ΔH_f⁰ 298.15 = 40.1 ± 3 kcal. mole⁻¹

S⁰ 298.15 = 46.5 cal. deg⁻¹ mole⁻¹

Ground State Quantum Weight = 2

Vibrotional Frequencies and Degeneracies

ω, cm ⁻¹
3173 (1)
1499 (1)
3220 (1)

Bond Distance: N-H = 1.024 Å

Bond Angle: H-N-H = 103°

Product of the Moments of Inertia: I_AI_BI_C = 8.5 X 10⁻¹²⁰ g.³ cm.⁶

σ = 2

Heat of Formation.

The heat of formation of amidogen at 298.15°K., ΔH_f⁰ (NH₂, g) = 39.8 kcal. mole⁻¹ was obtained from the pyrolysis of N₂H₄ by J. A. Kerr, R. C. Sekhar and A. P. Trotman-Dickenson, J. Chem. Soc. 3217 (1953). They have reinvestigated the rate constants of the thermal decomposition N₂H₄ → 2NH₂ at different temperatures using the same techniques as M. Szwarc, J. Chem. Phys. 17, 505 (1949), and revised the activation energy to 57.1 kcal. mole⁻¹ for the reaction at 874°K. (instead of 60 kcal. mole⁻¹ at 1000°K. reported by Szwarc). The activation energy was assumed to be the same as the dissociation energy of the N-N bond in hydrazine. Using all JANAP auxiliary data, one obtains D₀ (H₂N-NH₂) = 55.4 ± 3 kcal. mole⁻¹ and ΔH_f⁰ 298 (NH₂, g) = 40.1 ± 3 kcal. mole⁻¹.

P. M. Page, Trans. Faraday Soc. 57, 1254 (1961), has measured the electron affinity of NH₂ and has applied the results to calculate the dissociation energy, D₀ (H-NH₂) = 102 ± 3 kcal. mole⁻¹. This value leads to the heat of formation ΔH_f⁰ 298 (NH₂, g) = 40.4 ± 3 kcal. mole⁻¹ which is in good agreement with the value selected. E. R. Lippincott and M. O. Dayhoff, Spectrochim. Acta, 15, 807 (1960) calculated theoretically the dissociation energy D₀ (H₂N-NH₂) = 59 kcal. mole⁻¹ which gives ΔH_f⁰ 298 (NH₂, g) = 41.9 kcal. mole⁻¹.

Heat Capacity and Entropy.

The bond distance and angle were measured from the electronic absorption spectra of NH₂ by K. Dressler and D. A. Ramey, Phil. Trans. Roy. Soc. London Ser. A 251, 553 (1959). The three principal moments of inertia are I_A = 0.1189 X 10⁻³⁹ g. cm.², I_B = 0.2149 X 10⁻³⁹ g. cm.² and I_C = 0.3338 X 10⁻³⁹ g. cm.²

The selected vibrational frequencies were obtained from the infrared spectrum of NH₂ by matrix isolation by D. E. Milligan and M. E. Jacox, J. Chem. Phys. 43, 4487 (1965). K. N. Tanner and R. L. King, Nature 181, 953 (1958) have also determined the vibrational frequencies ω₁ = 3200 cm.⁻¹ and ω₃ = 3280 cm.⁻¹ by flash photolysis and calculated ω₂ = 1060 cm.⁻¹. The symmetric and the enthalpy stretching frequencies are in good agreement. M. Taubol, Spectrochim. Acta 15, 505 (1960), has observed NH₂ bending frequencies, 1572 cm.⁻¹, 1619 cm.⁻¹ and 1623 cm.⁻¹, in HCONH₂(g), C₆H₅NH₂(g) and CH₃NH₂(g), respectively. In light of these observations and the adopted ω₂, Tanner and King's bending frequency seems to be in error.

T, °K.	C _p	S°	(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	Log K _p
0	0.000	0.000	INFINITE	2.416	52.580	INFINITE
100	7.950	50.564	-1.621	51.931	53.846	-117.674
200	8.095	48.889	-1.822	51.424	55.948	-61.134
298	8.737	52.223	-0.000	50.900	58.281	-42.719
300	8.753	52.277	-0.016	50.890	58.326	-42.689
400	9.784	54.932	-0.941	50.424	60.878	-33.260
500	10.877	57.234	-1.975	50.056	63.535	-27.770
600	11.882	59.307	-3.114	49.783	66.259	-24.134
700	12.768	61.067	-4.347	49.586	69.021	-21.548
800	13.584	62.564	-5.674	49.454	71.822	-19.016
900	14.331	63.860	-7.054	49.373	74.607	-16.518
1000	14.830	64.913	-8.507	49.334	77.412	-14.018
1100	15.356	65.770	-10.017	49.330	80.220	-11.538
1200	15.829	66.452	-11.576	49.354	83.029	-9.079
1300	16.252	66.985	-13.176	49.392	85.832	-6.642
1400	16.627	67.402	-14.813	49.407	88.632	-4.225
1500	16.967	67.725	-16.493	49.456	91.432	-1.825
1600	17.261	67.977	-18.219	49.634	94.237	0.544
1700	17.515	68.155	-19.984	49.733	97.041	2.923
1800	17.735	68.275	-21.792	49.850	100.845	5.302
1900	17.903	68.343	-23.646	49.950	104.649	7.681
2000	17.970	68.363	-25.545	50.066	108.453	10.060
2100	18.119	68.481	-27.489	50.184	112.257	12.439
2200	18.247	68.595	-29.478	50.305	116.061	14.818
2300	18.372	68.704	-31.512	50.429	119.865	17.197
2400	18.479	68.826	-33.591	50.553	123.669	19.576
2500	18.575	68.962	-35.715	50.676	127.473	21.955
2600	18.663	69.112	-37.884	50.801	131.277	24.334
2700	18.741	69.275	-39.997	50.925	135.081	26.713
2800	18.814	69.450	-42.064	51.049	138.885	29.092
2900	18.879	69.627	-44.094	51.174	142.689	31.471
3000	18.939	69.803	-46.087	51.296	146.493	33.850
3100	18.993	69.975	-48.044	51.418	150.297	36.229
3200	19.041	70.143	-50.000	51.538	154.101	38.608
3300	19.089	70.307	-51.957	51.656	157.905	40.987
3400	19.132	70.466	-53.914	51.774	161.709	43.366
3500	19.171	70.619	-55.871	51.888	165.513	45.745
3600	19.207	70.767	-57.828	51.999	169.317	48.124
3700	19.239	70.910	-59.785	52.109	173.121	50.503
3800	19.272	71.048	-61.742	52.213	176.925	52.882
3900	19.301	71.181	-63.699	52.322	180.729	55.261
4000	19.327	71.309	-65.656	52.423	184.533	57.640
4100	19.352	71.432	-67.613	52.522	188.337	60.019
4200	19.378	71.550	-69.570	52.617	192.141	62.398
4300	19.398	71.663	-71.527	52.709	195.945	64.777
4400	19.417	71.771	-73.484	52.801	199.749	67.156
4500	19.437	71.875	-75.441	52.887	203.553	69.535
4600	19.455	71.975	-77.398	52.971	207.357	71.914
4700	19.472	72.071	-79.355	53.052	211.161	74.293
4800	19.488	72.163	-81.312	53.129	214.965	76.672
4900	19.503	72.251	-83.269	53.203	218.769	79.051
5000	19.517	72.334	-85.226	53.274	222.573	81.430
5100	19.531	72.413	-87.183	53.342	226.377	83.809
5200	19.545	72.488	-89.140	53.408	230.181	86.188
5300	19.559	72.559	-91.097	53.471	233.985	88.567
5400	19.572	72.626	-93.054	53.527	237.789	90.946
5500	19.577	72.689	-95.011	53.581	241.593	93.325
5600	19.588	72.748	-96.968	53.632	245.397	95.704
5700	19.597	72.803	-98.925	53.680	249.201	98.083
5800	19.607	72.854	-100.882	53.726	253.005	100.462
5900	19.615	72.901	-102.839	53.766	256.809	102.841
6000	19.624	72.944	-104.796	53.804	260.613	105.220

Dec. 31, 1965

Point group C_{2v}
ΔH_f⁰ = 52.6 ± 5 kcal. mole⁻¹
ΔH_f⁰ 298.15 = 50.9 ± 5 kcal. mole⁻¹

S_{298.15} = [52.2] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 1

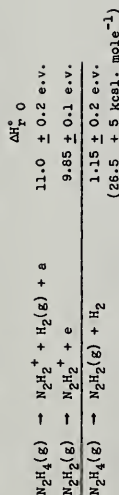
ω, cm. ⁻¹	ω, cm. ⁻¹
[3095](1)	[3205](1)
[1406](1)	[1495](1)
[1360](1)	[910](1)

Vibrational Frequencies and Degeneracies

Bond Distance: N-H = [1.014] Å N-N = [1.23] Å
Bond Angle: H-N-N = [100]°
Product of the Moments of Inertia: I_AI_BI_C = [1.3968] X 10⁻¹¹⁷ g.³ cm.⁶

Heat of Formation.

The standard enthalpy of formation, ΔH_f⁰ 298 (N₂H₂) = 50.9 kcal. mole⁻¹, was calculated from the appearance and ionization potentials of di-imide reported by S. N. Poner and R. L. Hudson, J. Chem. Phys. 29, 442 (1958), using the JANAF ΔH_f⁰ (N₂H₂) = 26.1 kcal. mole⁻¹ in calculation. For example:



From the above heat of formation and that for NH₃ in the JANAF Tables 12-31-65, one can calculate a N-N bond energy of 109.4 ± 5 kcal. mole⁻¹ at 0°K. This is in agreement with the N-N bond in molecules such as N₂P₂.

Heat Capacity and Entropy.

The bond distances and angle were obtained from a quantum-mechanical calculation by W. Wheland and P. S. K. Chen, J. Chem. Phys. 24, 67 (1956). The three principal moments of inertia are I_A = [0.3116] X 10⁻³⁹, I_B = [1.9666] X 10⁻³⁹ and I_C = [2.2802] X 10⁻³⁹ g. cm.²

Since there are 12 valency electrons in N₂H₂, A. D. Walsh, J. Chem. Soc. 2268 (1953), has predicted a bent ground state, existing in either a cis or a trans configuration for diimide. E. J. Blau and B. P. Hochheimer, J. Chem. Phys. 41, 1174 (1964), have measured the infrared spectrum of diimide which was frozen in a cold trap as one of the decomposition products of N₂H₄. The spectrum of the solid N₂H₂ at liquid nitrogen temperature agrees with the predicted non-linear planar structure, and the molecule N₂H₂ appears mainly in cis form. They have also assigned six fundamental vibrational frequencies for cis N₂H₂(s) which have been adopted here for gaseous cis N₂H₂. Blau and Hochheimer also observed two gas phase bands (1277 - 1314 and 3050 - 3190 cm.⁻¹). K. Rosenkrantz and G. C. Pimentel, J. Chem. Phys. 43, 507 (1965), have observed these bands in matrix isolation studies. They assigned ω₁ or ω₂ = 3074 cm.⁻¹ and ω₃ = 1279 cm.⁻¹ which are in satisfactory agreement with the selected frequencies.

Sodium Hydroxide, Dimeric (Na₂O₂H₂)

(Ideal Gas) Mol. Wt. = 79.99434

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	II°-H° ₂₉₈	ΔH° _f	Log K _p
0	0.000	0.000	INFINITE	INFINITE	INFINITE	INFINITE	INFINITE
100	11.929	56.308	86.409	4.135	-151.754	329.711	329.711
200	16.732	66.319	75.110	3.230	-152.961	162.130	162.130
298	18.949	73.442	73.442	0.000	-153.946	106.616	106.616
300	18.985	73.559	73.442	0.035	-154.815	105.916	105.916
400	20.248	84.070	75.714	2.016	-157.677	60.410	60.410
500	22.248	88.236	77.461	6.465	-158.287	48.002	48.002
600	24.381	91.922	79.269	8.857	-159.787	40.653	40.653
700	25.817	95.230	81.061	11.335	-159.203	34.448	34.448
800	26.381	100.681	84.486	16.495	-159.874	28.910	28.910
1000	26.681	103.520	86.103	19.158	-160.168	22.953	22.953
1200	27.324	105.878	87.654	21.869	-160.919	19.732	19.732
1300	27.720	108.081	89.141	24.652	-160.761	16.834	16.834
1400	28.008	110.059	90.599	26.235	-160.561	14.522	14.522
1500	28.288	112.008	91.937	28.088	-160.325	12.429	12.429
1600	28.571	113.937	93.257	30.088	-160.167	10.325	10.325
1700	28.824	115.683	94.526	35.968	-160.968	8.669	8.669
1800	29.151	117.343	95.748	38.972	-160.744	7.199	7.199
1900	29.458	118.866	96.926	42.742	-160.520	5.863	5.863
2000	29.738	120.435	98.064	47.705	-160.304	4.703	4.703
2100	29.704	121.681	99.164	47.705	-160.040	3.636	3.636
2200	29.853	123.266	100.228	50.683	-160.802	2.667	2.667
2300	29.968	124.596	101.259	53.675	-160.561	1.783	1.783
2400	30.062	125.612	102.258	56.680	-160.325	0.973	0.973
2500	30.221	127.108	103.228	59.696	-160.088	0.229	0.229
2600	30.322	128.294	104.169	62.724	-160.854	0.457	0.457
2700	30.414	129.440	105.084	65.761	-160.626	1.091	1.091
2800	30.498	130.547	105.974	68.806	-160.405	1.679	1.679
2900	30.576	131.617	106.840	71.857	-160.187	2.224	2.224
3000	30.546	132.657	107.683	74.921	-160.039	2.737	2.737
3100	30.711	133.663	108.505	77.989	-160.776	3.213	3.213
3200	30.771	134.639	109.306	81.063	-160.584	3.660	3.660
3300	30.826	135.586	110.088	84.143	-160.403	4.079	4.079
3400	30.874	136.506	110.850	87.229	-160.232	4.473	4.473
3500	30.924	137.403	111.598	90.318	-160.075	4.844	4.844
3600	30.968	138.275	112.327	93.413	-160.931	5.195	5.195
3700	31.008	139.124	113.040	96.512	-160.803	5.526	5.526
3800	31.046	139.951	113.737	99.614	-160.690	5.840	5.840
3900	31.084	140.757	114.417	102.717	-160.591	6.137	6.137
4000	31.114	141.546	115.088	105.831	-160.523	6.419	6.419
4100	31.145	142.314	115.743	108.943	-160.472	6.688	6.688
4200	31.173	143.065	116.384	112.059	-160.444	6.943	6.943
4300	31.200	143.799	117.013	115.178	-160.430	7.187	7.187
4400	31.226	144.516	117.626	118.293	-160.426	7.420	7.420
4500	31.249	145.218	118.236	121.423	-160.434	7.642	7.642
4600	31.271	145.906	118.830	124.549	-160.454	7.855	7.855
4700	31.292	146.578	119.413	127.677	-160.474	8.059	8.059
4800	31.312	147.237	119.986	130.808	-160.500	8.255	8.255
4900	31.331	147.884	120.550	133.940	-160.521	8.442	8.442
5000	31.348	148.516	121.102	137.074	-160.538	8.623	8.623
5100	31.365	149.137	121.645	140.209	-160.549	8.796	8.796
5200	31.380	149.746	122.180	143.347	-160.560	8.963	8.963
5300	31.395	150.344	122.706	146.485	-160.568	9.125	9.125
5400	31.409	150.932	123.222	149.623	-160.573	9.280	9.280
5500	31.423	151.508	123.732	152.761	-160.576	9.430	9.430
5600	31.435	152.074	124.273	155.910	-160.578	9.576	9.576
5700	31.447	152.631	124.726	159.054	-160.576	9.716	9.716
5800	31.459	153.178	125.212	162.200	-160.570	9.853	9.853
5900	31.470	153.712	125.692	165.342	-160.562	9.985	9.985
6000	31.480	154.244	126.162	168.493	-160.556	10.114	10.114

Mar. 31, 1988



MOL. WT. = 79.99434

(IDEAL GAS)

Point Group C_{2h}

$$\Delta H_f^\circ = -151.8 \pm 5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -154.8 \pm \text{kcal. mole}^{-1}$$

$$S_{298.15}^\circ = [73.4] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e , cm. ⁻¹	ω_e , cm. ⁻¹
[350](1)	[3700](1)
[209](1)	[3700](1)
[270](1)	[1250](1)
[201](1)	[1250](1)
[294](1)	[1250](1)
[313](1)	[1250](1)

Bond Distance: Ne-O = [2.17] Å O-H = [0.96] Å

Bond Angle: Ne-O-H = [90°] Ne-O-H = [110]°

Products of the Moments of Inertia: $I_A I_B I_C = [8.156754] \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

See NaOH(g) table for details.

Heat Capacity and Entropy.

S. H. Bauer, R. H. Diner and R. P. Porter, J. Chem. Phys. 29, 921 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. P. Porter, J. Chem. Phys. 31, 830 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances 0.2 Å larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meech and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have also postulated a model for Li₂(OH)₂(g) which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the angle O-H-O = 100°. The last one was adopted for the molecular configuration of Na₂(OH)₂, but the bond angle O-H-O in Na₂(OH)₂(g) was modified to 90° (i.e., a square planar configuration for sodium and oxygen atoms). The bond angle Na-O-H in Na₂(OH)₂(g) was assumed to be 110°. The bond distance O-H was estimated to be the same in H₂O(g). The three principal moments of inertia are $I_A = [14.0831] \times 10^{-39}$, $I_B = [18.1878] \times 10^{-39}$ and $I_C = [31.8449] \times 10^{-39} \text{ g. cm.}^2$

The first six selected vibrational frequencies were taken to be equal to those for Na₂F₂(g) (see Na₂F₂(g) table), and the rest were O-H stretching and bending frequencies which have been suggested by Berkowitz et al., loc. cit.



WATER (H₂O)

(IDEAL GAS)

MOL. WT. = 18.016

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	Log K _p
0	.000	INFINITE	-	2.367	- 57.103	INFINITE
100	7.961	36.396	52.202	- 1.581	- 56.557	123.600
200	11.756	52.837	35.737	- 3.793	- 55.763	60.792
298	14.875	65.106	23.106	- 5.198	- 54.568	40.048
300	8.077	45.155	45.106	.015	- 54.617	39.786
400	6.166	47.484	45.422	.825	- 53.519	29.240
500	6.415	49.334	46.026	1.454	- 52.277	22.686
600	6.474	50.891	46.710	2.500	- 50.500	18.633
700	6.964	52.299	47.406	3.390	- 48.710	15.156
800	9.246	53.464	48.089	4.300	- 46.843	13.289
900	9.587	54.570	48.749	5.240	- 44.905	11.498
1000	9.851	55.592	49.382	6.209	- 42.926	10.062
1100	10.152	56.545	49.991	7.210	- 40.904	8.983
1200	10.486	57.441	50.575	8.246	- 38.847	8.177
1300	10.773	58.288	51.136	9.298	- 36.756	7.644
1400	10.987	59.092	51.675	10.384	- 34.634	7.263
1500	11.233	59.859	52.196	11.495	- 32.497	6.925
1600	11.462	60.591	52.698	12.630	- 30.350	6.628
1700	11.676	61.293	53.183	13.787	- 28.202	6.361
1800	11.879	61.965	53.652	14.964	- 26.054	6.123
1900	12.068	62.612	54.107	16.160	- 23.906	5.914
2000	12.244	63.234	54.548	17.373	- 21.758	5.725
2100	12.346	63.834	54.974	18.602	- 19.610	5.556
2200	12.505	64.412	55.392	19.846	- 17.462	5.407
2300	12.634	64.971	55.796	21.103	- 15.314	5.277
2400	12.753	65.511	56.190	22.372	- 13.166	5.158
2500	12.863	66.034	56.573	23.653	- 11.018	5.049
2600	12.965	66.541	56.947	24.945	- 8.870	4.940
2700	13.059	67.032	57.311	26.244	- 6.722	4.841
2800	13.146	67.508	57.667	27.556	- 4.574	4.752
2900	13.228	67.971	58.014	28.875	- 2.426	4.673
3000	13.304	68.421	58.358	30.201	- 2.279	4.594
3100	13.374	68.858	58.698	31.535	- 2.131	4.515
3200	13.439	69.294	59.030	32.873	- 1.983	4.436
3300	13.503	69.698	59.358	34.223	- 1.835	4.357
3400	13.562	70.102	59.639	35.577	- 1.687	4.278
3500	13.617	70.496	59.943	36.936	- 1.539	4.199
3600	13.669	70.881	60.282	38.300	- 1.391	4.120
3700	13.718	71.256	60.536	39.669	- 1.243	4.041
3800	13.764	71.622	60.821	41.043	- 1.095	3.962
3900	13.808	71.980	61.103	42.422	- 0.947	3.883
4000	13.850	72.331	61.379	43.805	- 0.799	3.804
4100	13.890	72.673	61.651	45.191	- 0.651	3.725
4200	13.927	73.008	61.917	46.583	- 0.503	3.646
4300	13.963	73.336	62.179	47.977	- 0.355	3.567
4400	13.997	73.658	62.436	49.375	- 0.207	3.488
4500	14.030	73.973	62.689	50.777	- 0.059	3.409
4600	14.061	74.281	62.938	52.181	0.089	3.330
4700	14.091	74.584	63.182	53.583	0.237	3.251
4800	14.120	74.881	63.423	55.000	0.385	3.172
4900	14.148	75.172	63.660	56.413	0.533	3.093
5000	14.174	75.459	63.893	57.829	0.681	3.014
5100	14.201	75.750	64.122	59.248	0.829	2.935
5200	14.228	76.016	64.366	60.669	0.977	2.856
5300	14.254	76.287	64.571	62.093	1.125	2.777
5400	14.279	76.553	64.791	63.520	1.273	2.698
5500	14.303	76.816	65.007	64.949	1.421	2.619
5600	14.328	77.074	65.220	66.381	1.569	2.540
5700	14.351	77.327	65.430	67.815	1.717	2.461
5800	14.375	77.577	65.637	69.251	1.865	2.382
5900	14.398	77.823	65.842	70.690	2.013	2.303
6000	14.422	78.065	66.044	72.131	2.161	2.224

March 31, 1961

ΔH_f⁰ = -57.103 kcal. mole⁻¹ΔH_f⁰ 298.15 = -57.7979 kcal. mole⁻¹Point Group C_{2v}S_{298.15} = 45.106 cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

(W, cm. ⁻¹)
3657.05 (1)
1594.59 (1)
3755.79 (1)

Bond Length and Angle O-H distance = 0.9584 Å H-O-H angle = 104.45° σ = 2

Product of Moments of Inertia I_AI_BI_C = 5.7658 × 10⁻¹²⁰ g.³ cm.⁶

Heat of Formation

Taken from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952.

Heat Capacity and Entropy

A. S. Friedman and L. Haar, J. Chem. Phys. **22**, 2051 (1954), using the infra-red spectra analysis of W. S. Benedict, H. H. Claassen and J. H. Shaw, J. Research Natl. Bur. Standards **49**, 91 (1952), have calculated the thermodynamic functions for water including the anharmonic corrections. Friedman and Haar in comparing their calculation to that of a direct summation by Glatt, Adams, and Johnston, Ohio State University Res. Foundation Tech. Report No. 316-8 (1953), found that the difference between the two calculations was less than the uncertainty in the direct summation.

C_p values from 100° to 5000°K. are from Friedman and Haar. C_p from 5000° to 6000°K. was extrapolated linearly. Using the tabulated functions of Friedman and Haar C_p, S, and H₀-H₀ at T = 298.15°K. was calculated by the method of Lagrangian curvilinear interpolation, W. J. Taylor, J. Research Natl. Bur. Standards **35**, 151 (1945).

The bond length and angle were obtained from a compilation by L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chem. Soc., Burlington House, London W1, 1958.



Hydrogen Peroxide (H_2O_2)
(Gas) Mol. Wt. = 34.016

INTERIM TABLE

T, °K.	C_p	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	.000	INFINITE	2.594	31.025	31.025	INFINITE
100	0.013	44.558	52.538	1.798	31.682	29.559	64.598
200	0.013	50.316	54.701	.877	32.060	27.174	29.693
298	10.305	55.660	55.660	.000	32.530	25.208	18.877
300	10.330	55.724	55.660	.019	32.537	25.163	18.330
400	11.580	58.872	56.081	1.116	32.844	22.655	12.377
500	12.560	61.585	56.915	2.325	33.083	20.081	8.777
600	13.310	63.975	57.891	3.621	33.225	17.469	6.363
700	13.900	66.019	59.005	5.005	33.282	14.862	4.800
800	14.390	67.900	59.914	6.369	33.340	12.181	3.328
900	14.690	69.607	60.697	7.839	33.516	9.519	2.311
1000	15.026	71.173	61.468	9.325	33.576	6.850	1.497
1100	15.330	72.619	62.762	10.883	33.622	4.173	.829
1200	15.600	73.995	64.460	12.590	33.652	1.489	.429
1300	15.870	75.225	66.483	13.968	33.684	1.186	.199
1400	16.110	76.410	68.293	15.563	33.703	3.870	.604
1500	16.330	77.529	69.672	17.185	33.718	6.558	.955

Hydrogen Peroxide (H_2O_2) (Gas)

Mol. Wt. = 34.016

H_f° 298.15 = -32.53 kcal. mole⁻¹

$S_{298.15}^\circ$ = 55.660 cal. deg.⁻¹ mole⁻¹

Point Group C_2

C_p from P. A. Giguère and I. D. Lin, J. Am. Chem. Soc. 77, 6477 (1955). C_p below 298.15°K. estimated.



Sulfuric Acid (H₂SO₄)
(Liquid)

GFW = 98.07754

T, °K	C _p ^a	g/bb/mole	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log K _p
100								
200								
298	33.200	37.501	37.501	.000	-194.548	-194.548	-166.925	170.495
300	33.290	37.707	37.502	.062	-194.535	-194.535	-166.785	120.016
400	36.700	47.790	36.853	3.575	-194.237	-194.237	-154.912	84.640
500	38.650	56.206	41.506	7.350	-193.561	-193.561	-145.155	63.467
600	40.000	63.380	44.569	11.287	-192.691	-192.691	-135.551	49.172
600	40.830	65.601	45.741	13.260	-191.716	-191.716	-126.082	32.269
600	40.830	65.601	45.741	13.260	-191.716	-191.716	-126.082	32.269
800	41.900	80.015	53.777	23.614	-202.327	-202.327	-107.922	26.088
1000	42.178	84.445	56.626	27.819	-200.935	-200.935	-96.950	21.188
1100	42.307	86.471	59.341	32.044	-199.557	-199.557	-86.620	17.210
1200	42.400	88.551	61.382	36.523	-198.156	-198.156	-76.412	13.749
1300	42.450	90.672	63.422	41.172	-196.735	-196.735	-66.412	10.749
1400	42.500	92.793	65.462	45.882	-195.295	-195.295	-56.426	8.793
1500	42.500	101.634	68.953	48.022	-194.241	-194.241	-46.424	6.765



(LIQUID)

SULFURIC ACID (H₂SO₄)

OFW = 98.07754

$$\Delta H_f^{\circ} 298.15 = -194.548 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 2.56 \text{ kcal/mol}$$

$$\Delta H_v^{\circ} = [13.35] \text{ kcal/mol}$$

Heat of Formation.

The heat of combustion (ΔH_c°) of rhombic sulfur (c) to H₂SO₄(aq), i.e. S(c, rhombic) + 3/2 O₂(g) + H₂O(l) = H₂SO₄(aq), has been determined by many investigators. Based on the reported ΔH_c° data, values of ΔH_f° H₂SO₄(l) are derived using heats of solution and dilution for H₂SO₄(l), taken from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Technical Note 270-1, Natl. Bur. Std., 1965. The results obtained are presented in the table below. The value of ΔH_f° H₂SO₄(l) is adopted as -194.548 ± 0.10 kcal/mol, which is the same as that given by Technical Note 270-1, loc. cit.

Investigator	Product	ΔH_c° , kcal/mol	ΔH_f° , kcal/mol
1. McCullough et al. (1963)	H ₂ SO ₄ (70H ₂ O)	-143.58 ± 0.09	-194.400
2. Scott et al. (1956)	H ₂ SO ₄ (75H ₂ O)	-143.98 ± 0.22	-194.775
3. Good et al. (1960)	H ₂ SO ₄ (115H ₂ O)	-143.85 ± 0.06	-194.521
4. Manason and Sumner (1963)	H ₂ SO ₄ (115H ₂ O)	-143.93 ± 0.07	-194.601

- J. P. McCullough, S. Sumner, H. L. Finke, W. N. Hubbard, J. E. Orozco, R. E. Pennington, J. F. Measerly, W. D. Ood and G. Waddington, J. Am. Chem. Soc. **75**, 5075 (1953).
- D. W. Scott, J. P. McCullough, W. N. Hubbard, J. F. Measerly, I. A. Hoesenlopp, F. R. Frow and G. Waddington, J. Am. Chem. Soc. **78**, 5463 (1956).
- J. D. Good, J. L. Lachina and J. P. McCullough, J. Am. Chem. Soc. **82**, 5589 (1960).
- M. Manason and S. Sumner, Acta Chem. Scand. **17**, 723 (1963).

Heat Capacity and Entropy.

The heat capacities, 283.46 to 300°K, were measured by W. P. Olafue, E. W. Hornung, J. E. Kunzler, and R. R. Rubin, J. Am. Chem. Soc. **82**, 62 (1960). The Cp values above 300°K are obtained from graphical extrapolation. The value of S°₂₉₈ was reported by Olafue, Hornung, Kunzler and Rubin, loc. cit., based on low temperature heat capacity measurements of H₂SO₄(c).

Melting Data.

T_m and ΔH_m° are taken from T. R. Rubin and W. P. Olafue, J. Am. Chem. Soc. **74**, 800 (1952). The value, T_m=283.53°K, has been reported by C. M. Gable, H. F. Betz and S. H. Maron, J. Am. Chem. Soc. **72**, 1445 (1950), as well as J. E. Kunzler and W. P. Olafue, J. Am. Chem. Soc. **74**, 797 (1952). The heat of melting (ΔH_m°) has also been determined by the following investigators:

ΔH_m° kcal/mol	Source
2.35	Pickering, Proc. Roy. Soc. (London) 49 , 11 (1891).
2.25	Hantzsch, Z. Physik. Chem. 61 , 262 (1907).
2.24	Knietsch, quoted by Hantzsch, loc. cit.
2.55	Brönsted, Z. Physik. Chem. 68 , 693 (1910).
2.56	Rubin and Olafue, J. Am. Chem. Soc. 74 , 800 (1952).

Vaporization Data.

T_b is the temperature at which the Gibbs energy change (ΔG_v°) for the reaction H₂SO₄(l) = H₂SO₄(g) approaches zero. The difference between ΔH_f° for H₂SO₄(g) and H₂SO₄(l) at T_b is ΔH_v° . According to O. P. Luchinskii, Zh. Fiz. Khim. **30**, 1207 (1956), the total vapor pressure over H₂SO₄(l) reaches one atmosphere at 553°K with a vapor composition of 76.6 mole percent SO₃, 22.6% H₂SO₄, and 0.8% H₂O. This composition implies that the real liquid phase enhances the vapor decomposition by reducing the partial pressure of water vapor.

Dec. 31, 1960; Dec. 31, 1966



Sulfuric Acid (H₂SO₄)
(Ideal Gas)

GFW = 98.07754

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	INFINITE	-3.652	-173.425	-173.425	INFINITE
100	9.585	54.518	52.913	-2.840	-174.924	-170.138	370.138
200	14.549	52.396	50.748	-1.870	-176.142	-163.306	178.452
298	19.256	51.129	49.519	0.000	-177.000	-158.510	114.945
300	19.343	49.248	49.113	0.036	-177.013	-156.655	114.145
400	22.705	45.327	45.934	2.157	-178.107	-149.795	81.845
500	25.506	40.733	41.563	4.555	-178.775	-142.636	62.346
600	27.410	35.560	37.501	7.235	-179.195	-135.344	43.204
700	28.543	30.037	33.037	10.037	-179.417	-127.926	25.326
800	29.842	24.285	28.285	12.931	-179.462	-120.492	13.309
900	30.469	18.408	23.408	15.837	-179.357	-113.105	37.466
1000	31.425	12.501	18.539	19.162	-179.044	-104.315	22.798
1100	32.648	6.576	13.746	22.458	-178.495	-95.541	18.946
1200	34.052	0.624	8.921	25.523	-177.674	-86.814	15.811
1300	35.572	-5.224	4.079	28.400	-176.610	-78.115	13.137
1400	37.250	-10.943	-0.779	31.057	-175.350	-69.487	10.847
1500	39.031	-16.598	-5.434	33.457	-173.930	-60.859	8.867
1600	40.861	-22.184	-10.020	35.561	-172.300	-52.282	7.139
1700	42.681	-27.700	-14.536	37.350	-170.500	-43.799	5.615
1800	44.431	-33.156	-19.000	38.800	-168.580	-35.455	4.277
1900	46.151	-38.561	-23.414	39.950	-166.500	-27.210	3.100
2000	47.791	-43.826	-27.780	40.850	-164.220	-19.020	2.060
2100	49.381	-48.951	-32.100	41.550	-161.700	-10.840	1.140
2200	50.851	-53.931	-36.370	42.000	-159.000	-2.650	0.320
2300	52.221	-58.761	-40.600	42.250	-156.150	5.540	-0.480
2400	53.511	-63.451	-44.790	42.350	-153.100	13.690	-1.320
2500	54.741	-68.001	-48.940	42.300	-149.800	22.000	-2.210
2600	55.921	-72.411	-53.050	42.100	-146.200	30.450	-3.140
2700	57.051	-76.681	-57.120	41.750	-142.350	39.050	-4.110
2800	58.141	-80.811	-61.150	41.250	-138.300	47.800	-5.120
2900	59.191	-84.801	-65.140	40.600	-134.000	56.700	-6.170
3000	60.201	-88.651	-69.090	39.800	-129.500	65.750	-7.260
3100	61.171	-92.361	-72.990	38.850	-124.800	74.950	-8.390
3200	62.101	-95.931	-76.840	37.750	-119.900	84.300	-9.560
3300	62.991	-99.361	-80.640	36.500	-114.800	93.800	-10.770
3400	63.841	-102.651	-84.390	35.100	-109.500	103.400	-12.020
3500	64.651	-105.801	-88.090	33.550	-104.000	113.100	-13.310
3600	65.421	-108.811	-91.740	31.850	-98.300	122.900	-14.640
3700	66.151	-111.681	-95.340	30.000	-92.400	132.800	-16.010
3800	66.841	-114.411	-98.890	28.000	-86.300	142.800	-17.420
3900	67.491	-116.991	-102.390	25.850	-80.000	152.900	-18.870
4000	68.101	-119.421	-105.840	23.550	-73.500	163.100	-20.360
4100	68.671	-121.711	-109.140	21.100	-66.800	173.400	-21.890
4200	69.201	-123.861	-112.290	18.500	-60.000	183.800	-23.460
4300	69.691	-125.871	-115.290	15.750	-53.100	194.300	-25.070
4400	70.141	-127.741	-118.140	12.850	-46.100	204.900	-26.720
4500	70.551	-129.471	-120.840	9.800	-39.000	215.600	-28.410
4600	70.921	-131.061	-123.390	6.600	-31.800	226.400	-30.140
4700	71.251	-132.511	-125.790	3.250	-24.500	237.300	-31.910
4800	71.541	-133.821	-128.040	-0.250	-17.100	248.300	-33.720
4900	71.791	-135.001	-130.140	-2.800	-9.700	259.400	-35.570
5000	72.001	-136.051	-132.090	-5.300	-2.300	270.600	-37.460
5100	72.171	-136.971	-133.890	-7.800	5.100	281.900	-39.390
5200	72.301	-137.761	-135.540	-10.300	12.400	293.300	-41.360
5300	72.391	-138.421	-137.040	-12.800	19.700	304.800	-43.370
5400	72.441	-138.951	-138.360	-15.300	27.000	316.400	-45.420
5500	72.451	-139.361	-139.510	-17.800	34.300	328.100	-47.510
5600	72.421	-139.641	-140.490	-20.300	41.600	339.900	-49.640
5700	72.351	-139.891	-141.310	-22.800	48.900	351.800	-51.810
5800	72.241	-140.111	-141.970	-25.300	56.200	363.800	-54.020
5900	72.091	-140.301	-142.470	-27.800	63.500	375.900	-56.270
6000	71.901	-140.451	-142.910	-30.300	70.800	388.100	-58.560

Dec. 31, 1966

Sulfuric Acid (H₂SO₄)
(Ideal Gas)

GFW = 98.07754

H₂O, S

Point Group (C_{2v})
S°_{298.15} = (69.1) gibbs/mol
Ground State Quantum Weight = 1
ΔH°₀ = -173.4 ± 2 kcal/mol
ΔH°_{298.15} = -177.0 ± 2 kcal/mol

Vibrational Frequencies and Degeneracies

$\bar{\nu}$, cm ⁻¹	$\bar{\nu}$, cm ⁻¹	$\bar{\nu}$, cm ⁻¹
(4500) (1)	(380) (1)	883 (1)
(400) (1)	(400) (1)	(400) (1)
(380) (1)	(380) (1)	1450 (1)
3610 (1)	3610 (1)	[450] (1)
1159 (1)	1159 (1)	568 (1)

Bond Distance: S-O = (1.42) Å
Bond Angle: O-S-O = (125)°
Product of the Moments of Inertia: I_AI_BI_C = (4.237 x 10⁻¹⁴⁴) g³cm⁶
S-OH = (0.97) Å
HO-S-OH = [100]°
S-O-H = (105)°
O = 2

Heat of Formation

The vapor phase equilibria of the H₂SO₄, H₂O and SO₃ system have been studied by (1) E. Rodenstein and M. Katayama, Z. Elektrochem. 15, 244 (1909), Z. Physik. Chem. 69, 26 (1909); (2) G. P. Luchinskii, Zh. Fiz. Khim. 30, 1207 (1956), and (3) A. V. Suvorov, R. B. Dobrovin and S. M. Katayama, Russ. J. Inorg. Chem. (English Transl.) 10, 710 (1955). The data of Rodenstein and Katayama and of Suvorov et al. were obtained from PVT studies, while those of Luchinskii were based on vapor pressure measurements. A translation of Luchinskii's paper is not yet available, so it is not known whether he obtained the vapor composition experimentally or by calculation. Using the reported equilibrium values for the reaction H₂SO₄(g) = H₂O(g) + SO₃(g), we evaluate the corresponding enthalpy changes by both the second and third law methods. The results are presented in the table below. The value of H°₂₉₈ for H₂SO₄(g) is adopted as -177 ± 2 kcal/mol.

Investigator	Temp., °K	No. of Points	Second Law	Third Law	Drift
1. Rodenstein & Katayama (1909)	586-2-756.2	53	-22.95 ± 0.66	-24.55	-2.3 ± 1.0
2. Luchinskii (1956)	333-2-473.2	8	-24.02 ± 0.22	-24.43	-1.2 ± 0.5
3. Suvorov (1965)	583.0-713.0	40	-27.14 ± 0.45	-24.90	+3.3 ± 0.6

*Calculation based on the third law ΔH°₂₉₈ value.

Heat Capacity and Entropy

The molecular structure and bond angles (O-S-O, HO-S-OH) are estimated by comparison with those for SF₆(g) reported by D. R. Lide, D. E. Mann and R. M. Fristrom, J. Chem. Phys. 26, 734 (1957). The S-O and S-OH bond distances are assumed to be the same as those in H₂SO₄(c), determined by R. Pascard, Compt. Rend. 240, 2162 (1955). The OH distance and S-O-H angle are taken from those for H₂O(g). Electric deflection studies by A. Behler, J. L. Stauffer and K. Klemperer, J. Chem. Phys. 45, 605 (1967), indicate that H₂SO₄(g) is polar, which is consistent with the assumed C_{2v} structure.

The infrared absorption spectrum in the range 4000 to 400 cm⁻¹ of normal and deuterated H₂SO₄(g) above H₂SO₄(l) was observed by S. M. Chackalackal and P. R. Starford, J. Am. Chem. Soc. 88, 723 (1966). The authors assigned nine vibrational frequencies, which are adopted here. The three principal moments of inertia are: I_A = 1.570 x 10⁻³⁸, I_B = 1.586 x 10⁻³⁸, and I_C = 1.702 x 10⁻³⁸ g cm².

Four of the six missing frequencies are obtained from P. A. Giguère and R. Savoie, J. Am. Chem. Soc. 85, 287 (1963), which were estimated by comparison with infrared frequencies for the crystal and Raman values for the liquid. The remaining two frequencies, ν₇ = 450 and ν₁₄ = 450 cm⁻¹, are assigned arbitrarily so that the second and third law values for ΔH°_{298.15} derived from equilibrium data are in reasonable agreement.

H₂O, S

Tungstic Acid (H₂WO₄)

GFW = 249.86354

(Crystal)

TUNGSTIC ACID (H₂WO₄)

(CRYSTAL)

GFW = 249.86354

H₂O₄W

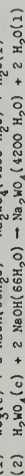
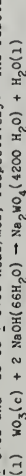
T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^c	Log K _p
0							
100							
200							
298	24.920	34.600	34.600	0.00	-270.500	-239.963	175.877
300	27.500	34.787	34.601	0.950	-270.500	-239.774	174.675
400	31.500	43.082	35.707	2.950	-270.305	-228.552	155.462
500	35.500	50.431	47.929	8.251	-269.763	-219.419	135.768
600	38.200	57.116	60.579	9.922	-269.915	-209.425	116.283
700	40.500	63.219	73.384	13.885	-267.832	-199.591	96.315
800	42.200	68.788	86.216	18.041	-266.611	-190.029	76.866
900	43.500	73.826	99.007	22.334	-265.295	-180.419	57.512
1000	44.500	78.472	111.724	26.743	-263.912	-171.061	37.395

ΔH₂₉₈^a = UnknownΔH_{298,15}^b = -270.5 ± 0.4 kcal/molS_{298,15}^c = [34.6 ± 6] gibbs/mol

Td = [393]°K

Heat of Formation

V. I. Spitsyn and N. N. Patsukova¹ have measured calorimetrically the heats of reaction (1) and (2) at 298°K as -13.80 ± 0.01 and -13.05 ± 0.02 kcal/mol, respectively. The reactions are given as follows:



Combination of reactions (1) and (2) gives ΔH₂₉₈^a = -0.75 ± 0.04 kcal/mol for WO₃(c) + H₂O(l) → H₂WO₄(c), which leads to ΔH₂₉₈^b(H₂WO₄, c) = -270.5 ± 0.4 kcal/mol.

To obtain WO₃(c) in a form soluble in the calorimetric solution, Spitsyn and Patsukova dehydrated H₂WO₄(c) at the relatively low temperature of 250°C. The resulting WO₃(c) was a very fine lemon-yellow powder which may have excess surface free energy compared with the JANAP standard state. The latter is WO₃ formed at high temperature in a calorimetric bomb. The actual heat of formation of tungstic acid should be less negative if this effect is significant.

The previously accepted value^{2,3,4} -280.2 ± 0.4 kcal/mol, was based on the pressure-temperature-composition studies of G. P. Huttig and B. Kurre⁵ for the WO₃-H₂O system. We suspect that the data do not correspond to equilibrium (see entropy section) for the reaction H₂WO₄(c) = WO₃(c) + H₂O(g).

Heat Capacity and Entropy

C_{p300} = 27.0 gibbs/mol is estimated using Kopp's rule. Since the decomposition temperature of H₂WO₄(c) is approximately 400°K, which is relatively low for hydrogen and oxygen to reach their maximum Cp contribution, we estimate Cp₄₀₀ = 31.0 gibbs/mol for H₂WO₄(c).

The entropy, S₂₉₈^b = 34.6 eu, is estimated so that the decomposition pressure of water is one atmosphere at 120°C. This value is quite uncertain as suggested by comparison with the following estimates. A lower limit may be obtained from S_{283.5}^c = 26.8 eu for H₂SO₄(c). Summation of the entropies for WO₃(c) and H₂O(c) [10.7 eu] yields 28.8 eu, an estimate which is somewhat larger than the lower limit. An upper limit may be obtained by assuming that the pressure of about 14 mm at 190°C corresponds to equilibrium for the reaction H₂WO₄(c) = WO₃(c) + H₂O(g). This pressure, based on the plateau in the temperature-composition data of Huttig and Kurre⁵, yields S₂₉₈^c = 46.5 eu when combined with the adopted ΔH₂₉₈^a and JANAP auxiliary data. Since the estimate appears to be unreasonably large, we suggest that this region of the curve may correspond to the reaction WO₃·0.5 H₂O(c) = WO₃(c) + 0.5 H₂O(g). In contrast, the observed pressures⁵ for samples having mole ratios (H₂O/WO₃) of 1.2 - 1.35 leads to S₂₉₈^c = 34 eu, if the reaction is WO₃·H₂O(c) = WO₃(c) + H₂O(g).

Temperature of Decomposition

Td is calculated as the temperature at which the Gibbs energy change of the reaction H₂WO₄(c) → WO₃(c) + H₂O(g) approaches zero.

Spitsyn and Patsukova¹ observed that some dehydration of stoichiometric H₂WO₄(c) occurs at temperatures as low as 90°C. Thermal studies^{6,7} on tungstic acid containing some excess water indicated the start of dehydration somewhere in the region of 60 - 120°C. These temperatures yield a lower limit for Td on the presumption that the experiments correspond to a partial pressure of water of less than one atmosphere.

References

1. V. I. Spitsyn and N. N. Patsukova, Russ. J. Inorg. Chem. (English Transl.) **10**, 1304 (1965).
2. D. D. Wagman, U.S. Natl. Bur. Std. Report 8919, July 1st, 1965.
3. M. P. Kohler, L. B. Pankratz and R. Barany, U.S. Bur. Mines RI 5973 (1962).
4. U. S. Natl. Bur. Std. Circ. 500, 1952.
5. G. P. Huttig and B. Kurre, Z. Anorg. Chem. **125**, 44 (1922); **125**, 167 (1923).
6. N. Wanek, Silikaty **5**, 70 (1962).
7. P. P. Kerr and P. Young, Am. Mineral. **29**, 192 (1944).

Dec. 31, 1962; June 30, 1963; Mar. 31, 1967

H₂O₄W

Tungstic Acid (H_2WO_4)

(Ideal Gas)

GFw = 249.86354

TUNGSTIC ACID (H_2WO_4)

(IDEAL GAS)

OPW = 249.86354

T, K	Cp ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	.000	INF INITE		5.034	-214.171		INF INITE
100	14.502	63.357	102.816	3.944	-215.386		460.647
200	20.190	75.182	86.218	2.207	-216.122		274.948
298	24.504	84.103	84.103	.000	-216.500		147.133
300	24.570	84.255	84.104	.045	-216.505		146.155
400	27.486	91.746	85.106	2.654	-216.599		106.713
500	29.394	98.093	87.085	5.504	-216.513		83.048
600	30.511	103.583	89.387	8.518	-216.320		67.281
700	31.793	108.219	91.757	11.655	-216.062		56.030
800	33.077	112.639	94.412	14.804	-215.764		46.848
900	34.277	116.639	96.412	18.204	-215.430		41.059
1000	34.956	120.197	98.615	21.589	-215.078		35.832
1100	34.534	123.466	100.728	25.012	-214.716		31.562
1200	34.932	126.459	102.750	28.486	-214.347		28.010
1300	35.158	129.202	104.683	32.010	-213.973		24.442
1400	35.598	131.722	106.534	35.534	-213.618		20.921
1500	35.787	134.383	108.313	39.105	-213.267		17.443
1600	35.991	136.699	110.016	42.694	-212.929		14.000
1700	36.166	138.687	111.650	46.302	-212.603		10.571
1800	36.449	140.452	113.234	49.925	-212.296		7.155
1900	36.449	142.025	114.784	53.565	-212.006		3.740
2000	36.584	144.798	116.190	57.215	-211.736		0.325
2100	36.565	146.585	117.596	60.877	-211.485		-0.904
2200	36.794	148.292	118.952	64.541	-211.259		-2.118
2300	37.002	150.000	120.263	68.210	-211.047		-3.325
2400	37.215	151.715	121.533	71.876	-210.841		-4.532
2500	36.945	153.005	122.762	75.607	-210.709		-5.735
2600	37.021	154.456	123.953	79.307	-210.569		-6.938
2700	37.072	155.854	125.109	83.012	-210.460		-8.139
2800	37.118	157.206	126.237	86.731	-210.364		-9.338
2900	37.158	158.506	127.321	90.431	-210.300		-10.532
3000	37.196	159.746	128.367	94.152	-210.393		-11.726
3100	37.230	160.986	129.411	97.874	-210.482		-12.919
3200	37.261	162.169	130.419	101.594	-210.644		-14.112
3300	37.291	163.313	131.384	105.314	-210.805		-15.305
3400	37.319	164.428	132.313	109.034	-210.966		-16.498
3500	37.339	165.512	133.246	112.789	-211.126		-17.691
3600	37.361	166.564	134.176	116.524	-211.171		-18.884
3700	37.382	167.588	135.095	120.261	-211.173		-20.077
3800	37.401	168.587	136.002	124.000	-211.169		-21.270
3900	37.418	169.557	136.892	127.740	-211.165		-22.463
4000	37.434	170.504	137.633	131.484	-211.212		-23.656
4100	37.449	171.429	138.446	135.228	-211.244		-24.849
4200	37.463	172.331	139.242	138.973	-211.264		-26.042
4300	37.476	173.213	140.022	142.720	-211.284		-27.235
4400	37.489	174.075	140.782	146.468	-211.304		-28.428
4500	37.500	174.917	141.535	150.214	-211.453		-30.051
4600	37.511	175.742	142.270	153.969	-211.523		-31.674
4700	37.521	176.548	142.991	157.720	-211.604		-33.297
4800	37.531	177.335	143.693	161.471	-211.679		-34.920
4900	37.540	178.112	144.383	165.221	-211.773		-36.543
5000	37.548	178.871	145.075	168.981	-211.878		-38.166
5100	37.556	179.615	145.745	172.734	-211.984		-39.789
5200	37.564	180.344	146.403	176.492	-212.094		-41.412
5300	37.571	181.059	147.049	180.250	-212.206		-43.035
5400	37.577	181.759	147.687	184.008	-212.319		-44.658
5500	37.584	182.451	148.312	187.764	-212.457		-46.281
5600	37.590	183.129	148.928	191.521	-212.591		-47.904
5700	37.595	183.784	149.534	195.282	-212.728		-49.527
5800	37.600	184.428	150.131	199.043	-212.866		-51.150
5900	37.606	185.091	150.717	202.805	-213.010		-52.773
6000	37.611	185.723	151.296	206.563	-213.162		-54.396

Dec. 31, 1982; June 30, 1983; Mar. 31, 1987

Point Group [C_{2v}]

S_{298.15} = [84] gibbs/mol

Round State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
[2200]	[100]	[570]	[100]
[1000]	[100]	[120]	[100]
[620]	[100]	[1100]	[100]
[500]	[2500]	[300]	[300]
[500]	[630]	[540]	[540]

Bond Distances: W-O = [1.81] Å

Bond Angle: O-W-O = [109.47]°

Product of the Moments of Inertia: I_AI_BI_C = [1.443 x 10⁻¹¹³] g³ cm⁶

Heat of Formation: ΔH_f° = -216.5 ± 1.0 kcal/mol

The adopted heat of formation, ΔH_f° = -216.5 ± 1.0 kcal/mol, is derived from equilibrium data^{1,2,3,4,5} obtained by the transpiration method. The data are in reasonable agreement and they are summarized below. Beilstein and McCarron¹ have precedence that W₂O₃ is the species responsible for the increased volatilization of W(c) and W₂O₃(c) in the presence of water vapor. Based on their data for W(c) and the earlier data for W₂O₃(c), Beilstein and McCarron ruled out the possibility of significant amounts of (W₂O₃)₂·H₂O and W₂O₃·2H₂O.

Investigator

Reaction*

Temp. (°K)

No. of Points

ΔH_f° (kcal/mol)

Drift (eu)

ΔH_f° (kcal/mol)

2nd law

3rd law

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

Equation

The vibrational frequencies are estimated by comparison with those for H₂SO₄(g) reported by P. A. Olgue and R. Savoie, J. Am. Chem. Soc. **85**, 287 (1963), and S. M. Chackalackal and P. B. Stafford, J. Am. Chem. Soc. **88**, 723 (1966). These frequencies are also adjusted so that S_{298.15} is 136.7 eu as reported by Beilstein and McCarron, loc. cit. This entropy was derived from second law analysis of the equilibrium constants for reaction A.

The configuration of W₂O₃ group is assumed to be tetrahedral. The bond angle W-O-H is estimated to be the same as the angle of H₂O(g). The bond distances are assumed to be the same as those in W₂O₃(g) and H₂O(g). The three principal moments of inertia are I_A = 2.328 x 10⁻³⁶, I_B = 2.487 x 10⁻³⁶ and I_C = 2.493 x 10⁻³⁶ g cm².

H₂O^W

Phosphorus Hydride (PH₂)

(Ideal Gas) Mol. Wt. = 32.991

T, °K.	C _p ^o	S ^o	-(H°-H ₂₉₈ °)/T	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.049	42.020	57.986	-2.301	30.504	INFINITE
200	8.019	47.550	51.549	-1.597	28.924	- 63.211
298	8.312	50.860	50.860	-1.000	27.333	- 20.867
300	8.319	50.851	50.800	-0.915	25.858	- 18.972
400	8.732	53.300	51.131	-0.867	25.003	- 16.836
500	9.185	55.297	51.770	-1.763	24.502	- 13.386
600	9.656	57.013	52.504	-2.705	23.240	- 10.158
700	10.057	58.491	53.206	-3.686	22.053	- 8.032
800	10.457	59.917	54.000	-4.728	20.932	- 6.389
900	10.951	61.183	54.804	-5.804	19.871	- 5.071
1000	11.300	62.356	55.438	-6.917	18.868	- 3.944
1100	11.604	63.447	56.118	-8.063	17.926	- 3.389
1200	11.864	64.468	56.843	-9.247	17.040	- 3.015
1300	12.092	65.427	57.401	-10.435	16.215	- 2.738
1400	12.286	66.331	58.007	-11.654	15.445	- 2.517
1500	12.454	67.184	58.590	-12.891	14.726	- 2.398
1600	12.599	67.993	59.153	-14.144	14.059	- 2.299
1700	12.724	68.764	59.696	-15.412	13.442	- 2.220
1800	12.834	69.491	60.220	-16.688	12.875	- 2.157
1900	12.930	70.187	60.726	-17.974	12.358	- 2.107
2000	13.014	70.853	61.216	-19.274	11.881	- 2.062
2100	13.088	71.489	61.690	-20.570	11.442	- 2.020
2200	13.153	72.097	62.148	-21.872	11.039	- 1.980
2300	13.213	72.686	62.595	-23.180	10.671	- 1.941
2400	13.265	73.249	63.027	-24.493	10.336	- 1.904
2500	13.311	73.792	63.447	-25.822	10.033	- 1.870
2600	13.353	74.315	63.855	-27.169	9.761	- 1.838
2700	13.392	74.819	64.252	-28.534	9.519	- 1.808
2800	13.425	75.307	64.638	-29.917	9.300	- 1.780
2900	13.456	75.779	65.014	-31.320	9.103	- 1.753
3000	13.484	76.235	65.380	-32.745	8.927	- 1.728
3100	13.510	76.678	65.738	-34.194	8.771	- 1.704
3200	13.533	77.107	66.087	-35.667	8.634	- 1.681
3300	13.555	77.524	66.427	-37.162	8.515	- 1.659
3400	13.575	77.929	66.759	-38.679	8.413	- 1.638
3500	13.593	78.323	67.084	-40.218	8.326	- 1.618
3600	13.610	78.704	67.401	-41.780	8.253	- 1.599
3700	13.625	79.079	67.712	-43.365	8.193	- 1.580
3800	13.639	79.442	68.016	-44.974	8.145	- 1.562
3900	13.653	79.797	68.313	-46.606	8.115	- 1.545
4000	13.665	80.143	68.605	-48.261	8.091	- 1.529
4100	13.676	80.480	68.890	-50.000	8.066	- 1.513
4200	13.687	80.809	69.167	-51.762	8.049	- 1.498
4300	13.697	81.132	69.445	-53.546	8.031	- 1.483
4400	13.707	81.447	69.714	-55.352	8.011	- 1.468
4500	13.715	81.755	69.978	-57.180	7.992	- 1.453
4600	13.723	82.057	70.237	-59.030	7.971	- 1.438
4700	13.731	82.352	70.492	-60.900	7.950	- 1.423
4800	13.738	82.641	70.742	-62.790	7.929	- 1.408
4900	13.745	82.925	70.988	-64.700	7.907	- 1.393
5000	13.752	83.202	71.229	-66.630	7.885	- 1.378
5100	13.758	83.473	71.467	-68.580	7.862	- 1.363
5200	13.763	83.742	71.700	-70.550	7.839	- 1.348
5300	13.769	84.004	71.930	-72.540	7.815	- 1.333
5400	13.774	84.262	72.156	-74.550	7.791	- 1.318
5500	13.779	84.514	72.378	-76.580	7.767	- 1.303
5600	13.783	84.763	72.597	-78.630	7.742	- 1.288
5700	13.788	85.007	72.813	-80.700	7.717	- 1.273
5800	13.792	85.247	73.025	-82.790	7.692	- 1.258
5900	13.796	85.482	73.234	-84.900	7.667	- 1.243
6000	13.800	85.714	73.441	-87.030	7.642	- 1.228

Dec. 31, 1960; Mar. 31, 1963

PHOSPHORUS HYDRIDE (PH₂)

(IDEAL GAS)

MOL. WT. = 32.991

Point Group [C_{2v}] $\Delta H_f^o = [30.6 \pm 23] \text{ kcal. mole}^{-1}$ $S_{298.15}^o = [50.8] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^o 298.15 = [30.1 \pm 23] \text{ kcal. mole}^{-1}$

Ground State Multiplicity = [2]

Vibrational Frequencies and Degeneracies

 $\omega, \text{ cm.}^{-1}$

[2327] (1)

[1020] (1)

[2322] (1)

Bond Distances: P-H = [1.419] Å

Bond Angle: H-P-H = [93.7]°

Product of Moments of Inertia: $I_{AB} I_C = [6.95 \times 10^{-119}] \text{ g.}^3 \text{ cm.}^6$ $\sigma = 2$

Heat of Formation.

$\Delta H_f^o 298.15$ was estimated by V. N. Distefano, R. L. Potter, and S. N. Fox, "The Thermodynamic Functions of Some Combustion Products Containing Phosphorus-I.", American Cyanamid Company. The $\Delta H_f^o 298.15$ was estimated by taking 63% of the dissociation energy of PH₃ and using it as the dissociation energy of PH₂. D. Wiles and C. Winkler, J. Phys. Chem. 61, 902 (1957) have estimated the $\Delta H_f^o 298.15$ for PH₂(g) to be 30 kcal. mole⁻¹.

Heat Capacity and Entropy.

The vibrational spectra of PH₂ from the flash photolysis of PH₃ has been reported by D. A. Ramsay, Nature 179, 375 (1956) and in N. Y. Acad. Sci. 61, 485, (1957). Similarities between the spectra of NH₂ and PH₂ were found. For NH₂ and NH₃ bond angles and bond distances were reported to be about the same. By analogy then the bond angles and bond distances of PH₂ and PH₃ should be nearly the same. The moments of inertia for PH₂ were therefore calculated from the molecular constants for PH₃. The principal moments were found to be $I_A = 3.587 \times 10^{-40} \text{ g. cm.}^2$, $I_B = 2.959 \times 10^{-40} \text{ g. cm.}^2$, and $I_C = 6.546 \text{ g. cm.}^2 \times 10^{-40}$.

Distefano and Potter (loc. cit.) have assumed the ground state degeneracy to be 2, because of the unpaired electron. The vibrational frequencies reported by Distefano and Potter (loc. cit.) have been used. They used a simple force field and the force constants of PH₃ to obtain the vibrational frequencies.

H₂PH₂P

Hydrogen Sulfide (H₂S)

(Ideal Gas) Mol. Wt. = 34.07994

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	.000	INFINITE	- 2.381	- 4.184	-	INFINITE
100	7.949	40.219	- 1.786	- 4.312	- 5.613	12.266
200	10.567	49.151	- 1.000	- 4.880	- 7.955	7.455
298	8.172	49.151	.000	- 4.880	- 7.955	5.831
300	8.176	49.202	.49151	- 4.888	- 7.974	5.809
400	8.504	51.597	4.476	- 4.872	- 8.918	4.872
500	8.889	53.536	50.100	- 6.615	- 9.596	4.194
600	9.306	55.193	50.813	- 7.262	- 10.129	3.689
700	9.737	56.660	51.546	- 7.812	- 10.538	3.290
800	10.162	57.988	52.269	- 8.262	- 10.862	2.932
900	10.567	59.209	52.973	- 8.612	- 11.107	2.673
1000	10.943	60.342	53.654	- 8.881	- 11.271	2.414
1100	11.281	61.401	54.311	- 9.068	- 11.358	2.155
1200	11.584	62.396	54.944	- 9.172	- 11.366	1.896
1300	11.853	63.334	55.553	- 9.200	- 11.309	1.637
1400	12.092	64.221	56.141	- 9.151	- 11.179	1.378
1500	12.303	65.063	56.708	- 9.025	- 10.977	1.119
1600	12.491	65.863	57.255	- 8.823	- 10.700	.860
1700	12.658	66.625	57.784	- 8.546	- 10.357	.601
1800	12.808	67.353	58.296	- 8.193	- 9.944	.342
1900	12.941	68.049	58.791	- 7.764	- 9.466	.083
2000	13.063	68.716	59.271	- 7.266	- 8.933	.000
2100	13.171	69.356	59.736	- 6.700	- 8.356	.000
2200	13.270	69.971	60.187	- 6.067	- 7.736	.000
2300	13.360	70.563	60.625	- 5.367	- 7.073	.000
2400	13.444	71.133	61.051	- 4.600	- 6.377	.000
2500	13.520	71.684	61.466	- 3.767	- 5.647	.000
2600	13.590	72.215	61.869	- 2.870	- 4.884	.000
2700	13.655	72.729	62.262	- 1.916	- 4.088	.000
2800	13.715	73.227	62.645	- .906	- 3.260	.000
2900	13.771	73.709	63.018	.050	- 2.400	.000
3000	13.824	74.177	63.382	.823	- 1.512	.000
3100	13.874	74.631	63.730	1.606	- .600	.000
3200	13.921	75.073	64.085	2.399	.323	.000
3300	13.965	75.502	64.425	3.102	1.026	.000
3400	14.007	75.919	64.756	3.716	1.699	.000
3500	14.047	76.326	65.081	4.241	2.342	.000
3600	14.085	76.722	65.399	4.676	2.950	.000
3700	14.122	77.108	65.710	5.022	3.523	.000
3800	14.156	77.485	66.015	5.279	4.061	.000
3900	14.190	77.854	66.314	5.446	4.564	.000
4000	14.223	78.213	66.607	5.523	5.033	.000
4100	14.254	78.565	66.895	5.512	5.468	.000
4200	14.285	78.909	67.177	5.412	5.870	.000
4300	14.314	79.245	67.453	5.223	6.239	.000
4400	14.343	79.575	67.725	4.946	6.576	.000
4500	14.371	79.897	67.992	4.581	6.881	.000
4600	14.397	80.213	68.254	4.126	7.156	.000
4700	14.423	80.523	68.512	3.581	7.403	.000
4800	14.450	80.827	68.765	2.946	7.623	.000
4900	14.475	81.125	69.015	2.221	7.817	.000
5000	14.500	81.418	69.260	1.406	7.986	.000
5100	14.523	81.705	69.501	.501	8.131	.000
5200	14.548	81.988	69.738	.000	8.254	.000
5300	14.571	82.265	69.972	.000	8.357	.000
5400	14.594	82.538	70.202	.000	8.441	.000
5500	14.616	82.806	70.429	.000	8.507	.000
5600	14.639	83.069	70.652	.000	8.556	.000
5700	14.661	83.328	70.873	.000	8.590	.000
5800	14.682	83.584	71.089	.000	8.610	.000
5900	14.705	83.835	71.303	.000	8.617	.000
6000	14.725	84.082	71.514	.000	8.612	.000

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965

HYDROGEN SULFIDE (H₂S)

(IDEAL GAS)

MOL. WT. = 34.07994

Point Group C_{2v}ΔH_f^o 0 = -4.18 ± 0.15 kcal. mole⁻¹ΔH_f^o 298.15 = -4.88 ± 0.15 kcal. mole⁻¹S_{298.15}^o = 49.15 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

Wavenumber, cm. ⁻¹
2614.56 (1)
1182.68 (1)
2627.48 (1)

Bond Distance: S-H = 1.328 Å

Bond Angle: H-S-H = 92.2°

Moments of Inertia: I_A I_B I_C = 4.89 × 10⁻¹¹ g.² cm.⁶

Heat of Formation.

The heat of formation of hydrogen sulfide has been calorimetrically measured by H. Zeumer and W. A. Roth, Z. Elektrochem. 40, 777 (1934), and A. P. Kapustinikii and R. T. Kankovskii, Zhur. Fiz. Khim. 32, 2810 (1958), as ΔH_f^o 293 = -4.80 ± 0.15 kcal. mole⁻¹ and ΔH_f^o 298 = -4.94 ± 0.08 kcal. mole⁻¹, respectively. A weighted average of these two values was taken for the standard enthalpy of formation of hydrogen sulfide.

Heat Capacity and Entropy.

The bond distance, angle and vibrational frequencies were obtained from H. C. Allen, Jr. and E. K. Plyler, J. Chem. Phys. 25, 1132 (1956).

J. S. Gordon, private communication, Feb. 7, 1961, has calculated C_p from 298 to 6000°K. by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes second order corrections for vibrational anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The correction constants were obtained from Allen and Plyler, loc. cit. Below 298°K. the rigid-rotator harmonic oscillator method was used to calculate the functions, but at 298°K. and above Gordon's thermodynamic functions were adopted in this tabulation.

H₂S

Titanium Dihydride (TiH₂)

(Crystal) Mol. Wt. = 49.916

June 30, 1963

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	3.030	1.512	12.312	1.010	32.508	32.508	INFINITE
200	3.430	2.011	10.312	0.845	32.508	32.508	30.714
298	7.1491	7.101	7.101	0.000	32.508	32.508	18.418
300	7.232	7.146	7.101	0.013	34.511	25.069	18.262
400	9.400	9.524	7.411	1.845	34.993	21.845	11.935
500	11.300	11.832	8.066	1.883	35.303	18.318	8.094
600	12.860	14.035	8.879	3.094	35.465	15.144	5.516
700	14.100	16.115	9.765	4.445	35.510	11.752	3.669
800	15.090	18.065	10.682	5.906	35.465	8.361	2.284
900	15.850	19.888	11.605	7.455	35.353	4.977	1.209
1000	16.380	21.588	12.519	9.066	35.198	1.611	0.392
1100	16.744	23.166	13.416	10.725	35.021	1.738	-0.345
1200	17.050	24.637	14.291	12.415	35.781	5.109	-0.930
1300	17.298	26.012	15.140	14.133	35.585	8.509	-1.430
1400	17.488	27.301	15.963	15.873	35.389	11.893	-1.856
1500	17.620	28.512	16.760	17.629	35.199	15.265	-2.224
1600	17.753	29.654	17.530	19.398	35.019	18.622	-2.544
1700	17.858	30.734	18.276	21.178	34.847	21.970	-2.824
1800	17.934	31.757	18.996	22.968	34.685	25.306	-3.072
1900	17.981	32.728	19.694	24.764	34.536	28.636	-3.294
2000	18.000	33.650	20.369	26.564	34.077	32.051	-3.502

TITANIUM DIHYDRIDE (TiH₂)

(CRYSTAL)

MOL. WT. = 49.916

$$\Delta H_f^0 = [-32.5 \pm 2.0] \text{ kcal. mole}^{-1}$$
$$\Delta H_f^{298.15} = [-34.5 \pm 2.0] \text{ kcal. mole}^{-1}$$
$$S_{298.15}^0 = 7.101 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Heat of Formation.

The heat of combustion of TiH_{1.73}(c), the stable species of titanium hydride, was reported to be -247.8 kcal. by A. Sieverts and A. Gotta, Z. anorg. allgem. Chem. 199, 394 (1931). From this data the value of ΔH_f⁰ 298.15 for TiH_{1.73}(c) was calculated to be -29.40 kcal. mole⁻¹. The heat of dissociation of titanium hydride having compositions between the rough limits TiH_{1.75}-TiH_{1.93} was given as 19.15 kcal. per mole of H₂ dissociated by T. R. P. Gibb, Jr., J. McSharry, and R. W. Bragdon, J. Am. Chem. Soc. 73, 1751 (1951). Assuming this value is applicable to compositions between the limits TiH_{1.73}-TiH₂, the difference in the heat of formation of titanium hydride between TiH_{1.73} and TiH₂ was estimated to be -5.17 kcal. mole⁻¹. Thus the value of ΔH_f⁰ 298.15 for TiH₂(c) was calculated.

Heat Capacity and Entropy.

The low temperature C_p for TiH_{1.97}(c), 24-363°K., were measured by B. Stalinski and Z. Bieganski, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 8, No. 5, 243 (1960). This data were adopted for TiH₂(c) due to lack of the measured C_p values. A small but well marked λ-type anomaly with a maximal value of C_p at 298.5°K. in the C_p vs. T curve was observed. S_{298.15} was reported by B. Stalinski and Z. Bieganski, loc. cit., based on S₂₅(extrap.) = 0.065 cal. deg.⁻¹ mole⁻¹.



(IDEAL GAS)

MOL. WT. = 17.03061

 $\Delta H_f^\circ = -9.30 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 298.15 = 46.03 \pm 0.1 \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = 298.15 = -10.97 \pm 0.1 \text{ kcal. mole}^{-1}$
AMMONIA (NH₃)
 Point Group C_{3v}
 $S_{298.15} = 46.03 \pm 0.1 \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 Round State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

Zero-order "Harmonic"	Observed Wave Numbers	
	$\bar{\nu}$, cm. ⁻¹	$\bar{\nu}$, cm. ⁻¹
$\bar{\nu}_1$	3506 (1)	3577 (2)
$\bar{\nu}_2$	1022 (1)	1691 (2)
$\bar{\nu}_3$	1691 (2)	950 (1)
$\bar{\nu}_4$	1627 (2)	

 Bond Length: N-H = 1.0124 Å
 Bond Angle: H-N-H = 106.67°
 Product of the Moments of Inertia: $I_A I_B I_C = 3.4826 \times 10^{-119} \text{ g}^3 \text{ cm}^6$

Heat of Formation

A weighted average based on analysis using JANAF functions was selected. Haber, Tammaru and Oeholm, Z. Elektrochem. **21**, 206 (1915) obtained $\Delta H_{298}^\circ = 11.10$ for NH₃ → 0.5 N₂ + 1.5 H₂ by flow calorimetry. Estimated uncertainty is 1% and the formation value was corrected by 0.025 kcal. for non-ideality of NH₃. Becker and Roth, *ibid.* **20**, 836 (1934) measured ΔH_f° for NH₃(g) + H₂O(l) → NH₄OH(aq), ΔH_f° for NH₃(g) + H₂O(l) → NH₄OH(aq), and the necessary ΔH_{soln} leading to $\Delta H_{298}^\circ = 182.9 \pm 0.24$ for 3H₂O(l) + N₂(g) → 1.5 O₂(g) + 2NH₃(g). Equilibrium data from Larson and Dodge, J. Am. Chem. Soc. **45**, 2918 (1923) and Haber, Tammaru and Ponnaz, Z. Elektrochem. **21**, 89 (1915) were analyzed as tabulated by Stephenson and McMahon, J. Am. Chem. Soc. **61**, 437 (1939) from the non-ideality corrections of Olliepie and Beattie, Phys. Rev. **35**, 743 (1930). Data (1000-3000 atm) from Minchieser and Dodge, A.I.Ch.E. Journal **2**, 431-6 (1956) were omitted because of uncertainty in non-ideality while data (1 atm) of Haber and Maschke, Z. Elektrochem. **21**, 128 (1915) were assumed ideal. High-temperature calorimetry of the direct decomposition includes Haber and Tammaru, Z. Elektrochem. **21**, 191 (1915) and Wittig and Schmets, *ibid.* **63**, 470 (1959).

Sources

Method	ΔH_f° 298 (kcal. mole ⁻¹)	Drift (e.u.)
Haber, Tammaru, Oeholm (1915)	Flow calorimetry at 298°K	-11.07
Becker, Roth (1934)	Indirect calorimetry at 294°K	-11.02±0.12
Larson, Dodge (1923)	K _p from K _p (10-1000 atm, 600-800°K)	-0.17±0.05
Haber, Tammaru, Ponnaz (1915)	K _p from K _p (30 atm, 800-1200°K)	0.04±0.05
Haber, Maschke (1915)	K _p (1 atm, 900-1400°K)	-0.89(-10.95±0.05)*
Haber, Tammaru (1915)	Flow calorimetry (739-932°K)	-0.87(-10.60±0.1)*
Wittig, Schmets (1959)	Flow calorimetry at 823°K	-10.97
	Flow calorimetry at 823°K	-10.98

*Third law values for equilibrium data are followed by second law values in parentheses.
 Heat Capacity and Entropy.

The functions are an approximation of the non-rigid rotator anharmonic oscillator based on calculations of Harrison and Kobe, Chem. Eng. Progr. **49**, No. 7, 349 (1953) and Yungman, Olurich and Ritscheva, Trudy Gosudarst. Inst. Priklad. Khim. **49**, 20 (1962). In these calculations anharmonicity of ν_2 associated with inversion doubling was treated by summation over the energy levels. Both calculations include rotational distortion corrections while Yungman, at el., also allow for anharmonicity and vibration-rotation interaction of the other fundamentals. JANAF functions agree with the results to within 0.02 e.u. in the range 298-1500°K.

Two sets of rigid rotator harmonic oscillator functions were also tested for consistency with the ammonia data (see below). These were obtained from molecular dimensions and either calculated zero order frequencies ($\bar{\nu}$) or observed wave numbers ($\bar{\nu}$) obtained by Benedict and Plyler, Can. J. Phys. **35**, 1235 (1957) from high resolution infrared studies. Herzberg, "Infrared and Raman Spectra", pp. 503-4, 1945 states that $\bar{\nu}$ should be used and the RRHO¹ functions give better, but not perfect, agreement with the observed C_p for NH₃. Principal moments of inertia are $I_A = 4.414 \times 10^{-40}$ end $I_B = I_C = 2.809 \times 10^{-40} \text{ g. cm}^2$. Electron diffraction studies by Bastiansen and Bagley, Acta Chem. Scand. **18**, 2077 (1964) give slightly different constants (bond distance 1.015 Å and angle = 109.1°).

T, °K	Heat Capacity, C _p	Observed JANAF	Entropy, S°	
			Observed	JANAF
253.15	8.271(a)	8.269	239.72	44.23(b,c)
298.15	8.521(a)	8.515	298.15	44.21
423.15	9.422(a)	9.423	360.61	46.03
800.	12.070-2(f)	12.225	500.	55.99

- (e) N. S. Osborne, H. P. Stinson, T. S. Sligh, Jr., and G. S. Crago, NBS Sci. Papers **20**, 65 (1954-6) measured C_p of gaseous NH₃ (258 to 423°K and 0.5 to 20 atm) within an estimated maximum error of 0.3% (about 0.03 cal. deg.⁻¹ mole⁻¹) and obtained C_p by use of a suitable equation of state.
- (f) R. Overstreet and W. P. Dismuke, J. Am. Chem. Soc. **59**, 254 (1937) determined the entropy of the real gas at the normal boiling point as $S_{298.72}^\circ = 44.06 \pm 0.10 \text{ cal. deg}^{-1} \text{ mole}^{-1}$.
- (c) (S°) $S_{298.72}^\circ = 0.17 \text{ cal. deg}^{-1} \text{ mole}^{-1}$ from the virial coefficient equation derived by Hirschfelder, McClure and Weeks, J. Chem. Phys. **10**, 201 (1942) from the PVT data of Meyers and Jessup, Refrig. Eng. **11**, 345 (1925).
- (d) Combination of ΔH_f° 800 = -12.85 kcal. mole⁻¹ from the calorimetric measurement of F. E. Wittig and W. Schmets, Z. Elektrochem. **63**, 470 (1959) with $\Delta H_{298}^\circ = 9.315 \text{ kcal. mole}^{-1}$ from equilibrium data (f).
- (e) Second law analysis of the equilibrium data (f).
- (f) K_p values based on the equilibrium data of Haber, Tammaru and Ponnaz and those of Larson and Dodge were analyzed by regression analysis to give $\Delta H_{800}^\circ = 9.315 \pm 0.004$, $\Delta H_{800}^\circ = -12.666 \pm 0.017$ and ΔC_p 800 = -2.31 ± 0.20.

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Hydronium Unipositive Ion (H₃O⁺)



(Ideal Gas) GFW = 19.02276

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ₂₉₈ °)/T	IP ^o - H ₂₉₈ ^o	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0						
100						
200						
298	8.400	45.924	+0.00	138.900	144.983	- 106.275
300						
350	8.411	45.076	-0.14	138.899	145.020	- 105.647
400	8.401	46.485	-0.80	138.899	145.057	- 104.919
450	8.473	50.599	-1.89	138.905	149.112	- 103.177
500						
550	8.604	52.465	-2.863	139.099	151.165	- 101.505
600	8.615	54.150	-3.957	139.147	153.159	- 99.818
650	8.626	55.789	-5.129	139.184	155.107	- 98.132
700	8.637	57.390	-6.333	139.204	157.016	- 96.444
750	8.648	58.959	-7.566	139.216	158.888	- 94.756
800	8.659	60.494	-8.824	139.224	160.724	- 93.068
850	8.670	62.000	-10.100	139.230	162.524	- 91.380
900	8.681	63.474	-11.396	139.234	164.289	- 89.692
950	8.692	64.917	-12.711	139.236	166.019	- 88.004
1000	8.703	66.330	-14.046	139.237	167.714	- 86.316
1100	8.714	67.714	-15.390	139.238	169.374	- 84.628
1200	8.725	69.067	-16.749	139.239	171.000	- 82.940
1300	8.736	70.390	-18.124	139.240	172.592	- 81.252
1400	8.747	71.684	-19.514	139.241	174.150	- 79.564
1500	8.758	72.950	-20.919	139.242	175.674	- 77.876
1600	8.769	74.187	-22.339	139.243	177.164	- 76.188
1700	8.780	75.394	-23.774	139.244	178.620	- 74.500
1800	8.791	76.567	-25.224	139.245	180.042	- 72.812
1900	8.802	77.707	-26.689	139.246	181.430	- 71.124
2000	8.813	78.814	-28.169	139.247	182.784	- 69.436
2100	8.824	79.889	-29.664	139.248	184.104	- 67.748
2200	8.835	80.934	-31.174	139.249	185.390	- 66.060
2300	8.846	81.949	-32.699	139.250	186.642	- 64.372
2400	8.857	82.934	-34.239	139.251	187.860	- 62.684
2500	8.868	83.889	-35.794	139.252	189.044	- 61.000
2600	8.879	84.814	-37.364	139.253	190.194	- 59.312
2700	8.890	85.709	-38.949	139.254	191.310	- 57.624
2800	8.901	86.574	-40.549	139.255	192.394	- 55.936
2900	8.912	87.409	-42.164	139.256	193.444	- 54.248
3000	8.923	88.214	-43.794	139.257	194.460	- 52.560
3100	8.934	89.000	-45.439	139.258	195.442	- 50.872
3200	8.945	89.754	-47.099	139.259	196.390	- 49.184
3300	8.956	90.479	-48.774	139.260	197.304	- 47.496
3400	8.967	91.164	-50.464	139.261	198.184	- 45.808
3500	8.978	91.819	-52.169	139.262	199.030	- 44.120
3600	8.989	92.444	-53.889	139.263	199.842	- 42.432
3700	8.999	93.039	-55.624	139.264	200.610	- 40.744
3800	9.010	93.604	-57.374	139.265	201.344	- 39.056
3900	9.021	94.139	-59.139	139.266	202.044	- 37.368
4000	9.032	94.644	-60.919	139.267	202.704	- 35.680
4100	9.043	95.119	-62.714	139.268	203.324	- 33.992
4200	9.054	95.564	-64.524	139.269	203.904	- 32.304
4300	9.065	95.979	-66.349	139.270	204.444	- 30.616
4400	9.076	96.364	-68.189	139.271	204.944	- 28.928
4500	9.087	96.719	-70.044	139.272	205.404	- 27.240
4600	9.098	97.044	-71.914	139.273	205.824	- 25.552
4700	9.109	97.339	-73.799	139.274	206.204	- 23.864
4800	9.120	97.604	-75.699	139.275	206.544	- 22.176
4900	9.131	97.839	-77.614	139.276	206.844	- 20.488
5000	9.142	98.044	-79.544	139.277	207.104	- 18.800
5100	9.153	98.219	-81.489	139.278	207.324	- 17.112
5200	9.164	98.364	-83.449	139.279	207.504	- 15.424
5300	9.175	98.479	-85.424	139.280	207.644	- 13.736
5400	9.186	98.564	-87.414	139.281	207.744	- 12.048
5500	9.197	98.619	-89.419	139.282	207.804	- 10.360
5600	9.208	98.644	-91.439	139.283	207.824	- 8.672
5700	9.219	98.639	-93.474	139.284	207.804	- 6.984
5800	9.230	98.594	-95.524	139.285	207.744	- 5.296
5900	9.241	98.509	-97.589	139.286	207.644	- 3.608
6000	9.252	98.374	-99.669	139.287	207.504	- 1.920

June 30, 1966

HYDRONIUM UNIPOSITIVE ION (H₃O⁺) (IDEAL GAS)

OPW = 19.02276

Point Group [C_{3v}]

ΔH_f^o = 139.1 ± 3 kcal/mol

S_{298.15}^o = [45.92] gibbs/mol

ΔH_f^o298.15 = 138.9 ± 3 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[3760](1)	[3760](2)
[1050](1)	[1050](2)

Bond Distance: H-O = [0.96] Å

Bond Angle: H-O-H = [109]°

Product of the Moments of Inertia: I_AI_BI_C = [2.39] X 10⁻¹¹⁹ g³ cm⁶

σ = 3

Heat of Formation

The proton affinity of water has been measured by the ion impact method as -169 kcal/mol by V. L. Tal'rose and E. L. Frenkivitch, Doklady Akad. Nauk SSSR 111, 376 (1956), J. An. Chem. Soc. 80, 2344 (1958). The selected heat of formation of hydronium ion, ΔH_f^o(H₃O⁺, g) = 139.1 kcal/mol, was derived from the ΔH_f^o = -169 kcal/mol for H₂O(g) + H⁺(g) → H₃O⁺(g), using the JANAF ΔH_f^o(H₂O, g) = -57.1 and ΔH_f^o(H⁺, g) = 385.2 kcal/mol.

The values of 195 and 207 kcal/mol for the heat of formation of H₃O⁺(g) have also been reported by P. M. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957, and R. R. Berner and P. A. Long, J. Phys. Chem. 65, 1565 (1961), respectively. These two values were based on the electron impact studies which may involve unaccounted excitations and excess energy in the fragments. Other literature values have been reviewed by D. W. Bishop, J. Chem. Phys. 43, 4453 (1965).

J. A. Green and T. M. Sugden, Ninth Symposium (International) on Combustion, Academic Press, New York, 1963, based on the studies of the positive ions in flames by mass spectrometry, prefer the value derived from the proton affinity of water obtained by Tal'rose and Frankvitch, rather than the electron impact data. From the approximate equilibrium constant calculations for the reaction HCO⁺(g) + H₂O(g) ⇌ H₃O⁺(g) + CO(g), D. G. Clifton, AD444078, G. M. Defense Research Laboratory, General Motors Corp., Santa Barbara, Calif., July 1964, has also found that the heat of formation of H₃O⁺(g) derived from the proton affinity of water, not from the electron impact data, leads to agreement with the experimental data given by Green and Sugden.

Heat Capacity and Entropy

Since the molecule H₃O⁺(g) has the same number of valence electrons as NH₃(g), a pyramidal molecular configuration (C_{3v}) is assumed for H₃O⁺(g) in the tabulation. D. G. Clifton, J. Chem. Phys. 41, 3656 (1964), has obtained a bond distance O-H of 0.95 Å from an application of covalent bond radii and the effect of electric charge, and a bond angle H-O-H of 109° by extrapolating a plot of bond length versus bond angle for NH₃(g) and PH₃(g) to 0.95 Å. Both values are adopted in the tabulation. The three principal moments of inertia are I_A = 0.4004 X 10⁻³⁹, I_B = I_C = 0.2445 X 10⁻³⁹ g cm². D. M. Bishop, loc. cit., has calculated theoretically the bond distance H-O of 0.96 Å and the bond angle H-O-H of 114° 26' with a planar D_{3h} molecular configuration. The vibrational frequencies were calculated by the valence force method from the estimated stretching and bending force constants of Clifton.



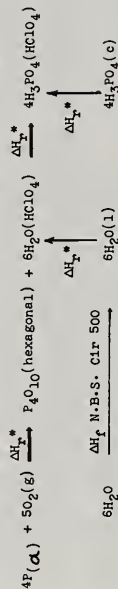
Orthophosphoric Acid (H_3PO_4)
(Crystal) Mol. Wt. = 97.999

T. °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _f
0	0.00	0.00	INFINITE	-	-297.541	-297.541	INFINITE
100	10.249	8.255	28.510	-4.059	-298.461	-298.461	330.2293
200	18.139	17.830	28.510	-2.136	-300.826	-297.449	93.293
298	25.384	26.421	26.421	0.000	-301.530	-264.604	193.951
300	25.480	26.421	26.421	0.047	-301.537	-264.276	194.589
300	33.000	31.258	27.479	2.832	-301.749	-251.947	137.651
500	33.250	41.023	29.615	6.005	-301.657	-239.502	104.681
600	35.700	47.915	32.151	9.458	-300.945	-227.096	82.716
700	37.400	53.555	34.813	13.120	-300.945	-214.749	67.044
800	38.800	58.649	37.479	16.936	-320.867	-207.781	56.760
900	39.500	63.285	40.092	20.856	-320.079	-193.691	47.932
1000	40.000	67.253	42.022	24.831	-319.274	-179.690	39.269
1100	40.600	71.292	45.056	28.860	-318.453	-165.773	32.934
1200	41.000	74.842	47.393	32.940	-317.613	-151.929	27.669
1300	41.400	78.140	49.632	37.060	-316.767	-138.156	23.225
1400	41.700	81.219	51.780	41.215	-315.916	-124.449	19.426
1500	42.000	84.106	53.840	45.400	-315.068	-110.800	16.143

ORTHOPHOSPHORIC ACID (H_3PO_4)
(CRYSTAL)
MOL. WT. = 97.999

$\Delta H_f^0 = -297.5 \pm 0.3 \text{ kcal. mole}^{-1}$
 $\Delta H_m^0 = 3.100 \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = 26.42 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 315.51^\circ \text{K}$

Heat of Formation.
The heat of formation was determined by W. S. Holmes [private communication July 5, 1962, Albright and Wilcoxon (WPG) Ltd., Oldbury, Birmingham, Great Britain (in press by Faraday Society)]. W. S. Holmes measured the enthalpy of combustion of white phosphorus (α form) in oxygen in a bomb calorimeter. The product, P_4O_{10} (hexagonal), was hydrolyzed in 10N perchloric acid to give H_3PO_4 . Measurement of the enthalpy of solution of $H_3PO_4(c)$ then enabled the ΔH_f^0 298.15 to be calculated according to the following cycle:



* All ΔH_f^0 's were measured.

E. P. Egan, Jr. and B. B. Luff, J. Phys. Chem., 65, 523 (1961), from partial molal heat contents of H_3PO_4 solutions found that a smooth extrapolation to 100% H_3PO_4 would give them a ΔH_f^0 298.15 for $H_3PO_4(c)$ which was 755 cal. mole⁻¹ greater than the ΔH_f^0 298.15 reported in the National Bureau of Standards Circular 500. The Circular 500 (loc. cit.) heat of formation refers to the work of Thomson, "Thermochimische Untersuchungen," Vol. 2, Barth, Leipzig (1882-1886). The heats of formation summarized:

ΔH_f^0 298.15	Source
-305.7 $\pm$ 0.3 kcal. mole ⁻¹	W. S. Holmes (loc. cit.)
-306.2 kcal. mole ⁻¹	Circular 500 (loc. cit.)
-305.4 kcal. mole ⁻¹	Egan and Luff (loc. cit.)
The selected ΔH_f^0 298.15, -305.7 $\pm$ 0.3 kcal. mole ⁻¹ , was corrected by +4.17 kcal. mole ⁻¹ , which is the ΔH_f^0 298.15 of white (α) phosphorus.	

Heat Capacity and Entropy.

Third law entropy was calculated from the low temperature heat capacities measured by E. P. Egan, Jr. and Z. T. Wakefield, J. Phys. Chem. 61, 1500 (1957).

Melting.

The heat of fusion, ΔH_m , was reported by E. P. Egan, Jr. and B. B. Luff, J. Phys. Chem. 65, 523 (1961) from ΔH_m data measured by E. P. Egan, Jr. and Z. T. Wakefield, J. Phys. Chem. 61, 1500 (1957). The melting point $T_m = 315.51^\circ \text{K}$ was taken from the work of W. H. Ross and R. M. Jones, J. Am. Chem. Soc. 47, 2165 (1925).

H_3O_4P

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f kcal. mole ⁻¹	ΔF° _f	Log K _p
0						
100						
200						
298	48.000	34.993	0.000	-298.810	-264.440	193.830
300	48.000	35.289	0.089	-298.776	-264.227	192.480
400	48.000	49.088	6.889	-296.972	-252.986	136.218
500	48.000	59.809	40.431	-295.253	-242.190	105.856
600	48.000	68.561	66.413	-293.614	-231.733	84.402
700	48.000	75.960	88.404	-292.056	-221.543	69.165
800	48.000	82.369	92.258	-290.569	-211.684	59.247
900	48.000	88.023	95.924	-289.154	-202.220	49.832
1000	48.000	93.080	99.391	-287.806	-193.739	42.340
1100	48.000	97.655	102.665	-286.514	-185.242	36.242
1200	48.000	101.832	105.758	-285.276	-176.747	31.187
1300	48.000	105.674	108.682	-284.090	-168.261	26.931
1400	48.000	109.231	111.453	-282.954	-159.771	23.301
1500	48.000	112.542	114.083	-281.866	-151.284	20.171
1600	48.000	115.640	116.585	-280.827	-142.791	17.445
1700	48.000	118.550	118.969	-279.836	-134.291	15.031
1800	48.000	121.294	121.244	-278.891	-125.784	12.933
1900	48.000	123.889	123.421	-278.000	-117.271	11.047
2000	48.000	126.351	125.507	-277.162	-108.756	9.357

June 30, 1962

Orthophosphoric Acid (H₃PO₄) (Liquid)

Mol. Wt. = 97.999
ΔH°_f 298.15 = -298.81 ± 0.5 kcal. mole⁻¹
S°_{298.15} = 35.0 cal. deg.⁻¹ mole⁻¹
T_m = 315.61°K
ΔH°_m = 3.100 kcal. mole⁻¹
Heat of Formation. Calculated from ΔH°_f 298.15 for H₃PO₄(c) and ΔH°_m given by E. P. Egan, Jr., and B. B. Luff, J. Phys. Chem. 65, 523 (1961) using the ΔH°_m data reported by E. P. Egan, Jr., and Z. T. Wakefield, J. Phys. Chem. 61, 1500 (1957).

Heat Capacity and Entropy. The heat capacity is estimated. The entropy at 298.15°K. is calculated using S°_{298.15} of H₃PO₄(c) and the ΔH°_m at 298.15°K.

Melting Data. T_m reported by W. H. Ross and R. M. Jones, J. Am. Chem. Soc. 41, 2165 (1925). ΔH°_m from E. P. Egan, Jr., and Z. T. Wakefield (loc. cit.).



Phosphine (PH₃)

(Ideal Gas) Mol. Wt. = 33.999

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈)/T	H° - H ₂₉₈	keal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	6.945	∞	∞
100	7.949	57.622	2.423	6.945	6.945	13.514	13.514
200	8.111	56.877	1.628	6.511	5.992	5.992	5.992
298	8.156	56.238	1.000	5.470	5.470	4.452	4.452
300	8.167	56.238	1.016	5.458	5.458	4.427	4.427
400	8.487	52.997	50.600	4.959	4.827	6.380	6.380
500	11.110	55.347	51.319	2.014	4.262	6.835	6.835
600	12.157	57.468	52.149	3.179	3.776	7.395	7.395
700	13.130	59.527	53.067	4.485	3.306	8.063	8.063
800	13.945	61.227	53.976	5.801	2.843	8.816	8.816
900	14.729	62.918	54.876	7.238	2.397	9.628	9.628
1000	15.368	64.504	55.761	8.744	1.977	10.507	10.507
1100	15.915	65.995	56.624	10.308	1.583	11.455	11.455
1200	16.376	67.400	57.468	11.923	1.216	12.468	12.468
1300	16.776	68.728	58.280	13.592	0.874	13.546	13.546
1400	17.115	69.984	59.071	15.277	0.556	14.684	14.684
1500	17.405	71.175	59.839	17.004	0.262	15.882	15.882
1600	17.655	72.306	60.583	18.757	0.000	17.137	17.137
1700	17.868	73.380	61.303	20.533	-0.222	18.448	18.448
1800	18.058	74.410	62.004	22.330	-0.439	19.814	19.814
1900	18.222	75.391	62.683	24.144	-0.642	21.234	21.234
2000	18.365	76.329	63.342	25.978	-0.832	22.707	22.707
2100	18.491	77.228	63.992	27.817	-1.008	24.232	24.232
2200	18.600	78.092	64.636	29.662	-1.171	25.807	25.807
2300	18.701	78.920	65.269	31.517	-1.321	27.431	27.431
2400	18.794	79.718	65.891	33.411	-1.458	29.103	29.103
2500	18.868	80.487	66.509	35.294	-1.582	30.823	30.823
2600	18.919	81.228	67.125	37.165	-1.693	32.593	32.593
2700	18.962	81.928	67.729	39.022	-1.791	34.413	34.413
2800	19.000	82.596	68.322	40.865	-1.876	36.283	36.283
2900	19.112	83.306	68.915	42.694	-1.948	38.203	38.203
3000	19.159	83.955	69.519	44.507	-2.008	40.173	40.173
3100	19.202	84.584	69.511	46.295	-2.056	42.193	42.193
3200	19.278	85.187	70.481	48.058	-2.093	44.263	44.263
3300	19.311	85.767	70.921	49.794	-2.120	46.383	46.383
3400	19.331	86.363	70.921	51.503	-2.138	48.553	48.553
3500	19.361	86.973	71.370	53.183	-2.148	50.773	50.773
3600	19.349	87.448	71.809	54.837	-2.151	53.043	53.043
3700	19.419	88.517	72.661	56.465	-2.148	55.363	55.363
3800	19.441	89.514	73.479	58.067	-2.138	57.733	57.733
3900	19.462	90.495	74.253	59.643	-2.119	60.153	60.153
4000	19.481	91.468	75.000	61.193	-2.093	62.623	62.623
4100	19.495	92.431	75.753	62.719	-2.060	65.143	65.143
4200	19.516	93.372	76.508	64.223	-2.019	67.713	67.713
4300	19.532	94.291	77.262	65.705	-1.971	70.333	70.333
4400	19.546	95.181	78.018	67.167	-1.916	73.003	73.003
4500	19.558	96.044	78.766	68.605	-1.854	75.723	75.723
4600	19.567	96.881	79.500	69.999	-1.786	78.493	78.493
4700	19.573	97.694	80.221	71.349	-1.712	81.313	81.313
4800	19.576	98.481	80.928	72.657	-1.633	84.183	84.183
4900	19.576	99.244	81.601	73.917	-1.549	87.103	87.103
5000	19.573	99.981	82.244	75.129	-1.460	90.073	90.073
5100	19.567	100.694	82.857	76.293	-1.366	93.093	93.093
5200	19.558	101.381	83.441	77.407	-1.267	96.163	96.163
5300	19.546	102.044	83.996	78.471	-1.163	99.283	99.283
5400	19.532	102.681	84.623	79.485	-1.054	102.453	102.453
5500	19.516	103.291	85.223	80.449	-0.940	105.673	105.673
5600	19.495	103.874	85.783	81.363	-0.821	108.943	108.943
5700	19.468	104.431	86.357	82.227	-0.697	112.263	112.263
5800	19.437	104.964	86.944	83.041	-0.569	115.633	115.633
5900	19.400	105.473	87.544	83.805	-0.437	119.053	119.053
6000	19.357	105.958	88.157	84.519	-0.301	122.523	122.523

June 30, 1962

H₃P

(IDEAL GAS)

MOL. WT. = 33.999

$$\Delta H_f^o 298.15 = +5.5 \pm 0.4 \text{ kcal/mole}^{-1}$$

$$S_{298.15}^o = 50.24 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

Point Group C_{3v}

Vibrational Levels and Multiplicities	ω, cm ⁻¹
2332.9 (1)	992 (1)
2327.7 (2)	1122.4 (2)

P-H distance 1.42 Å H-P-H angle = 93° 50' σ = 3

$$I_A = I_B = 6.29 \times 10^{-40} \text{ g cm}^2 \quad I_C = 7.24 \times 10^{-40} \text{ g cm}^2$$

Heat of Formation

The heat of formation was derived by S. R. Gunn and L. G. Green, J. Phys. Chem., **65**, 779 (1961). In order to obtain the $\Delta H_f^o 298.15$ they measured the heat of explosive decomposition of phosphine gas. There is a good deal of uncertainty about the heat of formation of PH₃(g), for instance:

$$\Delta H_f^o 298.15 = +3.6 \text{ kcal mole}^{-1}$$

The heat of reaction between gaseous PH₃ and saturated bromine water. M. J. Ogier, Ann. Chim. Phys., **20**, 5 (1880).

$$\Delta H_f^o 298.15 = +6.3 \text{ kcal mole}^{-1}$$

The heat of combustion of PH₃(g) in O₂(g) to form H₃PO₄. M. P. Lemoult, Compt. Rend., **115**, 374 (1907).

$$\Delta H_f^o 298.15 = -2.34 \text{ kcal mole}^{-1}$$

Equilibrium data of W. N. Ipatiew, and A. W. Frost, Ber. dtsh. chem. Ges., **63B**, 1104 (1930). Their data showed a wide variation in ΔH , as much as 11 kcal mole⁻¹.

$$\Delta H_f^o 298.15 = +1.6 \text{ kcal mole}^{-1}$$

National Bureau of Standards, Report No. 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds," 1 January 1962 (page 80-91).

The heats of formation have been reviewed by T. L. Cottrell, "The Strength of Chemical Bonds," Butterworth's Scientific Publications, London, (1958); and by F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of The Chemical Substances," Reinhold Publishing Corp., New York (1936).

The heat of formation selected was, $+1.3 \pm 0.4 \text{ kcal mole}^{-1}$, as reported by Gunn and Green (loc. cit.). The selected heat of formation was based on white (α) phosphorus and thus required an adjustment for the red (V) phosphorus reference state.

Heat Capacity and Entropy

The fundamental wave number and degeneracy assignments are from the infrared spectral data by V. N. McConaghie and H. H. Nielsen, J. Chem. Phys., **21**, 1836, (1953). The molecular constants are those obtained from infrared data by H. H. Nielsen, J. Chem. Phys., **20**, 759 (1952). Nielsen (loc. cit.) has reported the molecular constants after calculating the Coriolis coupling effect between the wave numbers 2 and 4, or (992 cm⁻¹) and (1122.4 cm⁻¹).

H₃P

INTERIM TABLE

T. °K.	C _p ^o	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$\int_0^T C_p dT$ S° - (F° - H _{298°)/T}	H° - H _{298°}	ΔH_f°	ΔF_f°	Log K _p
0							
100	14.540	27.000	27.000	.000	- 48.300	- 26.760	19.689
200	14.570	27.121	27.000	.036	- 48.300	- 26.766	19.811
300	21.271	32.960	29.331	2.036	- 48.300	- 26.801	10.545
400	21.271	37.910	29.331	4.290	- 51.688	- 10.972	4.796
500	22.980	42.251	31.130	6.673	- 55.710	- 2.003	.730
600	24.600	46.184	33.003	9.227	- 55.373	6.925	- 2.162
700	26.400	49.622	34.961	11.953	- 54.961	21.762	- 5.971
800	28.330	52.636	36.733	14.826	- 54.439	31.306	- 7.279
900	29.670	55.472	38.346	17.826	- 52.495	41.936	- 6.332
1000	31.570	59.562	40.317	21.169	- 51.403	50.475	- 9.152
1100	34.300	62.533	42.045	24.895	- 50.161	58.915	- 10.866
1200	35.000	65.389	43.732	28.154	- 48.509	75.507	- 11.001
1300	36.336	68.120	45.377	31.440	- 46.133	83.661	- 11.427
1400	37.304	70.717	46.981	35.404	- 43.224	91.734	- 11.763
1500	39.161	73.176	48.542	39.411	- 40.007	99.724	- 12.108
1600	40.042	75.465	50.059	43.224	- 36.586	107.506	- 12.461
1700	41.558	77.648	51.533	47.007	- 33.154	115.506	- 12.821
1800	42.711	79.657	52.961	50.724	- 29.724	123.506	- 13.181
1900	43.500	81.411	54.343	54.337	- 26.293	131.506	- 13.541
2000							

March 31, 1962

Ammonium Iodide (NH₄I)

(Crystal)

Mol. Wt. = 144.95

ΔH_f° 298.15 = -48.30 kcal. mole⁻¹

$S_{298.15}^\circ$ = 27.0 ± 1.5 cal. deg.⁻¹ mole⁻¹

ΔH_g° 798 = 40.280 kcal. mole⁻¹

T_g° = 260°K

ΔH_t° = 0.70 kcal. mole⁻¹

T_m° = 824°K

ΔH_m° = [5.0] kcal. mole⁻¹

ΔH_f° 298.15, T_g° , and T_m° . Taken from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties". $S_{298.15}^\circ$ was taken from K. K. Kelley, U. S. Bureau of Mines Bulletin 564, (1960). Sublimation data from N. W. Luft, Ind. Chemist, 31, 502 (1955).

Heat Capacity. Data extrapolated from Simon, Simeon, and Ruhemann Z. Phys. Chemie, 129, 339 (1927).

Hydrazine (N₂H₄)

(Liquid)

Mol. Wt. = 32.04528

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	(F°-H ₂₉₈)/T	II°-H ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0								
100	20.850	5.028	49.091	- 4.406	11.611	19.797	- 43.263	
200	22.250	19.910	31.166	- 2.451	11.857	27.880	- 30.484	
298	23.623	26.050	26.050	- .000	12.100	35.654	- 26.163	
300	23.650	26.106	26.050		12.106	35.640	- 26.108	
400	25.060	36.236	20.000	0.64	13.049	33.701	- 23.876	
500	27.860	42.218	31.861	5.179	13.054	51.444	- 22.485	
600	30.060	47.492	34.034	8.075	13.838	59.052	- 21.509	

HYDRAZINE (N₂H₄)

(LIQUID)

MOL. WT. = 32.04528

$$S_{298.15} = 29.05 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 274.69^\circ\text{K.}$$

$$T_b = 386.9^\circ\text{K.}$$

$$\Delta H_f^\circ 298.15 = 12.10 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = 3.025 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^\circ = 9.70 \text{ kcal. mole}^{-1}$$

Heat of Formation.

A. M. Hughes, R. J. Corruccini and E. C. Ollbert, J. Am. Chem. Soc. **61**, 2639 (1939), measured the heats of combustion of hydrazine and hydrazine monohydrate. The data, adjusted as suggested by L. O. Cole and E. C. Ollbert, J. Am. Chem. Soc. **73**, 5423 (1951), are summarized below. Heats of solution determined by V. C. Bushnell, A. M. Hughes and E. C. Ollbert, J. Am. Chem. Soc. **59**, 2142 (1937) interrelate N₂H₄(l) and N₂H₄·H₂O(l). An intermediate value was selected from the resulting heats of formation.

Source	Reaction	ΔH _f ° 298	ΔH _f ° 298
Hughes	N ₂ H ₄ (l) + O ₂ (g) → N ₂ (g) + 2H ₂ O(l)	-148.68 ± 0.06	12.05
Hughea	N ₂ H ₄ ·H ₂ O(l) + O ₂ (g) → N ₂ (g) + 3H ₂ O(l)	-147.00 ± 0.06	—
Bushnell	N ₂ H ₄ (l) + H ₂ O(l) → N ₂ H ₄ ·H ₂ O(l)	-1.80	12.17*

*From combination of second and third reactions.

Heat Capacity and Entropy.

Heat capacities (12-340°K) of hydrazine crystal and liquid were determined by D. W. Scott, O. D. Oliver, M. E. Oras, W. M. Hubbard and H. M. Huffman, J. Am. Chem. Soc. **71**, 2293 (1949). Values beyond the experimental range for the liquid were extrapolated linearly. The entropy was obtained from the heat of melting and the smoothed heat capacities of the crystal using S₁₂° = 0.023 cal. deg.⁻¹ mole⁻¹.

Melting Data.

Taken from Scott et al., loc. cit.

Vaporization Data.

The normal boiling point and heat of vaporization are those calculated for the ideal gas from these tables. The boiling point found for the real gas (387.3°K) by W. Hieber and A. Woerner, Z. Elektrochem. **40**, 252 (1934) is in good agreement. The selected heat of vaporization, ΔH_v° = 10.69 kcal. mole⁻¹, is based on the vapor pressure data of Scott et al., loc. cit., series III. Vapor pressure measurements of Hieber and Woerner, loc. cit., and E. T. Cheng and N. A. Okken, AD-458286, Defense Documentation Center, January, 1964, are in satisfactory agreement as shown below.

Source	Temp. Range °K.	ΔH _v ° 298 (kcal. mole ⁻¹) 2nd Law	3rd Law e.u.	3rd Law Drift
Scott, et al. (1949)	273-343	10.683 ± 0.003	10.696	0.05 ± 0.01
Cheng, Gocken (1964)	276-325	10.40 ± 0.03	10.68	0.91 ± 0.09
Hieber, Woerner (1934)	293-387	10.82 ± 0.03	10.71	-0.33 ± 0.07

The second law-third law consistency of Scott et al. reflects the use of these data in selection of the gas phase functions (see H₄N₂ gas).

Dec. 31, 1965

H₄N₂

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	(H ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹	ΔH _f ^o	Log K _p
0	-0.000	0.000	INFINITE	-2.755	26.155	INFINITE	
100	8.214	66.180	-1.956	24.751	26.878	-62.891	
200	9.718	52.717	-0.058	23.730	31.192	-62.868	
298	12.145	57.030	+0.000	22.790	38.042	-27.684	
300	12.194	57.106	-0.023	22.776	38.136	-27.781	
400	16.767	60.971	-2.033	21.522	43.135	-23.698	
500	16.861	64.498	-5.484	21.522	48.772	-21.317	
600	18.538	67.726	-59.843	4.730	21.183	54.257	-19.762
700	19.910	70.690	-61.184	6.954	20.975	54.780	-18.666
800	21.111	73.470	-63.897	10.866	20.849	54.842	-17.478
900	22.111	75.970	-65.225	13.124	20.897	54.901	-17.216
1000	23.030	78.348	-65.225	13.124	20.897	54.901	-16.709
1100	23.854	80.583	-66.570	15.469	21.002	54.911	-16.293
1200	24.592	82.690	-67.781	17.892	21.156	54.915	-15.945
1300	25.256	84.684	-68.862	20.390	21.326	54.915	-15.654
1400	25.862	86.579	-69.830	22.960	21.578	54.915	-15.389
1500	26.437	88.380	-70.713	25.551	21.826	54.915	-15.164
1600	26.836	90.097	-72.465	28.211	22.094	54.915	-14.963
1700	27.254	91.737	-74.151	30.916	22.382	54.915	-14.785
1800	27.690	93.300	-75.780	33.640	22.698	54.915	-14.628
1900	28.146	94.798	-77.359	36.400	23.042	54.915	-14.478
2000	28.628	96.250	-78.894	39.200	23.421	54.915	-14.345
2100	29.135	97.635	-80.390	42.000	23.835	54.915	-14.223
2200	29.666	98.968	-81.843	44.800	24.285	54.915	-14.110
2300	30.221	100.250	-83.250	47.600	24.770	54.915	-14.000
2400	30.797	101.480	-84.610	50.400	25.290	54.915	-13.890
2500	31.394	102.684	-85.920	53.200	25.845	54.915	-13.781
2600	31.995	103.838	-87.180	56.000	26.435	54.915	-13.673
2700	32.600	104.955	-88.400	58.800	27.060	54.915	-13.566
2800	33.209	106.030	-89.580	61.600	27.720	54.915	-13.460
2900	33.822	107.064	-90.720	64.400	28.415	54.915	-13.355
3000	34.439	108.100	-91.820	67.200	29.145	54.915	-13.250
3100	35.060	109.086	-92.880	70.000	29.910	54.915	-13.145
3200	35.685	110.000	-93.900	72.800	30.710	54.915	-13.040
3300	36.314	110.840	-94.880	75.600	31.545	54.915	-12.935
3400	36.947	111.610	-95.820	78.400	32.415	54.915	-12.830
3500	37.584	112.310	-96.720	81.200	33.320	54.915	-12.725
3600	38.225	112.940	-97.580	84.000	34.260	54.915	-12.620
3700	38.870	113.500	-98.400	86.800	35.230	54.915	-12.515
3800	39.519	114.000	-99.180	89.600	36.230	54.915	-12.410
3900	40.172	114.450	-99.920	92.400	37.260	54.915	-12.305
4000	40.829	114.850	-100.620	95.200	38.320	54.915	-12.200
4100	41.490	115.200	-101.280	98.000	39.410	54.915	-12.095
4200	42.155	115.500	-101.900	100.800	40.530	54.915	-11.990
4300	42.824	115.750	-102.480	103.600	41.680	54.915	-11.885
4400	43.496	115.950	-103.020	106.400	42.860	54.915	-11.780
4500	44.171	116.100	-103.520	109.200	44.070	54.915	-11.675
4600	44.849	116.200	-104.000	112.000	45.310	54.915	-11.570
4700	45.530	116.250	-104.440	114.800	46.580	54.915	-11.465
4800	46.213	116.250	-104.840	117.600	47.880	54.915	-11.360
4900	46.900	116.200	-105.200	120.400	49.210	54.915	-11.255
5000	47.590	116.100	-105.520	123.200	50.570	54.915	-11.150
5100	48.282	115.950	-105.800	126.000	51.960	54.915	-11.045
5200	48.976	115.750	-106.040	128.800	53.380	54.915	-10.940
5300	49.672	115.500	-106.240	131.600	54.830	54.915	-10.835
5400	50.370	115.200	-106.400	134.400	56.310	54.915	-10.730
5500	51.070	114.850	-106.520	137.200	57.820	54.915	-10.625
5600	51.772	114.450	-106.600	140.000	59.360	54.915	-10.520
5700	52.476	114.000	-106.640	142.800	60.930	54.915	-10.415
5800	53.182	113.500	-106.640	145.600	62.530	54.915	-10.310
5900	53.890	112.950	-106.600	148.400	64.160	54.915	-10.205
6000	54.600	112.350	-106.520	151.200	65.820	54.915	-10.100

Dec. 31, 1960; Dec. 31, 1965

HYDRAZINE (N₂H₄)

(IDEAL GAS)

Point Group C₂ΔH_f^o = 26.16 kcal. mole⁻¹ΔH_f^o 298.15 = 22.79 ± 0.2 kcal. mole⁻¹S_{298.15} = 57.03 ± 0.4 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

w _i , cm. ⁻¹	w _i , cm. ⁻¹	w _i , cm. ⁻¹
------------------------------------	------------------------------------	------------------------------------

3350	875	3280
------	-----	------

1312	780	1275
------	-----	------

1098	337	966
------	-----	-----

3350	3350	3350
------	------	------

1098	1098	1098
------	------	------

337	337	337
-----	-----	-----

780	780	780
-----	-----	-----

1275	1275	1275
------	------	------

3280	3280	3280
------	------	------

966	966	966
-----	-----	-----

3350	3350	3350
------	------	------

1098	1098	1098
------	------	------

337	337	337
-----	-----	-----

780	780	780
-----	-----	-----

1275	1275	1275
------	------	------

3280	3280	3280
------	------	------

966	966	966
-----	-----	-----

3350	3350	3350
------	------	------

1098	1098	1098
------	------	------

337	337	337
-----	-----	-----

780	780	780
-----	-----	-----

1275	1275	1275
------	------	------

3280	3280	3280
------	------	------

966	966	966
-----	-----	-----

3350	3350	3350
------	------	------

1098	1098	1098
------	------	------

337	337	337
-----	-----	-----

780	780	780
-----	-----	-----

1275	1275	1275
------	------	------

3280	3280	3280
------	------	------

966	966	966
-----	-----	-----

3350	3350	3350
------	------	------

1098	1098	1098
------	------	------

337	337	337
-----	-----	-----

780	780	780
-----	-----	-----

1275	1275	1275
------	------	------

3280	3280	3280
------	------	------

966	966	966
-----	-----	-----

3350	3350	3350
------	------	------

1098	1098	1098
------	------	------

337	337	337
-----	-----	-----

780	780	780
-----	-----	-----

1275	1275	1275
------	------	------

3280	3280	3280
------	------	------

966	966	966
-----	-----	-----

3350	3350	3350
------	------	------

1098	1098	1098
------	------	------

337	337	337
-----	-----	-----

780	780	780
-----	-----	-----

ΔH_f^o = 26.16 kcal. mole⁻¹ΔH_f^o 298.15 = 22.79 ± 0.2 kcal. mole⁻¹S_{298.15} = 57.03 ± 0.4 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

w_i, cm.⁻¹w_i, cm.⁻¹w_i, cm.⁻¹

3350

875

3280

1312

780

1275

337

966

3350

1098

337

780

1275

3280

966

3350

1098

337

780

1275

3280

966

3350

1098

337

780

1275

3280

966

3350

1098

337

780

1275

3280

966

3350

1098

337

780

1275

3280

966

3350

1098

337

ΔH_f^o = 26.16 kcal. mole⁻¹ΔH_f^o 298.15 = 22.79 ± 0.2 kcal. mole⁻¹S_{298.15} = 57.03 ± 0.4 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

w_i, cm.⁻¹w_i, cm.⁻¹w_i, cm.⁻¹

3350

875

3280

1312

780

1275

337

966

3350

1098

337

780

1275

3280

966

3350

1098

337

780



(Ideal Gas) Mol. Wt. = 32.122

Silane (SiH_4) (Ideal Gas)

Mol. Wt. = 32.122
 $\Delta H_f^\circ 298.15 = 7.3 \pm 0.3 \text{ kcal. mole}^{-1}$
 $\Delta S_f^\circ 298.15 = 48.789 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Point Group T_d

Vibrational Frequencies and Degeneracies

$\omega \text{ cm.}^{-1}$	
2183 (3)	
910 (3)	
978 (2)	
2187 (1)	

SI-H distance = $1.457 \text{ \AA}$ H-Si-H angle = $109^\circ 28'$ $\epsilon = 12$
 Product of Moments of Inertia: $I_{ABC} = 0.84659 \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation, $\Delta H_f^\circ 298.15$ was determined by S. Gunn and L. Greene, J. Phys. Chem. **65**, 773 (1961). A value of $7.8 \text{ kcal. mole}^{-1}$ was selected by J. S. Gordan, Thiel Chemical Corp., Reaction Motors Division, Danville, N. J., "Thermodynamic Data for Combustion Products", January, 1960.

Heat Capacity and Entropy. Molecular constants were taken from J. S. Gordan, op. cit., G. Janz and Y. Mikawa, Bull. Chem. Soc. Japan, **34**, 1485 (1961) reported slightly different values for the vibrational levels.

T, K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	10.000	INFINITE	2.519	10.085	INFINITE	10.085	INFINITE
100	12.303	40.216	1.149	7.017	7.541	7.541	7.541
200	14.139	55.035	2.473	6.394	7.541	7.541	7.541
298	16.236	68.789	4.879	7.800	7.541	7.541	7.541
300	16.274	68.852	4.879	7.784	7.541	7.541	7.541
400	18.303	82.088	4.216	7.017	7.541	7.541	7.541
500	19.139	92.035	3.473	6.394	7.541	7.541	7.541
600	19.751	99.759	3.143	3.969	5.917	19.473	7.093
700	20.186	105.294	2.822	5.616	5.570	21.763	6.794
800	20.344	109.664	2.542	7.392	5.332	24.093	6.581
900	20.356	112.885	2.278	9.278	5.180	26.449	6.422
1000	20.208	115.972	2.024	11.258	5.099	28.816	6.297
1100	20.024	118.925	1.782	13.315	5.072	31.190	6.194
1200	19.805	121.777	1.549	15.439	5.090	33.564	6.113
1300	19.552	124.532	1.321	17.617	5.138	35.934	6.041
1400	19.264	127.191	1.096	19.842	5.209	38.302	5.979
1500	18.944	129.752	0.874	22.107	5.293	40.663	5.924
1600	18.597	132.213	0.652	24.406	5.385	43.016	5.875
1700	18.230	134.576	0.430	26.733	5.480	45.376	5.846
1800	17.844	136.844	0.208	29.086	5.573	47.746	5.821
1900	17.440	139.011	0.000	31.460	5.666	50.116	5.800
2000	17.019	141.079	0.000	33.852	5.759	52.486	5.780
2100	16.584	143.046	0.000	36.262	5.852	54.856	5.760
2200	16.135	144.911	0.000	38.686	5.945	57.226	5.740
2300	15.672	146.674	0.000	41.122	6.038	59.596	5.720
2400	15.197	148.335	0.000	43.570	6.131	61.966	5.700
2500	14.712	149.896	0.000	46.028	6.224	64.336	5.680
2600	14.217	151.357	0.000	48.495	6.317	66.706	5.660
2700	13.712	152.718	0.000	50.971	6.410	69.076	5.640
2800	13.197	153.979	0.000	53.453	6.503	71.446	5.620
2900	12.672	155.140	0.000	55.942	6.596	73.816	5.600
3000	12.137	156.201	0.000	58.436	6.689	76.186	5.580
3100	11.592	157.162	0.000	60.938	6.782	78.556	5.560
3200	11.037	158.023	0.000	63.444	6.875	80.926	5.540
3300	10.472	158.784	0.000	65.954	6.968	83.296	5.520
3400	9.897	159.445	0.000	68.468	7.061	85.666	5.500
3500	9.312	160.006	0.000	70.986	7.154	88.036	5.480
3600	8.717	160.467	0.000	73.508	7.247	90.406	5.460
3700	8.112	160.828	0.000	76.033	7.340	92.776	5.440
3800	7.497	161.089	0.000	78.561	7.433	95.146	5.420
3900	6.872	161.250	0.000	81.091	7.526	97.516	5.400
4000	6.247	161.311	0.000	83.621	7.619	99.886	5.380
4100	5.612	161.272	0.000	86.150	7.712	102.256	5.360
4200	4.967	161.133	0.000	88.679	7.805	104.626	5.340
4300	4.312	160.894	0.000	91.208	7.898	106.996	5.320
4400	3.647	160.555	0.000	93.736	7.991	109.366	5.300
4500	2.982	160.116	0.000	96.261	8.084	111.736	5.280
4600	2.307	159.577	0.000	98.786	8.177	114.106	5.260
4700	1.622	158.938	0.000	101.308	8.270	116.476	5.240
4800	0.937	158.199	0.000	103.826	8.363	118.846	5.220
4900	0.252	157.360	0.000	106.341	8.456	121.216	5.200
5000	0.000	156.421	0.000	108.850	8.549	123.586	5.180
5100	0.000	155.382	0.000	111.359	8.642	125.956	5.160
5200	0.000	154.243	0.000	113.868	8.735	128.326	5.140
5300	0.000	152.904	0.000	116.377	8.828	130.696	5.120
5400	0.000	151.365	0.000	118.886	8.921	133.066	5.100
5500	0.000	149.726	0.000	121.395	9.014	135.436	5.080
5600	0.000	147.987	0.000	123.904	9.107	137.806	5.060
5700	0.000	146.148	0.000	126.413	9.200	140.176	5.040
5800	0.000	144.209	0.000	128.922	9.293	142.546	5.020
5900	0.000	142.170	0.000	131.431	9.386	144.916	5.000
6000	0.000	140.031	0.000	133.940	9.479	147.286	4.980

December 31, 1960.



T, °K.	C _p	S°	$-(F^{\circ}-H^{\circ}_{298})/T$	$H^{\circ}-H^{\circ}_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	0.000	INFINITE	-	2.233	.000	.000	.000
100	5.797	6.899	12.148	1.268	.000	.000	.000
200	6.519	13.148	12.188	1.268	.000	.000	.000
298	6.867	18.171	18.171	.000	.000	.000	.000
300	6.864	18.212	18.171	.012	.000	.000	.000
400	6.855	21.575	18.171	.463	.000	.000	.000
500	6.835	21.570	18.171	1.325	.000	.000	.000
600	6.806	22.752	19.463	1.974	.000	.000	.000
700	6.768	24.034	22.250	16.649	.000	.000	.000
800	6.768	25.498	25.266	17.166	.000	.000	.000
900	6.768	27.253	27.660	18.135	.000	.000	.000
1000	6.768	29.406	29.687	18.135	.000	.000	.000
1100	6.768	31.338	31.338	18.636	.000	.000	.000
1200	6.768	32.768	32.768	19.133	.000	.000	.000
1300	6.768	34.110	34.110	19.630	.000	.000	.000
1400	6.768	35.362	35.362	20.127	.000	.000	.000
1500	6.768	36.521	36.521	20.623	.000	.000	.000
1600	6.768	37.591	37.591	21.120	.000	.000	.000
1700	6.768	38.572	38.572	21.617	.000	.000	.000
1800	6.768	39.465	39.465	22.114	.000	.000	.000
1900	6.768	40.270	40.270	22.610	.000	.000	.000
2000	6.768	40.985	40.985	23.107	.000	.000	.000
2100	6.768	41.612	41.612	23.604	.000	.000	.000
2200	6.768	42.150	42.150	24.101	.000	.000	.000
2300	6.768	42.698	42.698	24.598	.000	.000	.000
2400	6.768	43.256	43.256	25.094	.000	.000	.000
2500	6.768	43.824	43.824	25.591	.000	.000	.000
2600	6.768	44.401	44.401	26.088	.000	.000	.000
2700	6.768	44.988	44.988	26.585	.000	.000	.000
2800	6.768	45.585	45.585	27.082	.000	.000	.000
2900	6.768	46.192	46.192	27.578	.000	.000	.000
3000	6.768	46.809	46.809	28.075	.000	.000	.000
3100	6.768	47.436	47.436	28.572	.000	.000	.000
3200	6.768	48.073	48.073	29.069	.000	.000	.000
3300	6.768	48.720	48.720	29.566	.000	.000	.000
3400	6.768	49.377	49.377	30.062	.000	.000	.000
3500	6.768	50.044	50.044	30.559	.000	.000	.000
3600	6.768	50.721	50.721	31.056	.000	.000	.000
3700	6.768	51.408	51.408	31.553	.000	.000	.000
3800	6.768	52.105	52.105	32.050	.000	.000	.000
3900	6.768	52.812	52.812	32.547	.000	.000	.000
4000	6.768	53.529	53.529	33.044	.000	.000	.000
4100	6.768	54.256	54.256	33.541	.000	.000	.000
4200	6.768	54.993	54.993	34.038	.000	.000	.000
4300	6.768	55.740	55.740	34.535	.000	.000	.000
4400	6.768	56.497	56.497	35.032	.000	.000	.000
4500	6.768	57.264	57.264	35.529	.000	.000	.000
4600	6.768	58.041	58.041	36.027	.000	.000	.000
4700	6.768	58.828	58.828	36.525	.000	.000	.000
4800	6.768	59.625	59.625	37.023	.000	.000	.000
4900	6.768	60.432	60.432	37.521	.000	.000	.000
5000	6.768	61.249	61.249	38.019	.000	.000	.000
5100	6.768	62.076	62.076	38.518	.000	.000	.000
5200	6.768	62.913	62.913	39.018	.000	.000	.000
5300	6.768	63.760	63.760	39.518	.000	.000	.000
5400	6.768	64.617	64.617	40.018	.000	.000	.000
5500	6.768	65.484	65.484	40.519	.000	.000	.000
5600	6.768	66.361	66.361	41.021	.000	.000	.000
5700	6.768	67.248	67.248	41.523	.000	.000	.000
5800	6.768	68.145	68.145	42.027	.000	.000	.000
5900	6.768	69.052	69.052	42.532	.000	.000	.000
6000	6.768	69.969	69.969	43.037	.000	.000	.000

December 31, 1961

MERCURY (Hg)

(REFERENCE STATE)

MOL. WT. = 200.61

The reference state is chosen as follows:

O° to 234.29°K Crystal

234.29° to 629.73°K Liquid

629.73° to 800°K Ideal Gas

$$S^{\circ}_{298.15} = 18.171 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H^{\circ}_{f, 298.15} = 14.652 \pm 0.015 \text{ kcal. mole}^{-1}$$

$$\Delta H^{\circ}_m = 0.5486 \pm 0.0001 \text{ kcal. mole}^{-1}$$

$$\Delta H^{\circ}_{f, 629.73} = 14.133 \pm 0.020 \text{ kcal. mole}^{-1}$$

$$T_m = 234.29^{\circ}\text{K}$$

$$T_b = 629.73^{\circ}\text{K}$$

Heat Capacity.

The heat capacities of P. L. Smith and N. M. Wolcott, Phil. Mag. 1 (8), 854 (1956), 1.2°-20.2°K, R. H. Busey and W. P. Olsauque, J. Am. Chem. Soc. 75, 806 (1953), 15°-350°K, and N. B. Douglass, A. P. Ball, and D. C. Oirmings, J. Research Natl. Bur. Standards, 46, 334 (1951), 300°-770°K, have been smoothly joined. There is fair agreement between the selected values and those of O. L. Pickard and P. E. Simon, Proc. Phys. Soc. A61, 1 (1948), L. G. Carpenter and P. H. Oakley, Phil. Mag. 12, 511 (1931), L. O. Carpenter and L. G. Stoodley, Phil. Mag. 10, 249 (1930), E. Cohen, C. I. Krushner, and A. L. Moenvald, Z. phys. Chem. A95, 437 (1920), A. L. Dixon and W. H. Rodenbush, J. Am. Chem. Soc. 49, 1182 (1927), P. Simon, Z. phys. Chem. 107, 282 (1923), Ann. Physik 68, 241 (1922), J. N. Brünsted, Z. Elektrochem. 16, 714 (1912), and P. Pollitzer, Z. Elektrochem. 17, 5 (1911).

Melting Data.

From Busey and Olsauque, loc. cit.

Boiling Point and Heat of Vaporization.

Calculated from the vapor pressures determined by K. D. Carlson, R. J. Thorn, and P. W. Gilles, private communication, October 1961, P. M. Ernberger and H. W. Pitman, Rev. Sci. Instrum. 26, 584 (1955), P. H. Spedding and J. L. Dye, J. Phys. Chem. 59, 561 (1955), and J. A. Beattie, B. E. Blaisdell, and J. Kaminsky, Proc. Am. Acad. Arts Sciences 71, 375 (1937). Earlier measurements are less accurate and have not been used. Gas imperfection has been allowed for by the method of Busey and Olsauque, loc. cit.

Hg

Mercury (Hg)

(Liquid) Mol. Wt. = 200.61

MOL. WT. = 200.61

(LIQUID)

MERCURY (Hg)

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0						
100						
200						
298	9.687	18.171	.000	.000	.000	.000
300	9.688	18.212	.012	.000	.000	.000
400	9.552	20.115	18.431	.000	.000	.000
500	9.495	21.570	18.919	.000	.000	.000
600	9.446	22.752	19.463	.000	.000	.000
700	9.393	23.738	20.006	.000	.000	.000
800	9.337	24.581	20.506	.000	.000	.000
900	9.277	25.311	21.030	.000	.000	.000
1000	9.212	25.941	21.504	.000	.000	.000
1100	9.147	26.463	21.953	.000	.000	.000
1200	9.082	26.898	22.379	.000	.000	.000
1300	9.017	27.258	22.789	.000	.000	.000
1400	8.952	27.548	23.181	.000	.000	.000
1500	8.887	27.782	23.556	.000	.000	.000
1600	8.822	27.972	23.916	.000	.000	.000
1700	8.757	28.128	24.261	.000	.000	.000
1800	8.692	28.258	24.591	.000	.000	.000
1900	8.627	28.363	24.907	.000	.000	.000
2000	8.562	28.445	25.209	.000	.000	.000

$\Delta H_f^\circ 298.15 = 0$
 $S_{298.15}^\circ = 18.171 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 234.29^\circ \text{K}$
 $T_b = 629.73^\circ \text{K}$

$\Delta H_v^\circ 298.15 = 14.651 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta H_m^\circ = 0.5486 \pm 0.0001 \text{ kcal. mole}^{-1}$
 $\Delta H_v^\circ 629.73 = 14.134 \pm 0.020 \text{ kcal. mole}^{-1}$

See notes on reference state for sources of data.

December 31, 1961

Hg

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T cal. mole ⁻¹	H°-H° ₂₉₈ ΔH° _f kcal. mole ⁻¹	ΔF° Log K _p
0	.000	INFINITE	1.481	INFINITE
100	4.948	36.366	15.404	15.404
200	4.948	36.211	15.493	12.745
298	4.948	36.160	15.493	10.114
300	4.948	36.152	15.493	10.114
300	4.948	41.794	.000	7.609
300	4.948	41.824	.000	7.565
400	4.948	41.794	14.649	7.565
500	4.948	41.794	14.649	5.511
600	4.948	41.794	14.649	5.511
700	4.948	41.794	14.649	5.511
800	4.948	41.794	14.649	5.511
900	4.948	41.794	14.649	5.511
1000	4.948	41.794	14.649	5.511
1100	4.948	41.794	14.649	5.511
1200	4.948	41.794	14.649	5.511
1300	4.948	41.794	14.649	5.511
1400	4.948	41.794	14.649	5.511
1500	4.948	41.794	14.649	5.511
1600	4.948	41.794	14.649	5.511
1700	4.948	41.794	14.649	5.511
1800	4.948	41.794	14.649	5.511
1900	4.948	41.794	14.649	5.511
2000	4.948	41.794	14.649	5.511
2100	4.948	41.794	14.649	5.511
2200	4.948	41.794	14.649	5.511
2300	4.948	41.794	14.649	5.511
2400	4.948	41.794	14.649	5.511
2500	4.948	41.794	14.649	5.511
2600	4.948	41.794	14.649	5.511
2700	4.948	41.794	14.649	5.511
2800	4.948	41.794	14.649	5.511
2900	4.948	41.794	14.649	5.511
3000	4.948	41.794	14.649	5.511
3100	4.948	41.794	14.649	5.511
3200	4.948	41.794	14.649	5.511
3300	4.948	41.794	14.649	5.511
3400	4.948	41.794	14.649	5.511
3500	4.948	41.794	14.649	5.511
3600	4.948	41.794	14.649	5.511
3700	4.948	41.794	14.649	5.511
3800	4.948	41.794	14.649	5.511
3900	4.948	41.794	14.649	5.511
4000	4.948	41.794	14.649	5.511
4100	4.948	41.794	14.649	5.511
4200	4.948	41.794	14.649	5.511
4300	4.948	41.794	14.649	5.511
4400	4.948	41.794	14.649	5.511
4500	4.948	41.794	14.649	5.511
4600	4.948	41.794	14.649	5.511
4700	4.948	41.794	14.649	5.511
4800	4.948	41.794	14.649	5.511
4900	4.948	41.794	14.649	5.511
5000	4.948	41.794	14.649	5.511
5100	4.948	41.794	14.649	5.511
5200	4.948	41.794	14.649	5.511
5300	4.948	41.794	14.649	5.511
5400	4.948	41.794	14.649	5.511
5500	4.948	41.794	14.649	5.511
5600	4.948	41.794	14.649	5.511
5700	4.948	41.794	14.649	5.511
5800	4.948	41.794	14.649	5.511
5900	4.948	41.794	14.649	5.511
6000	4.948	41.794	14.649	5.511

December 31, 1961

 $\Delta H_{f0}^{\circ} = 15.404 \pm 0.015$ kcal. mole⁻¹ $\Delta H_{f298.15}^{\circ} = 14.652 \pm 0.015$ kcal. mole⁻¹Ground State Configuration $1s^2$ $S_{298.15}^{\circ} = 41.794$ cal. deg⁻¹ mole⁻¹

Electronic Levels and Multiplicities

E_1 , cm ⁻¹	E_1 , cm ⁻¹	E_1 , cm ⁻¹	E_1 , cm ⁻¹
0	1	5	12
37645	1	69826	79703
39412	3	71240	80603
44043	5	71364	81510
54069	3	73468	82622
62350	3	76812	83580
63928	1	77191	601

Heat of Formation.

The same as the heat of vaporization; see notes on reference state.

Heat Capacity and Entropy.

The electronic levels and multiplicities are from C. E. Moore, Natl. Bur. Standards Circular 487, Vol. 3 (1956).

Mercury Moniodide (HgI)

(Ideal Gas) Mol. Wt. = 327.52 INTERIM TABLE

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f keal. mole ⁻¹	ΔF _f keal. mole ⁻¹	Log K _p
0	∞	∞	∞	33.179	33.179	∞
100	6.549	57.402	1.742	33.176	29.054	63.495
200	6.929	63.877	6.883	32.684	25.052	27.374
298	7.055	67.068	10.000	31.900	21.459	15.729
300	7.056	67.128	10.017	31.893	21.395	15.586
400	7.139	69.781	17.424	29.556	18.026	9.848
500	7.208	71.788	24.060	26.060	15.670	6.849
600	7.272	73.473	29.859	23.686	14.007	5.102
700	7.333	74.907	34.623	21.691	13.966	4.354
800	7.387	76.157	38.527	19.650	14.155	3.615
900	7.435	77.257	41.700	17.653	14.455	2.885
1000	7.478	78.265	44.240	15.775	15.775	2.165
1100	7.517	79.195	46.279	14.007	14.007	1.447
1200	7.552	80.050	47.837	12.453	12.453	0.729
1300	7.583	80.833	48.993	11.096	11.096	0.011
1400	7.611	81.557	49.766	9.937	9.937	-0.711
1500	7.636	82.227	50.259	8.971	8.971	-1.431
1600	7.658	82.847	50.583	8.186	8.186	-2.151
1700	7.677	83.420	50.757	7.543	7.543	-2.871
1800	7.693	83.950	50.800	7.027	7.027	-3.591
1900	7.707	84.442	50.730	6.613	6.613	-4.311
2000	7.719	84.895	50.560	6.284	6.284	-5.031
2100	7.729	85.316	50.300	6.027	6.027	-5.751
2200	7.737	85.703	49.960	5.829	5.829	-6.471
2300	7.743	86.053	49.550	5.684	5.684	-7.191
2400	7.747	86.373	49.080	5.589	5.589	-7.911
2500	7.749	86.673	48.560	5.532	5.532	-8.631
2600	7.749	86.950	47.990	5.512	5.512	-9.351
2700	7.747	87.203	47.380	5.527	5.527	-10.071
2800	7.743	87.433	46.730	5.576	5.576	-10.791
2900	7.737	87.639	46.050	5.659	5.659	-11.511
3000	7.729	87.820	45.350	5.776	5.776	-12.231
3100	7.719	87.977	44.630	5.927	5.927	-12.951
3200	7.707	88.110	43.890	6.112	6.112	-13.671
3300	7.693	88.220	43.130	6.330	6.330	-14.391
3400	7.677	88.307	42.350	6.581	6.581	-15.111
3500	7.658	88.373	41.550	6.864	6.864	-15.831
3600	7.636	88.419	40.730	7.179	7.179	-16.551
3700	7.611	88.445	40.000	7.527	7.527	-17.271
3800	7.583	88.450	39.260	7.907	7.907	-17.991
3900	7.552	88.435	38.510	8.319	8.319	-18.711
4000	7.517	88.399	37.760	8.764	8.764	-19.431
4100	7.478	88.343	37.010	9.242	9.242	-20.151
4200	7.435	88.267	36.260	9.753	9.753	-20.871
4300	7.387	88.171	35.510	10.297	10.297	-21.591
4400	7.333	88.056	34.760	10.874	10.874	-22.311
4500	7.272	87.923	34.010	11.484	11.484	-23.031
4600	7.208	87.773	33.260	12.127	12.127	-23.751
4700	7.139	87.607	32.510	12.802	12.802	-24.471
4800	7.055	87.427	31.760	13.508	13.508	-25.191
4900	6.929	87.233	31.010	14.245	14.245	-25.911
5000	6.758	87.027	30.260	15.012	15.012	-26.631
5100	6.549	86.810	29.510	15.809	15.809	-27.351
5200	6.299	86.583	28.760	16.636	16.636	-28.071
5300	6.000	86.347	28.010	17.493	17.493	-28.791
5400	5.659	86.103	27.260	18.380	18.380	-29.511
5500	5.276	85.850	26.510	19.297	19.297	-30.231
5600	4.850	85.588	25.760	20.244	20.244	-30.951
5700	4.383	85.316	25.010	21.221	21.221	-31.671
5800	3.875	85.035	24.260	22.228	22.228	-32.391
5900	3.327	84.745	23.510	23.265	23.265	-33.111
6000	2.740	84.445	22.760	24.332	24.332	-33.831

December 31, 1961

MERCURY MONIODE (HgI)

Ground State Configuration 2_2

$\Delta H_f^\circ 298.15 = 31.9 \pm 1.1$ kcal mole⁻¹

$S_{298.15}^\circ = 67.068$ cal deg⁻¹ mole⁻¹

Electronic Level and Multiplicity

$\frac{E, \text{cm}^{-1}}{0}$

$\frac{g_i}{2}$

$\omega_e = 125.0$ cm⁻¹

$\omega_e x_e = 1.00$ cm⁻¹

$\sigma = 1$

$B_e = [0.0351]$ cm⁻¹

$\alpha_e = [0.0003]$ cm⁻¹

$r_e = [2.49]$ Å

Heat of Formation

K. Wieland and A. Herzog, Helv. Chim. Acta, **32**, 869 (1949) gave 8.3 ± 1.1 kcal for the heat of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants were taken from K. Wieland, Zeits. f. Elektrochemie **54**, 761 (1960). Rotational constants were estimated using equation III 123, p. 108, G. Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York 1950. The bond length was estimated to be 0.965 of the mercuric bond length by analogy with the mercury chlorides.

HgI

(IDEAL GAS)

MOL. WT. = 327.52

HgI

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0						
100						
200						
298	16.582	43.336	43.336	.000	- 24.427	17.905
300						
300	16.600	43.453	43.336	.034	- 24.422	17.791
400	17.600	48.941	48.080	1.944	- 24.014	13.120
573	20.105	54.917	45.809	4.554	- 21.925	9.583
600						
600	20.105	56.583	46.442	38.226	- 18.417	6.781
700	20.105	64.387	51.135	51.777	- 13.815	4.313
800	20.105	66.735	52.739	50.566	- 8.431	2.303
900	20.105	68.853	54.287	49.958	- 3.124	.759
1000						
1000	20.105	70.769	55.443	48.351	- 2.114	.462
1100						
1100	20.105	72.686	56.463	46.747	- 7.292	1.449
1200	20.105	74.128	57.252	45.142	- 12.414	2.261
1300	20.105	75.618	58.240	43.538	- 17.487	2.940
1400						
1400	20.105	77.005	59.440	41.930	- 22.514	3.514
1500						
1500	20.105	78.440	60.565	40.319	- 27.496	4.006

March 31, 1952

MERCURY DIIODIDE (HgI₂)

(Crystal)

Mol. Wt. = 454.43
 $\Delta H_f^{298.15} = -25.2 \pm 0.4$ kcal. mole⁻¹
 $S_{298.15}^{298.15} = [43.338] \pm 1.5$ cal. deg.⁻¹ mole⁻¹
 $T_c = 402^\circ K$
 $\Delta H_c = 0.601 \pm 0.04$ kcal. mole⁻¹
 $T_m = 530^\circ K$
 $\Delta H_m = 4.533 \pm 0.05$ kcal. mole⁻¹

Heat of Formation. Taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties", (1952).

Heat Capacity and Entropy. The heat capacity was calculated from the heat content data of M. Guinchant, Comp. Rend. 89, 145 (1907) and R. Ewald, Ann. d. Physik (4) 44, 1213 (1914). The entropy was estimated by adjusting its value to provide the best fit of the melting, sublimation and vaporization phenomena.

Transition. The heat and temperature of transition were taken from National Bureau of Standards Circular 500 (loc. cit.).

Melting. The heat of melting was taken from M. Guinchant (loc. cit.), the temperature of melting from National Bureau of Standards Circular 500 (loc. cit.).

T. °K.	C _p	S° - (F° - H° ₂₉₈)/T	(F° - H° ₂₉₈)	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100							
200	16.592	51.544	.000	20.862	22.536	16.519	
300	16.600	51.659	.034	20.868	22.546	16.424	
400	16.777	52.328	2.181	24.550	22.576	16.372	
500	24.400	53.771	4.661	31.222	22.672		
600	24.400	67.670	55.902	33.391	19.235	7.006	
700	24.400	71.431	57.559	66.525	15.375	6.800	
800	24.400	74.690	56.763	11.941	10.995	3.004	
900	24.400	77.563	61.565	44.403	9.762	1.571	
1000	24.400	80.134	63.313	16.921	43.405	2.614	
1100	24.400	82.460	64.950	19.261	42.369	1.415	.281
1200	24.400	84.583	66.599	21.701	41.335	5.349	.974
1300	24.400	86.536	67.966	24.141	40.301	9.198	1.546
1400	24.400	88.344	69.358	26.581	39.266	12.968	2.066
1500	24.400	90.028	70.680	29.021	38.239	16.662	2.527

March 31, 1962

MERCURY DIIODIDE (HgI₂) (Liquid)

Mol. Wt. = 454.43
 ΔH_f^o 298.15 = [-20.862] ± 0.45 kcal. mole⁻¹
 ΔF_f^o 298.15 = [51.544] ± 1.5 cal. deg.⁻¹ mole⁻¹
 T_m = 530°K
 ΔH_m = 4.533 ± 0.05 kcal. mole⁻¹
 T_b = 627°K
 ΔH_v = 14.141 ± 0.25 kcal. mole⁻¹

Heat of Formation. Calculated from ΔH_f^o 298(c).

Heat Capacity and Entropy. Heat capacity measurements were obtained from the data of M. Guinchant, Comp. Rend. 68, 145 (1907) in the range 540-600°K and were assumed constant above and below this range. A glass type transition was assumed at 353°K below which the heat capacity was that of HgI₂(c). The entropy was calculated from the entropy of the crystal and the measured entropy of fusion.

Fusion and Vaporization. T_m and T_b are taken from National Bur. of Standards (U.S.) Circular 500 (1952). ΔH_m is from the data of M. Guinchant (loc. cit.) and ΔH_v was obtained from the data of E. B. R. Pridoux, J. Chem. Soc. (London) 97, 2032 (1910) and F. M. G. Johnson, J. Amer. Chem. Soc. 53, 777 (1911).

Mercury Monoxide (HgO)

(Crystal) Mol. Wt. = 216.61

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H° ₂₉₈)/T cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	INFINITE	2.176	20.605	20.605	INFINITE
100	6.796	7.371	1.776	20.969	16.741	40.855
200	9.173	12.872	.969	21.119	16.581	17.564
298	10.551	16.795	.000	21.699	13.993	10.250
300	10.551	16.860	.020	21.698	13.935	10.151
400	11.550	20.037	1.126	21.608	11.356	6.206
500	12.340	22.703	1.858	21.429	8.615	3.853
600	12.935	25.008	2.587	21.191	6.315	2.300
700	13.400	26.931	3.295	20.937	4.286	.714
800	13.745	28.551	3.983	20.675	2.387	-.641
900	14.012	30.486	4.652	20.409	6.922	1.681
1000	14.200	31.973	5.310	20.140	11.440	2.500

MERCURY MONOXIDE (HgO)

(CRYSTAL)

MOL. WT. = 216.61

$$\Delta H_f^0 298.15 = -21.699 \pm 0.024 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 16.795 \pm 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_{\text{decomp}} = 749^\circ\text{K.}$$

Heat of Formation.

Obtained from the entropy obtained by T. W. Bauer and H. L. Johnston, J. Am. Chem. Soc. 75, 2217 (1953) and the free energy of formation as determined from the numerous cell measurements described by Bauer and Johnston. The value adopted for $\Delta F_f^0 298.15$ was $-42,707 \pm 14 \text{ cal. mole}^{-1}$.

Heat Capacity and Entropy.

The heat capacity has been measured from 15° to 298°K. by Bauer and Johnston loc. cit. The extrapolation below 15°K was done assuming a T^3 law and gave $S_{15}^0 = 0.264 \text{ e.u.}$ Above 298° the data was extrapolated smoothly and adjusted to give the observed decomposition vapor pressures of G. B. Taylor and G. A. Hulett, J. Phys. Chem. 17, 565 (1913).

Decomposition.

According to Taylor and Hulett, loc. cit., the vapor pressure reaches 1.89 atmospheres at 749°K. This corresponds to the decomposition to 2 Hg(g) + O₂(g), the equilibrium constant being unity at 1.89 atm.

June 30, 1962

HgO

T, °K	C _p ^o	$\frac{g\text{bbs}}{\text{mol}}$ S ^o	$-(G^o-H^o_{298})/T$	H ^o -H ^o ₂₉₈	ΔH ^o kcal/mol	ΔG ^o	Log K _p
0	.000	.000	INFINITE	- 2.153	11.117	11.117	INFINITE
100	6.969	49.187	63.768	- 1.458	11.057	11.057	19.884
200	7.340	54.103	57.837	- 1.000	10.804	7.235	7.906
298	7.859	57.134	57.134	- .000	10.000	5.688	4.170
300	7.868	57.183	57.134	-.015	9.994	5.662	4.125
400	8.236	59.500	57.448	-.821	9.786	4.250	2.322
500	8.469	61.365	58.051	-1.657	9.605	2.888	1.282
600	8.650	62.923	58.736	-2.512	9.433	1.560	.568
700	8.788	64.431	60.111	-3.250	9.272	.275	.258
800	8.894	65.891	61.115	-3.895	9.122	.004	.004
900	8.954	67.400	62.760	-5.139	8.983	3.722	1.021
1000	8.988	67.405	61.379	-6.024	8.826	4.671	1.021
1100	8.934	68.235	61.966	-6.916	8.651	5.622	1.117
1200	8.900	69.052	62.552	-7.811	8.464	6.580	1.266
1300	8.900	69.752	63.052	-8.711	8.266	7.550	1.422
1400	9.012	70.419	63.555	-9.611	8.066	8.528	1.587
1500	9.033	71.062	64.033	-10.513	7.863	9.504	1.761
1600	9.052	71.675	64.490	-11.417	7.655	10.489	1.942
1700	9.066	72.264	64.933	-12.323	7.442	11.476	2.128
1800	9.076	72.834	65.363	-13.231	7.226	12.464	2.319
1900	9.101	73.195	65.743	-14.140	7.009	13.452	2.514
2000	9.116	73.652	66.127	-15.051	6.793	14.440	2.713
2100	9.130	74.098	66.496	-15.964	6.577	15.428	2.916
2200	9.143	74.536	66.859	-16.879	6.362	16.416	3.122
2300	9.157	74.969	67.218	-17.792	6.147	17.404	3.331
2400	9.170	75.319	67.524	-18.706	5.932	18.392	3.541
2500	9.183	75.684	67.883	-19.626	5.717	19.380	3.752
2600	9.195	76.058	68.152	-20.545	5.502	20.368	3.963
2700	9.207	76.437	68.421	-21.464	5.287	21.356	4.174
2800	9.220	76.737	68.741	-22.383	5.072	22.344	4.385
2900	9.232	77.060	69.023	-23.309	4.857	23.332	4.596
3000	9.244	77.374	69.286	-24.233	4.642	24.320	4.807
3100	9.255	77.677	69.561	-25.158	4.427	25.308	5.018
3200	9.267	77.971	69.834	-26.082	4.212	26.296	5.229
3300	9.279	78.256	70.101	-27.003	3.997	27.284	5.440
3400	9.290	78.533	70.316	-27.940	3.782	28.272	5.651
3500	9.302	78.803	70.554	-28.870	3.567	29.260	5.862
3600	9.313	79.045	70.787	-29.800	3.352	30.248	6.073
3700	9.324	79.280	71.014	-30.729	3.137	31.236	6.284
3800	9.335	79.559	71.236	-31.658	2.922	32.224	6.495
3900	9.347	79.812	71.453	-32.589	2.707	33.212	6.706
4000	9.358	80.049	71.655	-33.534	2.492	34.200	6.917
4100	9.369	80.280	71.872	-34.471	2.277	35.188	7.128
4200	9.380	80.504	72.084	-35.408	2.062	36.176	7.339
4300	9.391	80.727	72.274	-36.347	1.847	37.164	7.550
4400	9.402	80.943	72.468	-37.286	1.632	38.152	7.761
4500	9.413	81.154	72.659	-38.227	1.417	39.140	7.972
4600	9.424	81.361	72.846	-39.169	1.202	40.128	8.183
4700	9.435	81.564	73.030	-40.105	0.987	41.116	8.394
4800	9.446	81.763	73.209	-41.042	0.772	42.104	8.605
4900	9.457	81.957	73.386	-42.001	0.557	43.092	8.816
5000	9.468	82.149	73.559	-42.947	0.342	44.080	9.027
5100	9.478	82.336	73.729	-43.894	0.127	45.068	9.238
5200	9.489	82.520	73.897	-44.841	0.000	46.056	9.449
5300	9.500	82.701	74.061	-45.782	0.000	47.044	9.660
5400	9.511	82.879	74.223	-46.723	0.000	48.032	9.871
5500	9.522	83.054	74.382	-47.665	0.000	49.020	10.082
5600	9.533	83.225	74.538	-48.607	0.000	50.008	10.293
5700	9.543	83.394	74.692	-49.550	0.000	51.000	10.504
5800	9.554	83.560	74.844	-50.554	0.000	52.000	10.715
5900	9.565	83.723	74.993	-51.512	0.000	53.000	10.926
6000	9.576	83.884	75.140	-52.469	0.000	54.000	11.137

June 30, 1967

(IDEAL GAS)

MERCURY MONOXIDE (HgO)

Ground State Configuration ¹Σ

ΔH_{f,0}^o = [11] kcal/mol

GFW = 216.5894

S_{298.15}^o = [57] gibbs/mol

ΔH_{f,298.15}^o = [10] kcal/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i
0	1

ω_eX_e = [680] cm⁻¹

ω_eX_e = [4.7] cm⁻¹

σ = 1

r_e = [1.84] Å

α_e = [0.00277] cm⁻¹

Heat of Formation

The heat of formation (ΔH_{f,298}^o) of HgO(g) is estimated to be 10 ± 15 kcal/mol. This value is obtained from the heat of formation of PbO(g) and comparison of the heats of formation of analogous lead and mercury compounds using the method of Karapet'yants (1). The corresponding dissociation energy (D₀) of HgO(g) is 64 ± 15 kcal/mol.

Heat Capacity and Entropy

The equilibrium internuclear separation (r_e) of HgO(g) is estimated from the corresponding quantity for PbO(g) and comparison of Hg-X and Pb-X bond distances for cases in which values of both distances are known. The rotational constant B_e is calculated from r_e. The fundamental vibrational frequency ω_e is estimated from Guggenheimer's relation for multiple bonded molecules (2). The anharmonic vibrational term ω_eX_e is calculated from ω_eX_e = ω_e²(4D₀ + 2ω_e). The value of α_e is calculated from the Morse potential function. The ground state configuration is estimated from the building-up principle (3), the united atom theory (3), and from analogy with BeO.

References

1. M. Kh. Karapet'yants, Russ. J. Inorg. Chem. (English Transl.) **10**, 837 (1965).
2. K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.



Mercury Monoiodide, Dimeric (Hg₂I₂)
(Crystal) Mol. Wt. = 655.04 INTERIM TABLE

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0								
100								
200								
298	25.300	57.670	57.670	.000	-28.462	-28.462	-24.545	19.457
300	25.323	57.677	57.670	.047	-28.463	-28.532	-24.532	19.328
400	26.120	61.816	61.816	2.643	-28.539	-32.182	-28.182	14.064
500	27.170	72.863	72.863	10.109	-32.315	-42.497	-32.182	10.109
600	27.740	76.249	76.249	12.812	-42.812	-52.812	-42.812	7.031
700	28.140	80.560	80.560	15.017	-52.812	-62.812	-52.812	3.881
800	28.540	84.387	84.387	16.228	-62.812	-72.812	-62.812	1.190
900	28.940	87.772	87.772	16.565	-72.812	-82.812	-72.812	.5975
1000	29.090	90.777	90.777	16.565	-82.812	-92.812	-82.812	.2502
1100	29.373	93.561	93.561	16.565	-92.812	-102.812	-92.812	.0000
1200	29.530	96.122	96.122	16.565	-102.812	-112.812	-102.812	.0000
1300	29.633	98.481	98.481	16.565	-112.812	-122.812	-112.812	.0000
1400	29.693	100.672	100.672	16.565	-122.812	-132.812	-122.812	.0000
1500	30.140	102.772	102.772	16.565	-132.812	-142.812	-132.812	.0000

MERCURY MONOIODIDE, DIMERIC (Hg₂I₂) (Crystal)

Mol. Wt. = 655.04
ΔH_f 298.15 = -28.462 ± 0.5 kcal. mole⁻¹
S° 298.15 = 57.670 ± 2.0 cal. deg.⁻¹ mole⁻¹
T_m = 563°K
ΔH_m = [6.5] ± 2.0 kcal. mole⁻¹

Heat of Formation. The average value of the cell measurements of W. C. Vosburgh, J. Amer. Chem. Soc. 50, 2386 (1928); E. Cohen Zeits. f. physik. Chemie 94, 210 (1920); T. Yoshida, J. Chem. Soc. Japan 48, 435 (1927); L. W. Øholm, Acta. Soc. Scientiarum Fennicae 41, 1 (1913) and the calorimetric values of R. Varot, Ann. Chim. Phys. (7) 9, 91 (1896) and W. Nernst, Zeits. f. physik. Chemie 2, 23 (1888) was adopted.

Heat Capacity and Entropy. The heat capacity at 298.15° was taken from National Bureau of Standards (U.S.) Circular 500 (1952) and was estimated above this by analogy with mercurous chloride. The entropy was obtained from the heat and free energy of formation obtained from the cell measurements listed under heat of formation.

Melting. P. Yvon, Comp. Rend. 76, 1607 (1973) gives 563°K for the melting point. The heat of melting was estimated by assuming the entropy of melting per atom to be the same as that for mercuric iodide.



Mercury Moniodide, Dimeric (Hg₂I₂)
(Liquid) Mol. Wt. = 655.04

INTERIM TABLE

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0								
100								
200								
298	25.300	66.068	66.668	.000	-23.021	-23.021	-23.021	17.479
300	25.323	67.025	66.868	.037	-23.022	-23.022	-23.021	17.374
400	25.600	74.872	67.689	2.780	-23.022	-23.022	-23.021	17.000
500	26.000	82.187	70.040	6.054	-23.022	-23.022	-23.021	16.791
600	26.600	88.099	72.568	9.314	-23.022	-23.022	-23.021	16.611
700	27.400	93.116	75.154	12.574	-23.022	-23.022	-23.021	16.461
800	28.400	97.469	77.807	15.834	-23.022	-23.022	-23.021	16.331
900	29.600	101.389	80.534	19.094	-23.022	-23.022	-23.021	16.211
1000	31.000	104.743	82.390	22.353	-23.022	-23.022	-23.021	16.101
1100	32.600	107.850	84.565	25.613	-23.022	-23.022	-23.021	16.001
1200	34.400	110.687	86.926	28.873	-23.022	-23.022	-23.021	15.911
1300	36.400	113.288	89.408	32.133	-23.022	-23.022	-23.021	15.831
1400	38.600	115.712	92.031	35.393	-23.022	-23.022	-23.021	15.761
1500	41.000	117.961	94.782	38.653	-23.022	-23.022	-23.021	15.701

March 31, 1962

MERCURY MONIODIDE, DIMERIC (Hg₂I₂)

(Liquid)

Mol. Wt. = 655.04

ΔH_f^o 298.15 = [-23.021 ± 2.5] kcal. mole⁻¹

S_{298.15}^o = [66.868 ± 5.0] cal. deg. ⁻¹ mole⁻¹

T_m = 563°K

ΔH_m = [6.5 ± 2.0] kcal. mole⁻¹

T_b = [530]°K (decomp.)

Heat of Formation. Calculated from ΔH_f^o (crystal) and the estimated heat of melting and heat capacity.

Heat Capacity and Entropy. C_p was estimated as 1.33 times the heat capacity of mercuric iodide. The entropy was calculated from S^o crystal, the estimated ΔH_m and the heat capacities of solid and liquid.

Melting and Vaporization. The melting point was given by P. Yvon, Comp. Rend. 76, 1607 (1873); the heat of melting was estimated from that of mercuric iodide, by assuming the entropies of melting per atom to be equal. Mercurous iodide decomposes to Hg(s) and HgI₂(s) at the boiling point which was estimated from the free energy change of the reaction.

Hg₂I₂

Hg₂I₂

Iodine, Monatomic (I)

(Ideal Gas) Mol. Wt. = 126.91

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
100	4.900	37.000	INFINITE	25.633	25.633	INFINITE
150	4.968	41.691	1.481	25.633	25.633	30.529
200	4.968	43.184	0.000	25.633	25.633	12.710
250	4.968	43.184	0.000	25.537	16.800	12.314
300	4.968	43.214	0.009	25.534	16.746	12.199
400	4.968	43.279	0.506	23.445	13.908	7.599
500	4.968	43.752	1.003	18.100	12.023	5.235
600	4.968	46.658	1.500	18.229	10.787	3.929
700	4.968	47.424	1.996	18.276	9.543	2.979
800	4.968	48.087	2.493	18.322	8.293	2.265
900	4.968	48.673	2.990	18.367	7.036	1.709
1000	4.970	49.196	3.487	18.412	5.775	1.262
1100	4.973	49.700	3.984	18.455	4.509	0.896
1200	4.977	50.103	4.482	18.498	3.239	0.590
1300	4.984	50.502	4.980	18.542	1.966	0.331
1400	4.993	50.871	5.479	18.585	0.690	0.108
1500	5.004	51.216	5.978	18.628	0.591	0.066
1600	5.018	51.539	6.479	18.672	1.873	0.256
1700	5.034	51.844	6.982	18.717	3.158	0.406
1800	5.052	52.132	7.486	18.762	4.447	0.540
1900	5.072	52.406	7.993	18.809	5.737	0.660
2000	5.093	52.667	8.416	18.857	7.031	0.768
2100	5.115	52.916	8.825	18.907	8.326	0.866
2200	5.137	53.154	9.225	18.958	9.624	0.956
2300	5.160	53.383	9.618	19.011	10.925	1.038
2400	5.182	53.603	9.995	19.066	12.227	1.113
2500	5.204	53.815	10.357	19.121	13.532	1.183
2600	5.226	54.020	10.709	19.179	14.840	1.247
2700	5.247	54.217	11.052	19.238	16.149	1.307
2800	5.267	54.408	11.386	19.298	17.460	1.363
2900	5.286	54.594	11.714	19.360	18.774	1.415
3000	5.304	54.773	12.033	19.422	20.091	1.464
3100	5.321	54.947	12.344	19.486	21.409	1.509
3200	5.336	55.116	12.647	19.551	22.729	1.552
3300	5.351	55.281	12.944	19.616	24.051	1.593
3400	5.364	55.441	13.237	19.682	25.376	1.631
3500	5.376	55.596	13.526	19.749	26.701	1.667
3600	5.387	55.748	13.812	19.816	28.030	1.702
3700	5.397	55.896	14.095	19.884	29.360	1.734
3800	5.406	56.040	14.375	19.952	30.692	1.765
3900	5.414	56.180	14.653	20.020	32.025	1.795
4000	5.421	56.316	14.929	20.089	33.362	1.823
4100	5.427	56.452	15.202	20.157	34.697	1.849
4200	5.432	56.582	15.472	20.225	36.035	1.875
4300	5.436	56.710	15.739	20.293	37.377	1.900
4400	5.439	56.835	16.004	20.360	38.720	1.923
4500	5.442	56.957	16.266	20.427	40.062	1.946
4600	5.444	57.077	16.525	20.494	41.404	1.967
4700	5.446	57.194	16.782	20.560	42.754	1.986
4800	5.446	57.309	17.037	20.626	44.101	2.006
4900	5.447	57.421	17.289	20.691	45.450	2.027
5000	5.447	57.531	17.538	20.755	46.801	2.046
5100	5.446	57.639	17.786	20.820	48.153	2.063
5200	5.445	57.745	18.032	20.882	49.507	2.081
5300	5.444	57.849	18.275	20.945	50.860	2.097
5400	5.442	57.950	18.515	21.006	52.214	2.113
5500	5.440	58.050	18.752	21.066	53.572	2.129
5600	5.438	58.148	18.987	21.126	54.931	2.144
5700	5.436	58.244	19.220	21.185	56.289	2.158
5800	5.433	58.339	19.452	21.243	57.648	2.172
5900	5.431	58.432	19.681	21.300	59.009	2.186
6000	5.428	58.523	19.907	21.356	60.370	2.199

December 31, 1961

IODINE, MONATOMIC (I)

(IDEAL GAS)

MOL. WT. = 126.91

$$\Delta H_{fO}^{\circ} = 25.633 \pm .010 \text{ kcal. mole}^{-1}$$

$$\Delta H_{fI}^{\circ} = 25.537 \text{ kcal. mole}^{-1}$$

$$S_{298}^{\circ} = 43.184 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$\text{Ground State} = 2P_{3/2}$$

Electronic Levels and Multiplicities

ω , cm. ⁻¹	g_1	ω , cm. ⁻¹	g_1	ω , cm. ⁻¹	g_1
0	4	67082.12	4	68549.77	8
7603.15	2	68586.98	2	68588.00	6
54633.46	6	64990.01	4	66812.02	4
61819.81	4	65844.49	6	71850.	14
60898.27	2	65870.00	8	72750.	24
56092.86	4	66020.64	8	75300.	80
85186.76	2	66355.21	4	77110.	64
84906.34	6	67298.45	4	79210.	128
				81440.	218

Thermodynamic Functions.

Atomic constants were taken from G. E. Moore [U. S. Natl. Bur. Standards Circ. 467, Vol. III (1958)]. The higher levels were averaged. Calculated thermodynamic functions are in good agreement with those of W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards, 55, 147 (1955)].

Heat of Formation.

The dissociation energy of diatomic iodine is given as $D_0^{\circ} = 12452.5 \pm 1.5 \text{ cm.}^{-1}$ by R. D. Verma [J. Chem. Phys. 32, 758 (1960)]. Converting to calories and combining with the heat of sublimation of iodine yields the heat of formation of the ideal monatomic gas. Evans, Munson, and Wagman [loc. cit.] list several investigations of the dissociation energy from equilibrium data. These are all less precise than the spectroscopic value and are not given any weight. The "best" average of the thermal data yields $D_0^{\circ} = 35.588 \text{ kcal. mole}^{-1}$ (spectroscopic = 35.608 kcal. mole⁻¹).

T, °K	Cp°	gibbs/mol	$-(G^{\circ}-H^{\circ}_{298})/T$	$H^{\circ}-H^{\circ}_{298}$	kcal/mol	ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	-	3.038	-	78.138	-	INFINITE
100	10.756	12.527	36.237	-2.371	-	78.250	-	170.206
200	12.074	20.500	26.565	-1.213	-	78.301	-	84.769
298	12.614	25.427	25.427	0.000	-	78.370	-	56.592
300	12.621	25.505	25.427	-0.073	-	78.372	-	56.238
400	12.890	29.172	25.921	-1.258	-	78.497	-	32.792
500	13.232	32.083	24.875	-2.604	-	86.196	-	75.023
600	13.695	34.534	27.953	-3.949	-	86.025	-	72.803
700	14.297	36.688	29.049	-5.387	-	85.793	-	70.617
800	14.971	38.578	30.175	-6.703	-	85.478	-	68.482
900	15.725	40.248	31.178	-8.384	-	85.122	-	66.392
1000	16.500	42.144	32.188	-9.956	-	84.688	-	64.301
1100	17.100	43.746	33.167	-11.637	-	103.093	-	61.262
1200	17.480	45.251	34.112	-13.364	-	102.314	-	57.493
1300	17.845	46.665	35.025	-15.145	-	101.485	-	53.151
1400	17.930	47.979	35.903	-16.905	-	100.687	-	48.847
1500	17.908	49.210	36.749	-18.492	-	99.908	-	43.066
1600	17.860	50.368	37.564	-20.486	-	99.008	-	39.575
1700	17.881	51.457	38.350	-22.283	-	98.166	-	36.152
1800	17.905	52.485	39.107	-24.082	-	97.384	-	32.890
1900	17.903	53.453	39.837	-25.882	-	96.664	-	29.786
2000	17.900	54.382	40.541	-27.682	-	95.984	-	26.847

Dec. 31, 1961; June 30, 1967

$\Delta H^{\circ}_0 = -78.14 \pm 0.1$ kcal/mol
$\Delta H^{\circ}_{298.15} = -78.37 \pm 0.1$ kcal/mol
$\Delta H^{\circ} = 5.74$ kcal/mol
$\Delta H^{\circ}_{298.15}(\text{to monomer}) = 48.37$ kcal/mol
$\Delta H^{\circ}_{298.15}(\text{to dimer}) = 55.84$ kcal/mol

 $S^{\circ}_{298.15} = 25.427$ gibbs/mol $T_m = 954^{\circ}\text{K}$

Heat of Formation

The heats of solution of KI(c) have been critically reviewed by V. B. Perker, U. S. Natl. Bur. Std. NBS-2, 1965. Six pertinent results are quoted in the table below. Adopting the best value, $\Delta H^{\circ}_{298} = 4.86 \pm 0.03$ kcal/mol, reported by Parker, and $\Delta H^{\circ}_{298} = -60.32$ and -13.19 kcal/mol for $\text{K}^+(\text{H}_2\text{O})$ and $\text{I}^-(\text{H}_2\text{O})$, respectively, obtained from U.S. Natl. Bur. Std. Tech. Note 270-1, 1965, we obtain $\Delta H^{\circ}_{298}(\text{KI}, \text{c}) = -78.37 \pm 0.1$ kcal/mol, which is adopted.

ΔH° , kcal/mol*	Temperature, °C	n**	Investigator
4.830 $\pm$ 0.05	19	200	J. Thomsen, <i>Thermochemische Untersuchungen</i> , J. Barth Verlag, Leipzig, 1887-86.
4.897 $\pm$ 0.04	25	18	J. Wüst and E. Lange, <i>Z. Physik. Chem.</i> 116 , 161 (1925).
4.873	25	500	E. Lange and W. Martin, <i>Z. Physik. Chem.</i> A180 , 233 (1937).
4.790 $\pm$ 0.10	20.5	600	M. M. Popov, S. M. Skuratov, and M. M. Strel'tsova, <i>Zhur. Obshch. Khim.</i> 10 , 2023 (1940).
5.020	24.5	18.5	M. Bobtelsky and R. D. Laisch, <i>J. Chem. Soc.</i> 1950 , 3612 (1950).
4.830 $\pm$ 0.07	25	75000	A. F. Kapustinskii and S. I. Drakin, <i>Zhur. Fiz. Khim.</i> 28 , 581 (1952).

*Values are adjusted to 298.15°K and to infinite dilution.

**n is the number of moles of H_2O per mole of KI(c) in solution.

Heat Capacity and Entropy

The low temperature heat capacities are based on those measured by W. T. Berg and J. A. Morrison, *Proc. Roy. Soc. (London)* **A242**, 467 (1957), 2.86 - 268.0°K. The adopted values are in good agreement with the Cp values reported by W. W. Seales, *Phys. Rev.* **112**, 49 (1958), 2 - 7°K. The data of K. Clusius, J. Goldmann, and A. Perlick, *Z. Naturforsch.* **4A**, 424 (1949), 10.27 - 269.9°K, appear to be too low in the temperature range 70 - 270°K and are not used. Low temperature enthalpies, 83 - 273°K, have been measured by F. Koref, *Ann. Physik* **5**, 49 (1911). The value of S°_{298} is derived based on the adopted low temperature heat capacities, using $S^{\circ}_{298} = 0.0033$ eu.

The high temperature enthalpies were determined by S. M. Skuratov and S. A. Lapushkin, *Russ. J. Gen. Chem. (English Transl.)* **21**, 2485 (1951), 623 - 923°K; A. S. Dworin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tenn., Dec. 1, 1964, 854 - 954°K; and C. B. Cooper, *J. Chem. Phys.* **21**, 777 (1953), 977 - 973°K. Heat Capacities are derived from the enthalpies by a curve fitting method which requires a smooth joint with the low temperature Cp. Enthalpy values used in the curve fit include smooth values calculated from the equation of Skuratov and the value $H^{\circ}_{954} - H^{\circ}_{298} = 9.2$ kcal/mol from Dworin. Deviation of the input values from the selected enthalpies are all less than 0.3 percent, while the deviations of the data of Cooper range from ± 1.0 percent at 570°K to ± 1.6 percent at 974°K. Since the latter point is 20° above the melting point, there appears to be an error in Cooper's measurement of temperature. Cp above the melting point is obtained by graphical extrapolation.

Melting Data

T_m has been reported to be 953, 952 and 954°K by R. C. Ray and V. Daval, *Trans. Faraday Soc.* **32**, 741 (1936); T. E. Phipps and E. G. Partridge, *J. Am. Chem. Soc.* **51**, 1331 (1929); and J. W. Johnson and M. A. Bredig, *J. Phys. Chem.* **52**, 604 (1958), respectively. The last value is adopted. The heat of melting was determined by A. S. Dworin and M. A. Bredig, *J. Phys. Chem.* **54**, 269 (1960), using drop calorimetry.

Heat of Sublimation

The difference between ΔH°_{298} for KI(g) and KI(c) is $\Delta H^{\circ}_{298}(\text{to monomer})$. The $\Delta H^{\circ}_{298}(\text{to dimer})$ is calculated as the enthalpy change for the following reaction: $2\text{KI}(\text{c}) = \text{K}_2\text{I}_2(\text{g})$.

Potassium Iodide (KI)
(Liquid) GFW = 166.0064

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
200	17.300	27.273	27.273	.000	- 74.771	- 74.156	54.358
300	17.300	27.380	27.273	.032	- 74.764	- 74.152	54.020
400	17.300	32.357	27.952	1.769	- 74.934	- 73.924	40.335
500	17.300	36.217	29.233	3.499	- 81.708	- 72.503	31.735
600	17.300	39.371	30.668	5.229	- 81.153	- 70.833	25.801
700	17.300	42.038	32.106	6.959	- 80.588	- 69.158	21.592
800	17.300	44.348	33.495	8.689	- 80.021	- 67.564	18.458
900	17.300	46.366	34.817	10.412	- 79.455	- 66.041	16.037
1000	17.300	48.208	36.066	12.142	- 78.888	- 64.580	14.114
1100	17.300	49.457	37.244	13.872	- 78.320	- 63.151	12.348
1200	17.300	51.363	38.361	15.602	- 77.752	- 61.761	10.744
1300	17.300	52.747	39.415	17.332	- 77.184	- 60.401	9.398
1400	17.300	54.029	40.414	19.062	- 76.616	- 59.072	8.253
1500	17.300	55.223	41.362	20.792	- 76.048	- 57.773	7.269
1600	17.300	56.339	42.263	22.522	- 75.480	- 56.504	6.415
1700	17.300	57.388	43.122	24.252	- 74.912	- 55.275	5.685
1800	17.300	58.377	43.943	25.982	- 74.344	- 54.086	5.009
1900	17.300	59.312	44.727	27.712	- 73.776	- 52.937	4.425
2000	17.300	60.200	45.479	29.442	- 73.208	- 51.828	3.904
2100	17.300	61.044	46.200	31.172	- 72.640	- 50.759	3.436
2200	17.300	61.849	46.893	32.902	- 72.072	- 49.730	3.019
2300	17.300	62.618	47.560	34.632	- 71.504	- 48.741	2.632
2400	17.300	63.354	48.203	36.362	- 70.936	- 47.792	2.285
2500	17.300	64.060	48.823	38.092	- 70.368	- 46.883	1.969

POTASSIUM IODIDE (KI)

(LIQUID)

GFW = 166.0064

$$S_{298.15}^{\circ} = 27.273 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = -74.771 \text{ kcal/mol}$$

$$T_m = 954^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 5.74 \text{ kcal/mol}$$

$$T_b = 1618^{\circ}\text{K}$$

$$\Delta H_v^{\circ} = 45.62 \text{ kcal/mol}$$

Heat of Formation

The heat of formation, ΔH_{298}° , is obtained from ΔH_{298}° (KI, c) by adding ΔH_m° and the difference between $H_{954}^{\circ} - H_{298}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is derived as 17.3 gibbs/mol from the enthalpy measurements, 954 - 1014°K, by A. S. Dworin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tenn., Dec. 1, 1964. This Cp value is adopted in the temperature range 298 - 2500°K. S_{298}° is obtained in a manner analogous to that of the heat of formation.

Melting Data

See KI(c) table for details.

Vaporization Data

The boiling point, $T_b = 1618^{\circ}\text{K}$, is calculated as the temperature at which the sum of the partial pressures of KI(g) and $K_2I_2(g)$ over KI(l) equals one atmosphere. The value of ΔH_v° is calculated as the heat required to produce one mole of vapor mixture, which contains 78 percent monomer (KI) and 22 percent dimer (K_2I_2) at T_b .

T_b was reported as 1603 and 1590°K by H. von Wartenberg and P. Albrecht, Z. Elektrochem. 21, 162 (1921), and O. Ruff and S. Mugdan, Z. Anorg. Chem. 117, 147 (1921), respectively.

Ground State Configuration $1s^2$ $S_{298.15}^\circ = 61.704$ gibbs/mol

$$\Delta H_f^\circ = -29.2 \pm 0.5 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -30.0 \pm 0.5 \text{ kcal/mol}$$

Electronic Levels and Quantum Weights

$$\frac{c_1, \text{ cm}^{-1}}{0} \quad \frac{g_1}{1}$$

$$\omega_e = 166.267 \pm 0.04 \text{ cm}^{-1} \quad \omega_e x_e = 0.0775 \pm 0.006 \text{ cm}^{-1} \quad \sigma = 1$$

$$B_e = 0.06072 \text{ cm}^{-1} \quad \alpha_e = 0.000267 \text{ cm}^{-1} \quad r_e = 3.0478 \text{ \AA}$$

Heat of Formation

The heat of formation is derived from the sublimation and vaporization data analyzed below. Many investigators have determined the total pressures of KI(g) and $K_2I_2(g)$ over KI(l) by static methods or "apparent" pressures by Knudsen effusion or transpiration. These pressures are converted to monomer pressures by use of functions [see $K_2I_2(g)$ table] which are consistent with the dimer-monomer equilibrium data of Batz (9). Second and third law analyses of the monomer pressures show reasonable agreement. The selected value of $\Delta H_f^{298} = -30.0 \pm 0.5$ kcal/mol is also in good agreement with -30.23 ± 1.15 and -30.46 kcal/mol derived from $D_0^\circ = 3.32 \pm 0.05$ and 3.33 eV reported by Gaydon (10) and Herzberg (11), respectively.

Investigator	Reaction**	Temperature *K	No. of Points	ΔH_{298}° , kcal/mol		Drift	$\Delta H_f^{298}^\circ$, kcal/mol
				Second Law	Third Law	eu	
1. Wartenberg-Albrecht	(B)	1336.2-1606.2	9	47.73 $\pm$ 0.36	44.76	-2.14 $\pm$ 0.2	-30.01
2. Ruff-Mugdan	(B)	1319.2-1590.2	12	49.38 $\pm$ 1.03	44.59	-3.34 $\pm$ 0.7	-30.18
3. Flock-Rodbusch	(B)	1116.1-1275.7	8	45.43 $\pm$ 0.03	44.75	-0.64 $\pm$ 0.1	-30.02
4. Grainer-Jellinek	(B)	1053.2	1	-	45.24	-	-29.53
5. Niwa	(A)	803.2-873.2	8	46.11 $\pm$ 0.35	48.30	2.64 $\pm$ 0.4	-30.07
6. Zimm-Mayer	(A)	616.4-892.9	10	48.66 $\pm$ 0.25	48.47	-0.44 $\pm$ 0.3	-29.90
7. Cugin-Kimball	(A)	721.5-897.7	29	48.52 $\pm$ 0.40	47.73	-1.14 $\pm$ 0.5	-30.64
8. Bridgers	(A)	697.5-891.7	25	48.48 $\pm$ 0.22	47.72	-1.12 $\pm$ 0.3	-30.65

*Based on the third law ΔH_{298}° value.

**(A) KI(c) = KI(g); (B) KI(l) = KI(g)

Heat Capacity and Entropy

The ground state configuration is obtained from Herzberg (11). The adopted values of ω_e , $\omega_e x_e$, B_e , α_e and r_e were determined using millimeter wave molecular beam spectroscopy by Rusk and Gordy (12), and corrected to the average isotopic species. Similar values were reported by Honig et al. (13) from microwave spectra, except ω_e which was given as 199.74 cm^{-1} . The value of ω_e was derived to be 200 and 173 cm^{-1} by Barrow and Caunt (14) and Rice and Klemperer (15). The moment of inertia is 4.5979×10^{-38} g cm^2 .

References

1. H. von Wartenberg and P. Albrecht, Z. Elektrochem., 2Z, 162 (1921).
2. O. Ruff and S. Mugdan, Z. Anorg. Chem. 11Z, 147 (1921).
3. E. F. Flock and W. H. Rodbusch, J. Am. Chem. Soc. 58, 2522 (1936).
4. B. Grainer and K. Jellinek, Z. Physik. Chem. (Leipzig) 165, 97 (1933).
5. K. Niwa, J. Fac. Sci. Hokkaido Imperial Univ., Ser. III, 2, 201 (1938).
6. B. H. Zimm and J. E. Mayer, J. Chem. Phys. 12, 362 (1944).
7. G. E. Cugin and G. E. Kimball, J. Chem. Phys. 16, 1035 (1948).
8. H. E. Bridgers, Ph.D. Thesis, The Ohio State University, 1953.
9. S. Batz, ORNL-2933, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1960.
10. A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.
11. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
12. J. R. Rusk and W. Gordy, Phys. Rev. 12Z, 617 (1962).
13. A. Honig, M. Mandel, M. L. Stitch and C. H. Townes, Phys. Rev. 86, 629 (1954).
14. R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) A219, 120 (1953).
15. S. A. Rice and W. Klemperer, J. Chem. Phys. 2Z, 573 (1957).

Dec. 31, 1961 June 30, 1967

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	0.000	INF	INF	2.484	-20.176	-20.176	INF
100	6.104	52.335	62.455	-1.712	-29.220	-32.376	71.447
200	6.700	56.191	62.512	-0.864	-29.582	-36.393	39.769
298	6.872	61.704	61.704	0.000	-30.000	-39.651	29.065
300	6.874	61.704	61.704	0.016	-30.000	-39.710	28.929
400	6.843	62.673	62.673	0.969	-30.000	-41.071	23.369
500	6.803	63.325	63.325	1.805	-30.024	-42.571	18.403
600	6.027	67.968	67.968	5.2736	-38.898	-45.736	16.659
700	6.055	69.362	69.362	3.610	-39.159	-46.855	14.629
800	6.081	70.572	70.572	4.517	-39.415	-47.937	13.006
900	6.107	71.664	71.664	5.426	-39.670	-48.980	11.859
1000	6.127	72.664	72.664	6.338	-39.932	-50.000	10.199
1100	6.148	73.475	73.475	7.252	-50.108	-50.980	9.930
1200	6.169	74.271	74.271	8.164	-50.144	-50.947	8.951
1300	6.190	75.006	75.006	9.086	-50.177	-50.913	8.122
1400	6.211	75.688	75.688	10.006	-50.210	-50.877	7.411
1500	6.231	76.324	76.324	10.924	-50.242	-50.836	6.795
1600	6.251	76.921	76.921	11.852	-50.272	-50.795	6.255
1700	6.272	77.482	77.482	12.774	-50.301	-50.753	5.779
1800	6.292	78.013	78.013	13.704	-50.330	-50.710	5.355
1900	6.312	78.516	78.516	14.636	-50.359	-50.667	4.976
2000	6.332	78.994	78.994	15.566	-50.387	-50.624	4.635
2100	6.351	79.449	79.449	16.501	-50.415	-50.582	4.325
2200	6.371	79.885	79.885	17.439	-50.446	-50.541	4.044
2300	6.391	80.302	80.302	18.377	-50.477	-50.500	3.788
2400	6.411	80.702	80.702	19.317	-50.509	-50.460	3.552
2500	6.431	81.087	81.087	20.259	-50.543	-50.420	3.335
2600	6.451	81.457	81.457	21.203	-50.583	-50.383	3.135
2700	6.470	81.814	81.814	22.149	-50.626	-50.349	2.950
2800	6.489	82.159	82.159	23.097	-50.675	-50.317	2.777
2900	6.508	82.492	82.492	24.046	-50.728	-50.287	2.616
3000	6.526	82.815	82.815	24.996	-50.781	-50.258	2.466
3100	6.549	83.128	83.128	25.953	-50.834	-50.228	2.326
3200	6.567	83.431	83.431	26.909	-50.890	-50.200	2.194
3300	6.588	83.726	83.726	27.867	-50.945	-50.175	2.070
3400	6.608	84.012	84.012	28.827	-51.001	-50.151	1.953
3500	6.628	84.291	84.291	29.788	-51.057	-50.128	1.842
3600	6.647	84.563	84.563	30.752	-51.113	-50.106	1.738
3700	6.667	84.827	84.827	31.718	-51.168	-50.082	1.638
3800	6.687	85.085	85.085	32.684	-51.223	-50.059	1.544
3900	6.706	85.338	85.338	33.650	-51.278	-50.036	1.456
4000	6.726	85.593	85.593	34.627	-51.333	-50.013	1.369
4100	6.746	85.824	85.824	35.600	-51.388	-50.000	1.288
4200	6.765	86.059	86.059	36.576	-51.443	-50.000	1.210
4300	6.785	86.289	86.289	37.554	-51.498	-50.000	1.136
4400	6.804	86.514	86.514	38.531	-51.553	-50.000	1.064
4500	6.824	86.734	86.734	39.514	-51.608	-50.000	0.995
4600	6.844	86.950	86.950	40.494	-51.663	-50.000	0.929
4700	6.864	87.162	87.162	41.481	-51.718	-50.000	0.865
4800	6.883	87.370	87.370	42.471	-51.773	-50.000	0.804
4900	6.903	87.576	87.576	43.460	-51.828	-50.000	0.744
5000	6.922	87.775	87.775	44.451	-51.883	-50.000	0.687
5100	6.942	87.971	87.971	45.444	-51.938	-50.000	0.631
5200	6.962	88.164	88.164	46.440	-51.993	-50.000	0.576
5300	6.981	88.354	88.354	47.437	-52.048	-50.000	0.523
5400	6.999	88.541	88.541	48.437	-52.103	-50.000	0.472
5500	7.021	88.725	88.725	49.437	-52.158	-50.000	0.422
5600	7.040	88.906	88.906	50.440	-52.213	-50.000	0.373
5700	7.059	89.083	89.083	51.445	-52.268	-50.000	0.325
5800	7.078	89.259	89.259	52.451	-52.323	-50.000	0.278
5900	7.097	89.431	89.431	53.456	-52.378	-50.000	0.231
6000	7.119	89.601	89.601	54.472	-52.433	-50.000	0.186

Lithium Iodide (LiI)

(Crystal) GFW = 133.8434

T, °K	Cp	gibbs/mol $S^\circ - (C^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0						
100						
200						
298	11.970	20.500	4.000	- 64.550	- 64.451	47.244
300	11.985	20.574	4.022	- 64.551	- 64.450	46.952
400	12.770	24.110	1.253	- 66.527	- 64.341	35.154
500	13.372	27.025	2.561	- 72.590	- 63.235	27.640
600	14.020	28.517	3.959	- 72.102	- 61.420	22.372
700	14.800	31.742	5.406	- 71.598	- 59.623	17.623
800	15.615	35.497	6.928	- 71.028	- 57.852	13.660
900	16.460	39.740	8.528	- 70.478	- 56.252	11.041
1000	17.200	37.480	10.221	- 69.880	- 54.639	11.041
1100	17.575	39.137	11.960	- 69.252	- 53.083	10.547
1200	17.915	40.618	13.731	- 68.598	- 51.589	9.829
1300	18.210	41.917	15.530	- 67.930	- 50.153	8.929
1400	18.435	43.052	17.330	- 67.255	- 48.744	7.909
1500	18.210	44.706	19.148	- 66.572	- 47.397	6.906
1600	18.210	45.681	20.969	- 65.880	- 46.094	6.296
1700	18.210	46.026	22.795	- 65.180	- 44.836	5.875
1800	18.210	46.631	24.631	- 64.471	- 43.619	5.515
1900	18.210	47.010	26.432	- 63.753	- 42.443	5.238
2000	18.210	49.944	28.253	- 63.033	- 41.318	5.070
2100	18.210	50.933	30.074	- 62.307	- 40.242	5.101
2200	18.210	51.460	31.895	- 61.576	- 39.215	5.286
2300	18.210	52.490	33.716	- 60.842	- 38.237	5.563
2400	18.210	53.265	35.537	- 60.108	- 37.308	5.909
2500	18.210	54.098	37.358	- 59.374	- 36.433	6.270

LITHIUM IODIDE (LiI)

(CRYSTAL)

OPW = 133.8434

ILI

 $\Delta H_f^\circ = \text{Unknown}$ $\Delta H_{298.15}^\circ = -64.55 \pm 0.1 \text{ kcal/mol}$ $\Delta H_m^\circ = 3.50 \text{ kcal/mol}$ $S_{298.15}^\circ = [20.5] \text{ gibbs/mol}$ $T_m = 742^\circ \text{K}$

Heat of Formation.

The heat of formation, $\Delta H_{298}^\circ(\text{LiI}, c) = -64.55 \text{ kcal/mol}$, was calculated from the heat of solution of lithium iodide (c) at infinite dilution and the ionic heats of formation of $\text{Li}^+(\text{aq})$ and $\text{I}^-(\text{aq})$.

V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-RS-NBS 2, Apr. 1, 1965, reviewed the literature heat of solution data and gave the "best" value, $\Delta H_{298}^\circ(\text{LiI}, c) = -66.49 \text{ kcal/mol}$ for $\text{LiI}(c) \rightarrow \text{Li}^+(\text{aq}) + \text{I}^-(\text{aq})$ at 298.15°K . The ionic heat of formation, $\Delta H_{298}^\circ(\text{Li}^+, \text{aq}) = -66.49 \text{ kcal/mol}$ was calculated from $\Delta H_{298}^\circ(\text{LiOH} \cdot \text{aq}) = -121.46 \text{ kcal/mol}$ (see JANAF LiOH(c) Table, Mar. 31, 1966) with $\Delta H_{298}^\circ(\text{OH}^-, \text{aq}) = -54.97 \text{ kcal/mol}$ from NBS Technical Note 270-1, "Selected Values of Chemical Thermodynamic Properties," Oct. 1, 1965. The value $\Delta H_{298}^\circ(\text{I}^-, \text{aq}) = -13.19 \text{ kcal/mol}$ was also obtained from NBS Technical Note 270-1. Combination of the ionic heats of formation of $\text{Li}^+(\text{aq})$ and $\text{I}^-(\text{aq})$ gives the heat of formation of $\text{LiI}(\text{aq})$, $\Delta H_{298}^\circ = -79.68 \text{ kcal/mol}$.

Heat Capacity and Entropy.

A. S. Dworin, private communication, Oak Ridge National Laboratory, Dec. 1964, has measured the enthalpy changes by the drop method ($642\text{--}802^\circ \text{K}$), yielding $(H_{742}^\circ - H_{298}^\circ) = 6.0 \text{ kcal/mol}$ for the crystal at the melting point. Heat capacities derived from his data were $C_p 692^\circ = 14.8$ and $C_p 772^\circ = 15.1 \text{ cal/deg-mol}$ for the crystal and liquid, respectively. The tabulated heat capacities were estimated based on these values and on the heat capacities of $\text{LiCl}(c)$, $\text{NaCl}(c)$ and $\text{NaI}(c)$.

The entropy, $S_{298.15}^\circ = 20.5 \text{ eu}$, was estimated by adding the entropy difference between $\text{NaI}(c)$ and $\text{NaCl}(c)$ to the entropy of lithium chloride (c) at 298.15°K . Comparisons with other alkali halides give results within $\pm 0.5 \text{ eu}$ of this value.

K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960), 592 (1961), has estimated the heat capacities ($C_p = 12.30 + 2.44 \times 10^{-3} T$ gibbs/mol) and the entropy ($S_{298}^\circ = 17.50 \text{ eu}$).

Melting Data.

The selected heat of fusion ($\Delta H_{298}^\circ = 3.50 \text{ kcal/mol}$) was obtained from enthalpy measurements in a drop calorimeter by A. S. Dworin and M. A. Bredig, J. Phys. Chem. 64, 289 (1960).

ILI

(Liquid) GFW = 133.8434

T, °K	Cp ^a	$\frac{\text{gkcal/mol}}{S^{\circ}}$	$-(G^{\circ}-H^{\circ}_{298})/T$	$H^{\circ}-H^{\circ}_{298}$	$\frac{\text{kcal/mol}}{\Delta H^{\circ}}$	ΔG°	Log Kp
0							
100							
200							
298	15.100	23.568	23.568	+0.00	- 61.749	- 62.564	45.861
300	15.100	23.601	23.568	+0.28	- 61.744	- 62.570	45.582
400	15.100	23.634	23.568	+0.56	- 61.739	- 62.575	45.303
500	15.100	23.667	23.568	+0.84	- 61.734	- 62.580	45.024
600	15.100	23.700	23.568	+1.12	- 61.729	- 62.585	44.745
700	15.100	23.733	23.568	+1.40	- 61.724	- 62.590	44.466
800	15.100	23.766	23.568	+1.68	- 61.719	- 62.595	44.187
900	15.100	23.799	23.568	+1.96	- 61.714	- 62.600	43.908
1000	15.100	23.832	23.568	+2.24	- 61.709	- 62.605	43.629
1100	15.100	23.865	23.568	+2.52	- 61.704	- 62.610	43.350
1200	15.100	23.898	23.568	+2.80	- 61.699	- 62.615	43.071
1300	15.100	23.931	23.568	+3.08	- 61.694	- 62.620	42.792
1400	15.100	23.964	23.568	+3.36	- 61.689	- 62.625	42.513
1500	15.100	23.997	23.568	+3.64	- 61.684	- 62.630	42.234
1600	15.100	24.030	23.568	+3.92	- 61.679	- 62.635	41.955
1700	15.100	24.063	23.568	+4.20	- 61.674	- 62.640	41.676
1800	15.100	24.096	23.568	+4.48	- 61.669	- 62.645	41.397
1900	15.100	24.129	23.568	+4.76	- 61.664	- 62.650	41.118
2000	15.100	24.162	23.568	+5.04	- 61.659	- 62.655	40.839
2100	15.100	24.195	23.568	+5.32	- 61.654	- 62.660	40.560
2200	15.100	24.228	23.568	+5.60	- 61.649	- 62.665	40.281
2300	15.100	24.261	23.568	+5.88	- 61.644	- 62.670	40.002
2400	15.100	24.294	23.568	+6.16	- 61.639	- 62.675	39.723
2500	15.100	24.327	23.568	+6.44	- 61.634	- 62.680	39.444

Sept. 30, 1961; June 30, 1968

LITHIUM IODIDE (LiI)

(LIQUID)

GFW = 133.8434

 $\Delta H^{\circ}_{298.15} = [23.568] \text{ gkcal/mol}$ $\Delta H^{\circ}_{298.15} = -61.749 \text{ kcal/mol}$ $\Delta H^{\circ}_{\text{m}} = 3.50 \text{ kcal/mol}$ $\Delta H^{\circ}(\text{to equilibrium mixture}) = 23.3 \text{ kcal/mol}$ $\Delta H^{\circ}(\text{to monomer only}) = [32.6] \text{ kcal/mol}$ $T_m = 742^{\circ}\text{K}$ $T_b(\text{to equilibrium mixture}) = 1449^{\circ}\text{K}$ $T_b(\text{to monomer only}) = [1497]^{\circ}\text{K}$

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding the heat of fusion and the difference between $H^{\circ}_{742} - H^{\circ}_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

A. S. Dworin, private communication, Oak Ridge National Laboratory, Dec. 1964, has derived the heat capacity, $C_p = 15.1 \text{ gkcal/mol}$, from enthalpy measurements, $742 - 802^{\circ}\text{K}$, by the drop method. The liquid heat capacity was assumed to be a constant, 15.1 gkcal/mol . The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See LiI(c) table for detail.

Vaporization Data.

T_b (to monomer only) is determined as the temperature at which the Gibbs energy change (ΔG°) for the reaction $\text{LiI(l)} = \text{LiI(g)}$ approaches zero. The corresponding enthalpy change (ΔH°) at boiling point is the heat of vaporization $\Delta H^{\circ}_{\text{v}}$ (to monomer only).

T_b (to equilibrium mixture) is the temperature at which the sum of the calculated partial vapor pressures of LiI(g) and $\text{Li}_2\text{I}_2(\text{g})$ reaches one atmosphere (trimer and higher polymer have been neglected in calculation). This value is in good agreement with the boiling point of 1444°K from the least squares fit of the total vapor pressure data measured by O. Ruff and S. Mugdan, Z. anorg. Chem. **117**, 147 (1921). $\Delta H^{\circ}_{\text{v}}$ (to equilibrium mixture) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 30.44 mole percent of dimer. For detailed information see LiI(g) and $\text{Li}_2\text{I}_2(\text{g})$ tables.

Lithium Iodide (LiI)

GFW = 133.8434

(IDEAL GAS)

OPW = 133.8434

[Li]

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-2.222	-21.290	-21.290	INFINITE
100	7.045	47.195	62.451	-1.526	-21.077	-24.892	54.401
200	7.742	52.280	56.719	-0.788	-20.606	-28.606	31.260
298	8.263	55.478	51.478	0.000	-21.750	-32.079	23.515
300	8.270	55.529	51.478	0.015	-21.758	-32.144	23.417
400	8.556	57.951	51.406	0.858	-21.122	-35.472	19.381
500	8.720	59.880	51.435	1.722	-20.437	-37.700	16.479
600	8.824	61.480	57.145	2.400	-20.721	-39.126	14.252
700	8.896	62.846	57.465	3.046	-20.984	-40.566	12.252
800	8.950	64.037	58.564	3.479	-21.234	-41.849	11.433
900	8.993	65.094	59.232	3.776	-21.480	-43.162	10.481
1000	9.029	66.043	59.866	4.177	-21.721	-44.446	9.714
1100	9.060	66.905	60.467	7.082	-21.958	-45.707	9.091
1200	9.087	67.693	61.037	7.989	-22.195	-46.948	8.583
1300	9.113	68.423	61.578	8.869	-22.424	-48.167	8.098
1400	9.136	69.099	62.091	9.811	-22.653	-49.369	7.707
1500	9.159	69.730	62.580	10.726	-22.877	-50.556	7.366
1600	9.180	70.322	63.045	11.643	-23.098	-51.726	7.065
1700	9.201	70.876	63.485	12.562	-23.316	-52.879	6.799
1800	9.221	71.406	63.915	13.483	-23.530	-54.005	6.559
1900	9.240	71.905	64.323	14.406	-23.739	-55.107	6.342
2000	9.260	72.379	64.714	15.331	-23.943	-56.186	6.146
2100	9.278	72.832	65.090	16.258	-24.143	-57.243	5.968
2200	9.297	73.266	65.451	17.189	-24.339	-58.278	5.805
2300	9.315	73.677	65.800	18.118	-24.531	-59.292	5.654
2400	9.334	74.074	66.137	19.050	-24.719	-60.285	5.513
2500	9.352	74.456	66.462	19.984	-24.904	-61.258	5.381
2600	9.370	74.823	66.776	20.920	-25.086	-62.211	5.258
2700	9.387	75.177	67.076	21.858	-25.265	-63.145	5.143
2800	9.405	75.518	67.376	22.798	-25.441	-64.059	5.036
2900	9.423	75.849	67.663	23.739	-25.614	-64.958	4.936
3000	9.440	76.168	67.941	24.682	-25.784	-65.843	4.842
3100	9.458	76.478	68.211	25.627	-25.951	-66.714	4.754
3200	9.475	76.777	68.471	26.574	-26.115	-67.572	4.671
3300	9.493	77.071	68.731	27.522	-26.276	-68.417	4.593
3400	9.510	77.354	68.980	28.473	-26.434	-69.249	4.520
3500	9.527	77.630	69.223	29.424	-26.589	-70.068	4.452
3600	9.545	77.899	69.461	30.378	-26.742	-70.874	4.388
3700	9.562	78.165	69.698	31.336	-26.892	-71.667	4.329
3800	9.579	78.416	69.918	32.299	-27.039	-72.447	4.274
3900	9.597	78.665	70.140	33.269	-27.183	-73.214	4.223
4000	9.614	78.908	70.356	34.210	-27.324	-73.968	4.174
4100	9.631	79.146	70.567	35.172	-27.462	-74.708	4.128
4200	9.648	79.377	70.771	36.130	-27.597	-75.434	4.084
4300	9.665	79.605	70.977	37.102	-27.729	-76.147	4.041
4400	9.682	79.828	71.176	38.069	-27.859	-76.847	4.000
4500	9.699	80.045	71.370	39.038	-27.986	-77.534	3.960
4600	9.717	80.250	71.563	40.008	-28.111	-78.208	3.921
4700	9.734	80.449	71.752	40.981	-28.234	-78.869	3.883
4800	9.751	80.673	71.932	41.956	-28.355	-79.517	3.846
4900	9.768	80.874	72.113	42.931	-28.474	-80.152	3.810
5000	9.785	81.072	72.290	43.909	-28.591	-80.774	3.775
5100	9.802	81.266	72.464	44.888	-28.706	-81.384	3.740
5200	9.819	81.456	72.635	45.869	-28.819	-81.981	3.705
5300	9.836	81.643	72.803	46.852	-28.930	-82.565	3.670
5400	9.853	81.827	72.969	47.837	-29.039	-83.137	3.635
5500	9.870	82.008	73.131	48.823	-29.146	-83.697	3.600
5600	9.887	82.186	73.292	49.811	-29.251	-84.244	3.565
5700	9.904	82.366	73.445	50.800	-29.354	-84.778	3.530
5800	9.921	82.534	73.594	51.791	-29.455	-85.300	3.495
5900	9.938	82.704	73.740	52.784	-29.554	-85.810	3.460
6000	9.955	82.871	73.888	53.779	-29.651	-86.308	3.425

Sept. 30, 1961; June 30, 1966

LITHIUM IODIDE (LiI)

(IDEAL GAS)

OPW = 133.8434

[Li]

Ground State Configuration 1Σ

ΔHf° = -21.3 ± 2 kcal/mol

ΔHf°_{298.15} = -21.75 ± 2 kcal/molS°_{298.15} = 55.478 gibbs/mol

Electronic Levels and Quantum Weights

$$\frac{\epsilon, \text{ cm}^{-1}}{g_i}$$
ω_e = 498.16 cm⁻¹

σ = 1

B_e = 0.44837 cm⁻¹r_e = 2.3919 Å

Heat of Formation.

The heat of formation (ΔHf°₂₉₈ (LiI, g) = -21.75 ± 2 kcal/mol) was calculated from the selected heat of sublimation and the heat of formation for lithium iodide (c). The heat of sublimation has been determined spectroscopically from the ion intensity measurement (2nd law method) by L. N. Gorokhov, Dokl. Akad. Nauk SSSR 142, 113 (1962), as ΔHs°(to monomer) = 42.9 ± 0.6 and ΔHs° (to dimer) = 43.2 ± 0.4 kcal/mol in the temperature range from 626-722°K. Gorokhov also reported the partial vapor pressure of monomeric lithium iodide (P_{monomer} = 3 X 10⁻³ mm Hg) and the ratio of dimer to monomer (P_{dimer}/P_{monomer} = 6) which have been used for third law calculation. Using the same technique, L. Friedman, J. Chem. Phys. 23, 477 (1955), reported the heats of sublimation as ΔHs°₇₂₇ (to monomer) = 41.9 ± 0.5 and ΔHs°₇₂₇ (to dimer) = 40.8 ± 0.5 kcal/mol in the temperature range from 630° to 730°K. J. Berkowitz, H. A. Tassman and W. A. Chupka, J. Chem. Phys. 36, 2170 (1962) have also studied the lithium iodide vapor in the mass spectrometer and reported the second law and third law values of the heat of dimerization at 800°K as 37.9 and 40.4 kcal/mol, respectively. Using the JANAF thermodynamic functions, all the heats of sublimation and dimerization at different temperatures have been reduced to 298°K and summarized in the following table. The total vapor pressure over the liquid has been measured by a boiling point method in the temperature range 1223° to 1413°K by O. Ruff and S. Muggen, Z. anorg. Chem. 117, 147 (1921). (Their data have been quoted by H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921).) In order to have good agreement between the calculated vapor pressure and the observed total vapor pressure, the heats of sublimation have been so chosen as ΔHs°₂₉₈ (to monomer) = 42.8 kcal/mol and ΔHs°₂₉₈ (to dimer) = 42.6 kcal/mol and the heat of dissociation of dimer, ΔHd°₂₉₈ = 43.0 kcal/mol. The calculated boiling point (to equilibrium mixture) is 1449°K which agrees with 1443°K reported by Wartenberg and Schulz, and also 1462°K by Ruff and Muggen.

Chemical Reaction	Investigator	ΔHf° ₂₉₈ kcal/mol	
		2nd law	3rd law
LiI(c) → LiI(g)	Gorokhov	44.7	42.2
	Friedman	43.9	—
2LiI(c) → Li ₂ I ₂ (g)	Gorokhov	46.0	41.3
	Friedman	44.1	—
Li ₂ I ₂ (g) → 2LiI(g)	Berkowitz et al.	38.8	41.3
	Friedman	43.7	—
	Gorokhov	43.2	43.1

Heat Capacity and Entropy.

The bond distance and the rotational constants (B_e and α_e), corrected to the isotopic abundance of 7.4% Li⁶ and 92.6% Li⁷, were obtained from the microwave studies by A. Honig, M. Mendel, M. L. Stich and C. H. Townes, Phys. Rev. 96, 629 (1954). The vibrational constants (ω_e and ω_ex_e) were determined from the infrared spectrum by W. Klemperer, W. O. Norris, A. Buchler and A. O. Enalle, J. Chem. Phys. 33, 1534 (1960).

The tabulated thermodynamic functions are in reasonable agreement with those calculated by R. L. Wilkins, J. Chem. Eng. Data 5, 337 (1960), who used slightly different molecular constants.

[Li]

T, °K	Cp°	S° -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔG° _f	Log Kp
0	∞.000	INFINITE	- 2.894	27.557	27.557	INFINITE
100	9.131	56.417	27.041	27.330	26.396	- 27.688
200	10.543	63.234	68.568	27.071	25.581	- 27.953
298	11.199	67.581	67.481	26.800	24.917	- 18.265
300	11.208	67.650	67.581	26.796	24.906	- 18.144
400	11.607	70.932	68.026	26.447	24.377	- 13.319
500	11.938	73.559	72.340	26.347	24.813	- 10.846
600	12.232	75.762	69.847	19.373	25.604	- 9.436
700	12.495	77.597	70.407	19.407	26.050	- 9.429
800	12.732	79.359	71.031	19.487	26.921	- 9.429
900	12.940	80.856	72.717	19.529	29.146	- 7.078
1000	13.026	82.026	73.600	19.529	30.218	- 6.604
1100	13.147	83.468	74.442	19.571	31.284	- 6.216
1200	13.278	84.616	75.242	19.612	32.349	- 5.891
1300	13.408	85.688	76.000	19.650	33.406	- 5.620
1400	13.537	86.670	76.732	19.690	34.464	- 5.380
1500	13.655	87.596	77.425	19.727	35.518	- 5.175
1600	13.764	88.466	78.089	19.761	36.571	- 4.995
1700	13.865	89.285	78.723	19.793	37.620	- 4.836
1800	13.958	90.059	79.324	19.822	38.664	- 4.696
1900	14.043	90.797	79.916	19.848	39.714	- 4.568
2000	14.120	91.496	80.478	19.872	40.757	- 4.454
2100	14.189	92.162	81.018	19.893	41.801	- 4.350
2200	14.252	92.797	81.540	19.910	42.844	- 4.256
2300	14.309	93.400	82.045	19.925	43.884	- 4.172
2400	14.361	93.980	82.528	19.937	44.920	- 4.099
2500	14.408	94.550	82.998	19.944	45.959	- 4.019
2600	14.450	95.089	83.453	19.950	47.010	- 3.952
2700	14.488	95.599	83.891	19.953	48.062	- 3.889
2800	14.522	96.079	84.311	19.954	49.114	- 3.829
2900	14.552	96.522	84.736	19.956	50.134	- 3.772
3000	14.578	96.939	85.139	19.958	51.174	- 3.728
3100	14.600	97.311	85.530	19.959	52.216	- 3.681
3200	14.618	97.648	85.905	19.960	53.259	- 3.637
3300	14.633	97.949	86.263	19.961	54.299	- 3.597
3400	14.645	98.217	86.605	19.962	55.334	- 3.557
3500	14.654	98.456	86.945	19.963	56.363	- 3.521
3600	14.661	98.667	87.267	19.964	57.384	- 3.486
3700	14.666	98.851	87.571	19.965	58.396	- 3.452
3800	14.669	99.019	87.858	19.966	59.400	- 3.423
3900	14.671	99.172	88.128	19.967	60.396	- 3.394
4000	14.672	99.311	88.379	19.968	61.384	- 3.366
4100	14.672	99.437	88.609	19.969	62.364	- 3.340
4200	14.672	99.551	88.819	19.970	63.336	- 3.315
4300	14.672	99.654	89.019	19.971	64.300	- 3.291
4400	14.672	99.748	89.209	19.972	65.256	- 3.269
4500	14.672	99.834	89.389	19.973	66.204	- 3.247
4600	14.672	99.911	89.559	19.974	67.144	- 3.227
4700	14.672	100.000	89.719	19.975	68.076	- 3.207
4800	14.672	100.099	89.869	19.976	68.999	- 3.187
4900	14.672	100.199	89.999	19.977	69.914	- 3.170
5000	14.672	100.299	90.119	19.978	70.820	- 3.153
5100	14.672	100.399	90.229	19.979	71.717	- 3.137
5200	14.672	100.499	90.329	19.980	72.606	- 3.121
5300	14.672	100.599	90.419	19.981	73.487	- 3.105
5400	14.672	100.699	90.509	19.982	74.360	- 3.090
5500	14.672	100.799	90.589	19.983	75.226	- 3.077
5600	14.672	100.899	90.659	19.984	76.084	- 3.064
5700	14.672	100.999	90.719	19.985	76.934	- 3.051
5800	14.672	101.099	90.769	19.986	77.776	- 3.039
5900	14.672	101.199	90.809	19.987	78.609	- 3.026
6000	14.672	101.299	90.839	19.988	79.434	- 3.015

Mar. 31, 1962; Dec. 31, 1966

Point Group C_∞ΔH°_f = [27.6 ± 5] kcal/molS°_{298.15} = [67.59] gibbs/molΔH°_f = [26.8 ± 5] kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm⁻¹

[1780] (1)

[440] (1)

[200] (1)

Bond Distance: O-N = [1.15] Å

N-I = [2.3] Å

Bond Angle: O-N-I = [120]°

Product of the Moment of Inertia: I_AI_BI_C = [7.742 × 10⁻⁴¹] g³ cm⁶

Heat of Formation.

The heat of formation (ΔH°_f 298.15) for INO (g) is estimated by comparison with those for FNO(g), ClNO(g), BrNO(g), and the related cyanogen halides.

Heat Capacity and Entropy.

The molecular structure and bond angle are estimated by comparison with those for ClNO(g) and BrNO(g). The N-O bond distance is assumed to be the same as that in NO(g). The N-I bond distance (r_{N-I}) is calculated based on an assumption that r_{ON-Cl} - r_{ON-I} = r_{ON-Cl} - r_{I-I}. The vibrational frequencies are estimated by comparison with those for FNO(g), ClNO(g) and BrNO(g). The three principal moments of inertia are: I_A = 8.834 × 10⁻⁴⁰, I_B = 2.916 × 10⁻³⁸ and I_C = 3.005 × 10⁻³⁸ g cm².

Sodium Iodide (NaI)

(Crystal) Mol. Wt. = 149.901

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	0.000	INFINITE	INFINITE	2.933	-68.615	-68.615	INFINITE
100	10.285	10.899	34.199	2.330	-68.498	-68.498	-68.498	14.9674
200	11.915	18.667	24.667	1.200	-68.743	-68.743	-68.743	74.589
298	12.482	23.542	23.542	0.000	-68.800	-68.800	-68.800	49.853
300	12.490	23.619	23.542	0.023	-68.801	-68.801	-68.801	49.852
400	12.860	27.265	24.077	1.293	-76.463	-76.463	-76.463	36.941
500	13.150	30.167	24.082	2.592	-76.664	-76.664	-76.664	28.916
600	13.440	32.591	26.034	3.922	-76.504	-76.504	-76.504	23.337
800	13.910	34.693	28.141	5.280	-76.302	-76.302	-76.302	19.361
900	14.266	38.193	29.221	8.076	-75.897	-75.897	-75.897	14.083
1000	14.508	39.706	30.155	9.513	-75.498	-75.498	-75.498	12.246
1100	14.766	41.103	31.124	10.977	-75.184	-75.184	-75.184	10.749
1200	15.020	42.399	32.010	12.466	-74.866	-74.866	-74.866	9.424
1300	15.278	43.611	32.856	13.971	-74.545	-74.545	-74.545	8.053
1400	15.528	44.752	33.659	15.491	-74.221	-74.221	-74.221	6.716
1500	15.778	45.832	34.441	17.087	-73.897	-73.897	-73.897	5.480
1600	16.027	46.858	35.185	18.677	-73.572	-73.572	-73.572	4.306
1700	16.273	47.837	35.901	20.292	-73.246	-73.246	-73.246	3.237
1800	16.518	48.764	36.580	21.931	-72.919	-72.919	-72.919	2.262
1900	16.760	49.674	37.255	23.593	-72.593	-72.593	-72.593	1.375
2000	17.000	50.540	37.898	25.283	-72.268	-72.268	-72.268	0.482

SODIUM IODIDE (NaI)

(CRYSTAL)

MOL. WT. = 149.901

$$\Delta H_f^o = -68.6 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o \text{ 298.15} = -68.8 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\Delta H_m = 5.64 \text{ kcal. mole}^{-1}$$

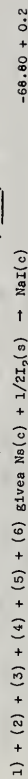
$$S_{298.15}^o = 23.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 933^\circ \text{K.}$$

Heat of Formation.

The heat of formation was obtained as follows:

- (1) $\text{HI} \cdot 100\text{H}_2\text{O} + \text{NaOH} \cdot 100\text{H}_2\text{O} \rightarrow \text{NaI} \cdot 20\text{H}_2\text{O}$
T. W. Richards, A. W. Rowe, J. Am. Chem. Soc. **44**, 684 (1922).
 $\Delta H_{298}^o (\text{kcal. mole}^{-1})$
-13.51 ± 0.02
- (2) $\text{Na(c)} + 100\text{H}_2\text{O(l)} \rightarrow \text{NaOH} \cdot 100\text{H}_2\text{O} + 1/2\text{H}_2(\text{g})$
S. R. Gunn, L. O. Green, J. Am. Chem. Soc. **80**, 4782 (1958).
-44.069 ± 0.006
- (3) $\text{NaOH} \cdot 100\text{H}_2\text{O} \rightarrow \text{NaOH} \cdot 100\text{H}_2\text{O} + 900\text{H}_2\text{O(l)}$
National Bureau of Standards Circular 500.
+0.031 ± 0.004
- (4) $1/2\text{H}_2(\text{g}) + 1/2\text{I}_2(\text{s}) \rightarrow \text{HI}(\text{g})$
JANAF Tables.
+6.30 ± 0.05
- (5) $\text{HI}(\text{g}) + 100\text{H}_2\text{O(l)} \rightarrow \text{HI} \cdot 100\text{H}_2\text{O}$
W. A. Roth, Z. Elektrochem. **50**, 107 (1944).
-19.30 ± 0.05
- (6) $\text{NaI} \cdot 20\text{H}_2\text{O} \rightarrow \text{NaI(c)} + 20\text{H}_2\text{O(l)}$
J. Wast, E. Lange, Z. physik. Chem. **116**, 161 (1925).
+1.75 ± 0.06
E. Lange, A. L. Robinson, Chem. Revs. **9**, 89 (1931).
Askew, Bullock, Smith, Tinkler, Gatty, Wolfenden, J. Chem. Soc., **1934**, 1368.



Heat Capacity and Entropy.

Smoothed heat capacities between 3° and 270°K. have been presented by W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) **242A**, 467 (1957). Above 270°K. the heat capacity was obtained by comparing with KI(c) on a reduced temperature plot of C_p/T versus T . The values so obtained were increased by 1.4% to bring them into line with the low temperature data.

Melting Data.

A. Dworkin and M. Bredig, J. Phys. Chem. **64**, 269 (1960) have measured both T_m and ΔH_m .

Sodium Iodide (NaI)

(Liquid) Mol. Wt. = 149.901

INa

SODIUM IODIDE (NaI)

(LIQUID)

MOL. WT. = 149.901

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	S°	(F° - H° ₂₉₈)/T	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0										
100	12.482	28.862	28.862	0.000	-	63.695	-	64.490	-	47.274
200	12.490	28.939	28.862	0.029	-	63.696	-	64.500	-	46.986
300	12.860	32.585	29.337	1.291	-	66.358	-	66.637	-	39.314
400	13.150	35.487	30.302	2.592	-	71.559	-	63.715	-	27.648
500	15.500	37.910	31.374	3.922	-	71.399	-	62.158	-	22.640
600	15.500	40.300	32.463	5.472	-	71.005	-	60.650	-	18.035
700	15.500	42.370	33.592	7.022	-	70.600	-	59.198	-	16.171
800	15.500	44.195	34.671	8.572	-	70.192	-	57.797	-	14.034
900	15.500	45.828	35.706	10.122	-	69.785	-	56.441	-	12.335
1000	15.500	47.306	36.695	11.672	-	69.384	-	55.128	-	10.982
1100	15.500	48.634	37.636	13.222	-	68.920	-	53.802	-	9.724
1200	15.500	49.895	38.532	14.772	-	68.430	-	52.470	-	8.436
1300	15.500	51.044	39.385	16.322	-	67.913	-	51.134	-	7.339
1400	15.500	52.113	40.198	17.872	-	67.377	-	49.791	-	6.395
1500	15.500	53.113	40.975	19.422	-	66.841	-	48.400	-	5.574
1600	15.500	54.053	41.717	20.972	-	66.245	-	47.059	-	4.854
1700	15.500	54.939	42.427	22.522	-	65.650	-	45.748	-	4.219
1800	15.500	55.777	43.107	24.072	-	65.057	-	44.469	-	3.654
1900	15.500	56.572	43.761	25.622	-	64.465	-	43.223	-	3.150
2000	15.500	57.326	44.389	27.172	-	63.872	-	42.006	-	2.696
2100	15.500	58.049	44.994	28.722	-	63.282	-	40.817	-	2.286
2200	15.500	58.738	45.577	30.272	-	62.692	-	39.652	-	1.915
2300	15.500	59.398	46.139	31.822	-	62.103	-	38.516	-	1.577
2400	15.500	60.031	46.682	33.372	-	61.516	-	37.406	-	1.268
2500	15.500	60.639	47.207	34.922	-	60.931	-	36.321	-	0.985
2600	15.500	61.224	47.715	36.472	-	60.348	-	35.261	-	0.724
2700	15.500	61.787	48.208	38.022	-	59.767	-	34.226	-	0.484
2800	15.500	62.331	48.686	39.572	-	59.188	-	33.216	-	0.262
2900	15.500	62.857	49.149	41.122	-	58.613	-	32.231	-	0.057

Sept. 30, 1963

 $S_{298.15}^{\circ} = 28.862 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^{\circ} 298.15 = -63.695 \text{ kcal. mole}^{-1}$ $\Delta H_m = 5.64 \text{ kcal. mole}^{-1}$ $T_m = 933^{\circ}\text{K.}$ $T_b = 1577^{\circ}\text{K. (equilibrium mixture)}$

Heat of Formation.

$\Delta H_f^{\circ} 298.15$ was calculated from the heat of formation of the crystal plus the heat of melting and the difference between $H_{933}^{\circ} - H_{293}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

C_p was estimated assuming each atom contributed $7/5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. $S_{298.15}^{\circ}$ was calculated in a manner similar to $\Delta H_f^{\circ} 298.15$.

Melting Data.

See table for crystal.

Vaporization Data.

The boiling point is that given by K. K. Kelley, U. S. Bureau of Mines Bulletin 363, 1955 from examination of the high temperature vapor pressure.

INa

Lead Moniodide (PbI)

(Ideal Gas) Mol. Wt. = 334.12

INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	2.470	26.451	26.451	INFINITE
100	8.262	57.411	1.723	26.410	22.279	-48.688
200	8.752	63.334	0.866	26.076	18.273	-19.967
298	8.870	66.855	0.000	25.700	14.522	-10.664
300	8.871	66.910	0.016	25.692	14.453	-10.528
400	8.920	69.470	0.016	23.344	10.836	-5.920
500	8.948	71.463	1.800	17.803	8.240	-3.602
600	8.966	73.086	2.696	17.561	6.350	-2.313
700	8.983	74.580	3.492	16.138	5.073	-1.465
800	8.993	75.980	4.092	15.138	4.073	-0.944
900	9.005	76.740	5.392	15.600	1.494	-0.13
1000	9.017	77.689	6.293	15.342	-0.059	0.13
1100	9.034	78.549	7.195	15.092	-1.588	0.315
1200	9.044	79.008	8.094	14.815	-2.478	0.770
1300	9.064	80.040	9.113	14.382	-6.047	0.944
1400	9.086	80.733	9.912	14.382	-6.047	1.092
1500	9.113	81.360	10.822	14.151	-7.497	1.220
1600	9.145	81.949	11.734	13.920	-8.932	1.331
1700	9.181	82.501	12.651	13.689	-10.353	1.434
1800	9.219	83.021	13.571	13.459	-11.763	1.531
1900	9.262	83.510	14.495	13.223	-13.157	1.623
2000	9.308	84.007	15.423	12.989	-14.539	1.715
2100	9.356	84.462	16.356	-	-15.907	1.808
2200	9.405	84.897	17.293	-	-17.260	1.901
2300	9.455	85.309	18.234	-	-18.600	2.000
2400	9.505	85.721	19.185	-	-19.927	2.100
2500	9.555	86.110	20.138	-	-21.250	2.200
2600	9.604	86.485	21.096	-	-22.569	2.300
2700	9.652	86.841	22.059	-	-23.884	2.400
2800	9.699	87.181	23.029	-	-25.195	2.500
2900	9.744	87.542	23.999	-	-26.503	2.600
3000	9.787	87.873	24.975	-	-27.808	2.700
3100	9.827	88.184	25.956	-	-29.110	2.800
3200	9.866	88.481	26.941	-	-30.411	2.900
3300	9.902	88.761	27.929	-	-31.713	3.000
3400	9.936	89.107	28.921	-	-33.015	3.100
3500	9.968	89.396	29.916	-	-34.318	3.200
3600	9.997	89.677	30.914	-	-35.621	3.300
3700	10.024	89.941	31.915	-	-36.925	3.400
3800	10.049	90.184	32.920	-	-38.229	3.500
3900	10.072	90.480	33.925	-	-39.534	3.600
4000	10.093	90.736	34.933	-	-40.838	3.700
4100	10.112	90.985	35.944	-	-42.143	3.800
4200	10.129	91.229	36.956	-	-43.447	3.900
4300	10.144	91.468	37.969	-	-44.752	4.000
4400	10.158	91.701	38.981	-	-46.056	4.100
4500	10.170	91.929	39.993	-	-47.361	4.200
4600	10.182	92.153	41.018	-	-48.665	4.300
4700	10.193	92.372	42.048	-	-49.969	4.400
4800	10.200	92.587	43.081	-	-51.274	4.500
4900	10.207	92.797	44.116	-	-52.578	4.600
5000	10.214	93.003	45.152	-	-53.883	4.700
5100	10.219	93.206	46.189	-	-55.187	4.800
5200	10.224	93.408	47.227	-	-56.492	4.900
5300	10.228	93.599	48.269	-	-57.796	5.000
5400	10.231	93.790	49.312	-	-59.101	5.100
5500	10.234	93.978	50.356	-	-60.405	5.200
5600	10.236	94.162	51.401	-	-61.710	5.300
5700	10.239	94.345	52.446	-	-63.014	5.400
5800	10.241	94.527	53.491	-	-64.319	5.500
5900	10.243	94.697	54.536	-	-65.623	5.600
6000	10.240	94.869	55.581	-	-66.928	5.700

June 30, 1952

Lead Moniodide (PbI)

(Ideal Gas)

Mol. Wt. = 334.12

ΔH_f⁰ 298.15 = 25.7 ± 9.2 kcal. mole⁻¹

S_{298.15} = 66.855 cal. deg.⁻¹ mole⁻¹

Ground State Configuration ²Π_{1/2}

Electronic Levels and Multiplicities

ε, cm. ⁻¹	ε ₁
0	2
[8000]	2

ω_e = 160.5 cm.⁻¹

ω_ex_e = 0.25 cm.⁻¹

B_e = [0.02940] cm.⁻¹

α_e = [0.00000] cm.⁻¹

σ = 1

Heat of Formation. ΔH_f⁰ 298.15 was calculated from the dissociation energy of PbI(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ω_e and ω_ex_e were obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950. B_e and α_e were estimated by comparison with the corresponding values for the other diatomic halide molecules. Electronic levels and multiplicities were estimated from those for Pb(g).

Titanium Monoiodide (TiI)
(Ideal Gas) GFW = 174.8044

TITANIUM MONOIODIDE (TiI) (IDEAL GAS)

GFW = 174.8044

Ground State Configuration [⁴F]

$\Delta H_f^\circ = [65.8 \pm 10.0] \text{ kcal/mol}$

$S_{298.15}^\circ = 64.22 \pm 2.0 \text{ gibbs/mol}$

$\Delta H_{f,298.15}^\circ = [65.5 \pm 10.0] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{ cm}^{-1}$	g_i
0	[4]
[1000]	[4]
[2000]	[4]
[4000]	[4]
[6000]	[4]
[8000]	[4]
[10000]	[4]

$\omega_e = [240] \text{ cm}^{-1}$ $\omega_e x_e = [1.67] \text{ cm}^{-1}$ $\sigma = 1$

$B_e = [0.062] \text{ cm}^{-1}$ $B_0 = [0.00043] \text{ cm}^{-1}$ $r_e = [2.8] \text{ \AA}$

Heat of Formation

The heat of formation, $\Delta H_{f,298}^\circ$ of TiI (g) is calculated from the dissociation energy, D_0° , which is estimated as 73 kcal/mol. This estimate is obtained from the relation $D(\text{TiI}) < D^\circ(\text{TiI}) < D^\circ(\text{TiI})$, where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF₂(g) by Zmbov and Margrave (1).

Heat Capacity and Entropy

The vibrational frequency, ω_e , and the anharmonic vibrational term, $\omega_e x_e$, are estimated from those of TiCl(g) and comparisons of the mercury and alkali monohalides. The interatomic distance is estimated from Guggenheimer's relation (2). B_e is calculated from r_e . The ground state term and electronic levels are estimated from the ground state multiplet of Ti⁺ (3). σ_e is estimated from the Morse potential function.

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
2. K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
3. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	$\log K_p$
0	7.900	INFINITE	-	2.964	65.864	65.864	INFINITE
100	7.786	54.962	72.005	-1.763	64.026	-134.312	-
200	6.647	60.668	65.048	-8.76	65.868	56.957	-62.240
298	6.192	64.225	64.225	0.000	65.500	52.673	-38.611
300	6.201	64.281	64.225	0.017	65.494	52.593	-38.315
400	6.412	66.193	64.225	1.967	65.494	52.593	-38.315
500	10.015	65.299	65.299	1.967	57.612	45.226	-10.768
600	10.239	71.040	66.106	2.961	57.712	42.715	-15.559
700	10.374	72.630	66.227	3.992	57.607	40.224	-15.559
800	10.451	74.021	67.129	5.033	57.488	37.769	-10.313
900	10.477	75.261	67.849	6.075	57.369	35.321	-7.865
1000	10.517	76.361	68.230	7.131	57.182	32.867	-7.179
1100	10.532	77.364	69.224	8.184	56.992	30.424	-6.045
1200	10.545	78.281	70.238	9.238	56.799	28.056	-5.110
1300	10.558	79.126	71.268	10.293	56.606	25.745	-4.328
1400	10.570	80.003	72.314	11.348	56.413	23.487	-3.682
1500	10.591	80.639	72.367	12.408	56.220	21.150	-3.082
1600	10.611	81.323	72.905	13.468	55.294	18.671	-2.578
1700	10.632	81.967	73.420	14.530	55.115	16.588	-2.134
1800	10.656	82.575	73.912	15.594	54.916	14.338	-1.781
1900	10.678	83.156	74.386	16.658	54.660	12.100	-1.481
2000	10.705	83.700	74.835	17.730	50.008	10.006	-1.093
2100	10.730	84.223	75.270	18.802	49.769	8.013	-0.834
2200	10.755	84.723	75.688	19.876	49.532	6.059	-0.599
2300	10.780	85.202	76.092	20.953	49.297	4.059	-0.386
2400	10.804	85.661	76.481	22.031	49.062	2.059	-0.193
2500	10.827	86.102	76.857	23.114	48.831	0.144	-0.113
2600	10.849	86.527	77.221	24.198	48.601	-1.800	-0.151
2700	10.870	86.937	77.573	25.283	48.372	-3.733	-0.302
2800	10.890	87.333	77.915	26.371	48.144	-5.659	-0.442
2900	10.909	87.715	78.251	27.461	47.916	-7.585	-0.581
3000	10.926	88.084	78.568	28.553	47.683	-9.505	-0.691
3100	10.943	88.447	78.881	29.647	47.449	-11.386	-0.803
3200	10.959	88.792	79.185	30.742	47.216	-13.284	-0.907
3300	10.974	89.127	79.491	31.838	47.024	-15.170	-1.005
3400	10.989	89.458	79.795	32.934	46.832	-17.070	-1.095
3500	11.002	89.776	80.051	34.036	46.592	-18.926	-1.182
3600	11.015	90.086	80.326	35.137	46.353	-20.533	-1.246
3700	11.028	90.388	80.593	36.239	46.115	-22.156	-1.306
3800	11.040	90.682	80.855	37.347	45.878	-23.796	-1.362
3900	11.051	90.970	81.116	38.453	45.641	-25.456	-1.416
4000	11.063	91.249	81.361	39.553	56.104	-27.132	-1.469
4100	11.074	91.522	81.605	40.660	56.345	-28.824	-1.520
4200	11.084	91.789	81.845	41.767	56.599	-30.532	-1.568
4300	11.095	92.050	82.079	42.874	56.863	-32.256	-1.614
4400	11.105	92.305	82.312	43.981	57.127	-33.996	-1.658
4500	11.116	92.555	82.533	45.088	57.424	-35.752	-1.700
4600	11.126	92.800	82.754	46.210	57.720	-37.524	-1.740
4700	11.137	93.039	82.970	47.333	58.025	-39.312	-1.778
4800	11.147	93.273	83.182	48.456	58.333	-41.116	-1.814
4900	11.158	93.503	83.392	49.579	58.649	-42.936	-1.848
5000	11.169	93.729	83.595	50.699	58.994	-44.776	-1.882
5100	11.180	93.950	83.796	51.766	59.332	-46.636	-1.914
5200	11.191	94.167	83.993	52.833	59.678	-48.516	-1.944
5300	11.201	94.379	84.188	53.899	60.030	-50.416	-1.972
5400	11.213	94.590	84.378	54.965	60.390	-52.336	-2.000
5500	11.225	94.794	84.566	56.027	60.754	-54.276	-2.026
5600	11.237	94.998	84.750	57.090	61.124	-56.236	-2.052
5700	11.249	95.197	84.932	58.152	61.498	-58.216	-2.078
5800	11.261	95.391	85.116	59.214	61.876	-60.216	-2.104
5900	11.274	95.586	85.296	60.276	62.256	-62.236	-2.128
6000	11.287	95.775	85.480	61.338	62.645	-64.276	-2.150

June 30, 1964; Sept. 30, 1964; June 30, 1968; Dec. 31, 1968

Zirconium Moniodide (ZrI)
(Ideal Gas) Mol. Wt. = 218.13

ZIRCONIUM MONIODIDE (ZrI) (IDEAL GAS)

MOL. WT. = 218.13

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔG _f ⁰	Log K _p
0	∞.000	∞.000	2.411	141.763	141.763	∞.000
100	7.464	56.651	1.684	137.330	137.330	14.120
200	8.385	62.385	0.861	132.144	132.144	13.144
298	8.593	63.668	0.000	128.575	128.575	12.244
300	8.625	65.923	65.868	128.497	128.497	93.605
400	8.924	66.477	66.216	128.356	128.356	67.943
500	9.093	67.075	66.875	128.239	128.239	52.991
600	9.205	72.116	67.616	128.171	128.171	43.200
700	9.269	73.510	68.381	128.101	128.101	36.387
800	9.309	74.722	69.082	128.029	128.029	31.176
900	9.316	75.794	69.769	127.955	127.955	27.155
1000	9.312	76.756	70.421	127.880	127.880	23.945
1100	9.304	77.629	71.037	127.805	127.805	21.325
1200	9.290	78.427	71.620	127.729	127.729	19.155
1300	9.271	79.163	72.172	127.653	127.653	17.339
1400	9.247	79.847	72.696	127.577	127.577	15.768
1500	9.219	80.485	73.194	127.501	127.501	14.419
1600	9.187	81.083	73.669	127.425	127.425	13.241
1700	9.151	81.647	74.122	127.349	127.349	12.204
1800	9.111	82.179	74.555	127.273	127.273	11.265
1900	9.068	82.684	74.969	127.197	127.197	10.465
2000	9.021	83.164	75.367	127.121	127.121	9.789
2100	8.971	83.622	75.750	127.045	127.045	9.065
2200	8.918	84.059	76.117	126.969	126.969	8.479
2300	8.862	84.478	76.472	126.893	126.893	7.952
2400	8.803	84.880	76.814	126.817	126.817	7.470
2500	8.741	85.267	77.144	126.741	126.741	7.026
2600	8.676	85.639	77.464	126.665	126.665	6.622
2700	8.609	85.998	77.773	126.589	126.589	6.266
2800	8.546	86.345	78.073	126.513	126.513	5.959
2900	8.478	86.680	78.364	126.437	126.437	5.577
3000	8.407	86.994	78.647	126.361	126.361	5.276
3100	8.333	87.290	78.922	126.285	126.285	4.994
3200	8.257	87.577	79.189	126.209	126.209	4.734
3300	8.179	87.857	79.449	126.133	126.133	4.490
3400	8.099	88.121	79.703	126.057	126.057	4.260
3500	8.017	88.379	79.950	125.981	125.981	4.043
3600	7.932	88.631	80.191	125.905	125.905	3.840
3700	7.847	88.878	80.426	125.829	125.829	3.646
3800	7.764	89.120	80.656	125.753	125.753	3.466
3900	7.679	89.358	80.881	125.677	125.677	3.295
4000	7.594	89.594	81.101	125.601	125.601	3.132
4100	7.509	90.036	81.316	125.525	125.525	2.979
4200	7.424	90.273	81.526	125.449	125.449	2.832
4300	7.340	90.505	81.732	125.373	125.373	2.693
4400	7.256	90.733	81.934	125.297	125.297	2.560
4500	7.171	90.955	82.132	125.221	125.221	2.435
4600	7.087	91.173	82.326	125.145	125.145	2.314
4700	7.003	91.387	82.517	125.069	125.069	2.199
4800	6.919	91.597	82.704	124.993	124.993	2.159
4900	6.835	91.803	82.887	124.917	124.917	2.083
5000	6.751	92.005	83.068	124.841	124.841	2.002
5100	6.667	92.204	83.245	124.765	124.765	1.923
5200	6.583	92.399	83.419	124.689	124.689	1.848
5300	6.500	92.591	83.590	124.613	124.613	1.773
5400	6.416	92.780	83.759	124.537	124.537	1.698
5500	6.332	92.966	83.925	124.461	124.461	1.623
5600	6.249	93.149	84.088	124.385	124.385	1.548
5700	6.165	93.329	84.248	124.309	124.309	1.473
5800	6.081	93.506	84.406	124.233	124.233	1.398
5900	6.000	93.680	84.562	124.157	124.157	1.323
6000	5.916	93.852	84.715	124.081	124.081	1.248

Sept. 30, 1964

$$\Delta H_f^0 = [141.8 \pm 10.0] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = [141.3 \pm 10.0] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = [65.87] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

<u>Electronic Levels and Multiplicities</u>		
ϵ	cm.^{-1}	g_i

$$\omega_e x_e = [1.2] \text{ cm.}^{-1}$$

$$\alpha'_e = [0.00020] \text{ cm.}^{-1}$$

$$r_e = [2.9] \text{ \AA}$$

Heat of Formation

The dissociation energy was estimated from a correlation of the JANAF values for TiCl(g) , TiI(g) , and ZrCl(g) . The resulting value, 29.7 kcal. mole⁻¹, was employed with auxiliary JANAF heats of formation for Zr(g) and I(g) in calculating $\Delta H_f^{298.15}$.

Heat Capacity and Entropy

The vibrational frequency was estimated from those of TiI(g) , TiCl(g) , and the alkali halides. The ground state configuration was assumed to be analogous to the ground term of TiCl(g) as given by E. A. Shenoyakaya, et al., Optics and Spectroscopy, 12, 359 (1962). The internuclear distance was estimated from those of TiBr(g) , TiI(g) and ZrI(g) .

T, K.	C _p	$\frac{\text{cal. mole}^{-1}\text{deg.}^{-1}}{S^\circ - (F^\circ - H_{298}^\circ)/T}$	$\frac{\text{kcal. mole}^{-1}}{H^\circ - H_{298}^\circ}$	ΔF°	Log K _P
0	0.000	14.581	36.810	0.000	0.000
100	10.911	22.696	28.930	0.000	0.000
200	12.395	27.758	21.758	0.000	0.000
298	13.011	27.758	21.758	0.000	0.000
300	13.026	27.758	21.758	0.000	0.000
400	13.251	27.758	21.758	0.000	0.000
500	13.488	27.758	21.758	0.000	0.000
600	8.980	39.152	17.616	0.000	0.000
700	9.005	43.447	18.515	0.000	0.000
800	9.030	47.742	19.414	0.000	0.000
900	9.055	52.037	20.313	0.000	0.000
1000	9.081	56.332	21.212	0.000	0.000
1100	9.077	73.983	22.132	0.000	0.000
1200	9.062	75.772	23.041	0.000	0.000
1300	9.047	77.561	23.950	0.000	0.000
1400	9.032	79.350	24.859	0.000	0.000
1500	9.017	81.139	25.768	0.000	0.000
1600	9.002	82.928	26.677	0.000	0.000
1700	8.987	84.717	27.586	0.000	0.000
1800	8.972	86.506	28.495	0.000	0.000
1900	8.957	88.295	29.404	0.000	0.000
2000	8.942	90.084	30.313	0.000	0.000
2100	8.927	91.873	31.222	0.000	0.000
2200	8.912	93.662	32.131	0.000	0.000
2300	8.897	95.451	33.040	0.000	0.000
2400	8.882	97.240	33.949	0.000	0.000
2500	8.867	99.029	34.858	0.000	0.000
2600	8.852	100.818	35.767	0.000	0.000
2700	8.837	102.607	36.676	0.000	0.000
2800	8.822	104.396	37.585	0.000	0.000
2900	8.807	106.185	38.494	0.000	0.000
3000	8.792	107.974	39.403	0.000	0.000
3100	8.777	109.763	40.312	0.000	0.000
3200	8.762	111.552	41.221	0.000	0.000
3300	8.747	113.341	42.130	0.000	0.000
3400	8.732	115.130	43.039	0.000	0.000
3500	8.717	116.919	43.948	0.000	0.000
3600	8.702	118.708	44.857	0.000	0.000
3700	8.687	120.497	45.766	0.000	0.000
3800	8.672	122.286	46.675	0.000	0.000
3900	8.657	124.075	47.584	0.000	0.000
4000	8.642	125.864	48.493	0.000	0.000
4100	8.627	127.653	49.402	0.000	0.000
4200	8.612	129.442	50.311	0.000	0.000
4300	8.597	131.231	51.220	0.000	0.000
4400	8.582	133.020	52.129	0.000	0.000
4500	8.567	134.809	53.038	0.000	0.000
4600	8.552	136.598	53.947	0.000	0.000
4700	8.537	138.387	54.856	0.000	0.000
4800	8.522	140.176	55.765	0.000	0.000
4900	8.507	141.965	56.674	0.000	0.000
5000	8.492	143.754	57.583	0.000	0.000
5100	8.477	145.543	58.492	0.000	0.000
5200	8.462	147.332	59.401	0.000	0.000
5300	8.447	149.121	60.310	0.000	0.000
5400	8.432	150.910	61.219	0.000	0.000
5500	8.417	152.699	62.128	0.000	0.000
5600	8.402	154.488	63.037	0.000	0.000
5700	8.387	156.277	63.946	0.000	0.000
5800	8.372	158.066	64.855	0.000	0.000
5900	8.357	159.855	65.764	0.000	0.000
6000	8.342	161.644	66.673	0.000	0.000

September 30, 1961

IODINE (I₂)

(REFERENCE STATE)

MOL. WT. = 253.82

0°K to 386.75°K Crystal
386.75°K to 458.59°K Liquid
458.59°K to 8000°K Ideal Diatomic Gas

Heat of Formation.

Zero by definition.

Heat Capacity of Crystal.

The recent measurements of D. A. Shirley and W. P. Giauque [J. Am. Chem. Soc. 81, 4778 (1959)] over the temperature range 13° to 327°K are adopted, no weight being given to the earlier work of E. Lange [Z. physik. Chem. 110, 343 (1924)], which deviate by 1% or more. L. G. Carpenter and T. P. Harle [Phil. Mag. 23, 193 (1937)] measured the heat capacity of crystalline and liquid iodine by an adiabatic method. Their data are in poor agreement with Shirley and Giauque in the range 275° to 330°K and are given no weight. K. J. Frederick and J. H. Hildebrand [J. Am. Chem. Soc. 80, 1436 (1958)] measured the enthalpy of crystalline and liquid iodine relative to 298°K by the method of mixtures. For calibration they used a slug of copper. The enthalpy of copper which they used now appears to be too high [K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960)]. The results of Frederick and Hildebrand were corrected by a factor which varied linearly from zero at 300°K to 0.995 at 400°K and 0.990 at 500°K. These corrected enthalpies and the heat capacities of Shirley and Giauque above 298°K were used to derive the equations for crystalline iodine:

$$H_f - H_{298} = -12.1048 T + 0.029506 T^2 - 6.686 \times 10^{-5} T^{-1} + 3228.65$$

$$C_p = -12.1048 + 0.059012 T + 6.686 \times 10^{-5} T^{-2}$$

Heat Capacity of Liquid, Melting Point, and Heat of Melting.

For the liquid, the corrected results of Frederick and Hildebrand give:

$$H_f - H_{298} = 19.281 T - 2516.5$$

$$C_p = 19.281$$

The melting point given by Frederick and Hildebrand is 113.6°C. The difference in the heat content equations at the melting point gives the heat of melting as 3706.7 cal. mole⁻¹.

Heat of Sublimation, Ideal Gas Functions.

See tables for ideal gases for details.

Iodine (I₂)
(Liquid) Mol. Wt. = 253.82

IODINE (I₂) (LIQUID) MOL. WT. = 253.82

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S° - (F°-H ₂₉₈ °)/T	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0							
100							
200							
298	14.281	35.936	35.936	.000	3.232	.794	.582
300	14.281	36.035	36.035	.036	3.268	.770	.587
400	14.281	37.205	37.205	1.169	3.200	.600	.500
500	14.281	38.405	38.405	3.492	2.595	.491	.389
600	14.281	39.620	39.620	5.820	1.564	2.891	1.053
700	14.281	40.842	40.842	8.148	7.535	4.719	1.773
800	14.281	42.071	42.071	10.476	6.588	7.951	1.931
900	14.281	43.305	43.305	12.804	5.641	9.389	2.052
1000	14.281	44.537	44.537	15.132	4.694		

ΔH_f^o 298 = +3.232 kcal. mole⁻¹
S₂₉₈^o = 35.936 cal. mole⁻¹ deg⁻¹
ΔH_m^o = 3708.7 cal. mole⁻¹
ΔH_v^o = 10025.5 cal. mole⁻¹

T_m = 386.75°K
T_b = 458.39°K

Heat of Formation.

Obtained as the heat of fusion calculated to 298.15°K by adding H_{386.75}-H_{298.15} for solid and subtracting H_{386.75}-H_{298.15} for liquid.

Heat Capacity.

The liquid heat capacity of 19.281 cal. mole⁻¹ deg⁻¹ derived from the data of Fradrick and Hildebrand (see Reference State) was extrapolated back to 298.15°K and up to 1000°K.

Entropy.

The value at 400°K calculated for the reference state was back calculated to 298.15°K by means of the constant heat capacity of 19.281 cal. mole⁻¹ deg⁻¹.

Vaporization.

See ideal gas tables for details.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	∞	∞	∞	15.660	∞	∞
100	7.920	53.037	69.958	15.657	11.811	INFINITE
200	8.619	58.797	63.083	15.657	11.811	25.812
300	8.814	62.281	-0.000	14.924	8.084	8.844
400	8.817	62.336	-0.016	14.916	4.631	3.327
500	8.901	62.605	-0.281	14.916	4.567	3.327
600	8.936	62.877	-0.553	14.916	4.567	3.327
700	8.980	63.111	-0.825	14.916	4.567	3.327
800	9.025	63.311	-1.097	14.916	4.567	3.327
900	9.064	63.484	-1.369	14.916	4.567	3.327
1000	9.097	63.633	-1.641	14.916	4.567	3.327
1100	9.127	63.763	-1.913	14.916	4.567	3.327
1200	9.154	63.877	-2.185	14.916	4.567	3.327
1300	9.178	63.977	-2.457	14.916	4.567	3.327
1400	9.199	64.066	-2.729	14.916	4.567	3.327
1500	9.217	64.146	-3.001	14.916	4.567	3.327
1600	9.232	64.217	-3.273	14.916	4.567	3.327
1700	9.245	64.280	-3.545	14.916	4.567	3.327
1800	9.256	64.336	-3.817	14.916	4.567	3.327
1900	9.265	64.386	-4.089	14.916	4.567	3.327
2000	9.272	64.432	-4.361	14.916	4.567	3.327
2100	9.277	64.474	-4.633	14.916	4.567	3.327
2200	9.280	64.513	-4.905	14.916	4.567	3.327
2300	9.282	64.549	-5.177	14.916	4.567	3.327
2400	9.283	64.582	-5.449	14.916	4.567	3.327
2500	9.284	64.613	-5.721	14.916	4.567	3.327
2600	9.284	64.642	-5.993	14.916	4.567	3.327
2700	9.284	64.669	-6.265	14.916	4.567	3.327
2800	9.284	64.694	-6.537	14.916	4.567	3.327
2900	9.284	64.718	-6.809	14.916	4.567	3.327
3000	9.284	64.741	-7.081	14.916	4.567	3.327
3100	9.284	64.763	-7.353	14.916	4.567	3.327
3200	9.284	64.785	-7.625	14.916	4.567	3.327
3300	9.284	64.807	-7.897	14.916	4.567	3.327
3400	9.284	64.829	-8.169	14.916	4.567	3.327
3500	9.284	64.851	-8.441	14.916	4.567	3.327
3600	9.284	64.873	-8.713	14.916	4.567	3.327
3700	9.284	64.895	-8.985	14.916	4.567	3.327
3800	9.284	64.917	-9.257	14.916	4.567	3.327
3900	9.284	64.939	-9.529	14.916	4.567	3.327
4000	9.284	64.961	-9.801	14.916	4.567	3.327
4100	9.284	64.983	-10.073	14.916	4.567	3.327
4200	9.284	65.005	-10.345	14.916	4.567	3.327
4300	9.284	65.027	-10.617	14.916	4.567	3.327
4400	9.284	65.049	-10.889	14.916	4.567	3.327
4500	9.284	65.071	-11.161	14.916	4.567	3.327
4600	9.284	65.093	-11.433	14.916	4.567	3.327
4700	9.284	65.115	-11.705	14.916	4.567	3.327
4800	9.284	65.137	-11.977	14.916	4.567	3.327
4900	9.284	65.159	-12.249	14.916	4.567	3.327
5000	9.284	65.181	-12.521	14.916	4.567	3.327
5100	9.284	65.203	-12.793	14.916	4.567	3.327
5200	9.284	65.225	-13.065	14.916	4.567	3.327
5300	9.284	65.247	-13.337	14.916	4.567	3.327
5400	9.284	65.269	-13.609	14.916	4.567	3.327
5500	9.284	65.291	-13.881	14.916	4.567	3.327
5600	9.284	65.313	-14.153	14.916	4.567	3.327
5700	9.284	65.335	-14.425	14.916	4.567	3.327
5800	9.284	65.357	-14.697	14.916	4.567	3.327
5900	9.284	65.379	-14.969	14.916	4.567	3.327
6000	9.284	65.401	-15.241	14.916	4.567	3.327

September 30, 1961

IODINE, DIATOMIC (I₂) (IDEAL GAS)

MOL. WT. = 253.82

$$\Delta H_f^0 = 15.66 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^0 = 14.924 \text{ kcal. mole}^{-1}$$

$$S_{298}^0 = 62.281 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$\omega_e = 214.52 \text{ cm.}^{-1}$$

$$\omega_e x_e = 0.6133 \text{ cm.}^{-1}$$

$$D_e = 0.455 \times 10^{-8} \text{ cm.}^{-1}$$

$$\alpha_e = 0.001206 \text{ cm.}^{-1}$$

$$\sigma = 2$$

Thermodynamic Functions.

The molecular constants are from the work of D. H. Rank and W. M. Baldwin [J. Chem. Phys. **19**, 1210 (1951)] with a revised value of $\omega_e = 214.52$ as given by R. D. Verma [J. Chem. Phys. **32**, 738 (1960)]. The value of $\omega_e x_e$ has been adjusted to allow for the dropping of higher order corrections not used in the computer program. The calculated thermodynamic functions are in good agreement with those of W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards **55**, 147 (1955)], who used very slightly different constants. L. Mathieson and A. L. O. Rees [J. Chem. Phys. **25**, 753 (1956)] give further refinements to the spectroscopic data which are negligible for our purpose. Their ω_e is also slightly low since it is based on Rank and Baldwin.

Heat of Formation.

The heat of sublimation of iodine was calculated from published vapor pressure data as follows, using thermodynamic functions of condensed and gaseous phases described above.

	ΔH_f^0 , kcal. mole ⁻¹
Baxter, Hickey, and Holmes ¹ (273° to 328°K)	15.657 ± .004
Baxter and Orsa ² (323° to 358°K)	15.657 ± .002
Ramsay and Young ³ (solid) (331° to 386°K)	15.871 ± .018
Ramsay and Young ³ (liquid) (386° to 454°K)	15.876 ± .007
Haber and Kerschbaum ⁴ (225° to 283°K)	15.765 ± .012
Ollieple and Fraser ⁵ (303° to 333°K)	15.655 ± .005
Skiyarenko, Markin, and Balyaeva ⁶ (293° to 303°K)	15.813
Neumann ⁷ (as given by Haber and Kerschbaum) (232° to 292°K)	15.899 ± .034
Wiedemann ⁸ (393° to 453°K)	15.635 ± .008
Breune and Stresemann ⁹ (305° to 358°K)	15.635 ± .012
Arctowski ¹⁰ (288° to 345°K)	15.623 ± .080
Wright ¹¹ (352° to 372°K)	15.659 ± .003
Dewar ¹² (273° to 303°K)	15.821 ± .103
Richter ¹³ (358° to 383°K)	15.639 ± .043

The uncertainties given are the average deviation from the mean. The data of Breune and Stresemann are as recalculated by Gerry and Ollieple¹⁴. The data of Haber and Kerschbaum appear systematically too high. The results of Skiyarenko, et al., Neumann, Arctowski, Dewar, and Richter are scattered and are not given any weight. A weighted average of the remaining data yield $\Delta H_f^0 = 15.66 \pm 0.01$ kcal. mole⁻¹, which calculates to $\Delta H_{298}^0 = 14.924$ cal. mole⁻¹.

References to Vapor Pressure Data

- (1) O. P. Baxter, C. H. Hickey, and W. C. Holmes, J. Am. Chem. Soc. **29**, 127 (1907).
- (2) O. P. Baxter and M. R. Orsa, J. Am. Chem. Soc. **37**, 1061 (1915).
- (3) W. Ramsay and S. Young, J. Chem. Soc. **49**, 453 (1886).
- (4) P. Haber and P. Kerschbaum, Z. Elektrochem. **20**, 286 (1914).
- (5) L. J. Ollieple and C. H. D. Fraser, J. Am. Chem. Soc. **58**, 2260 (1936).
- (6) S. I. Skiyarenko, B. I. Markin, and L. B. Balyaeva, Zhur. Fiz. Khim. **32**, 1916 (1958).
- (7) R. Neumann, Dissertation, Berlin (1907).
- (8) E. Wiedemann, Ber. deut. physikal. Ges. **3**, 159 (1905).
- (9) H. Breune and P. Stresemann, Z. physik. Chem. **143A**, 225 (1929).
- (10) H. Arctowski, Z. anorg. Chem. **12**, 427 (1898).
- (11) R. Wright, J. Chem. Soc. **107**, 1527 (1917).
- (12) J. Dewar, Proc. Chem. Soc. **13**, 241 (1899).
- (13) V. Richter, Ber. **19**, 1057 (1886).
- (14) H. T. Gerry and L. J. Ollieple, Phys. Rev. **40**, 269 (1932).

Potassium Iodide, Dimeric (K_2I_2)
(Ideal Gas) GFW = 332.0128

I_2K_2

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log Kp
0	.0000	.0000	INFINITE	-	99.541	99.541	INFINITE
100	14.157	73.647	111.819	3.817	99.734	103.939	227.158
200	19.408	86.759	96.351	1.920	100.255	107.952	117.984
298	19.660	94.556	94.556	.000	100.900	111.599	91.805
300	19.662	94.680	94.559	.034	100.914	111.665	91.348
400	19.753	100.351	95.331	2.004	106.742	114.776	62.711
500	19.796	104.764	96.793	3.985	117.774	115.727	50.584
600	19.819	108.375	98.431	5.064	118.162	115.982	41.991
700	19.833	111.431	100.074	7.940	118.490	117.777	35.835
800	19.842	114.080	101.664	9.933	118.831	118.224	31.205
900	19.848	116.418	103.176	11.917	119.175	113.628	27.593
1000	19.853	118.509	104.607	13.902	119.537	112.993	24.695
1100	19.854	120.401	105.958	15.889	119.732	110.972	21.909
1200	19.858	122.129	107.235	17.873	119.767	109.298	19.298
1300	19.860	123.719	108.462	19.859	119.756	107.658	17.000
1400	19.862	125.191	109.587	21.844	119.746	106.054	15.168
1500	19.863	126.561	110.673	23.832	119.740	104.506	13.560
1600	19.864	127.883	111.707	25.818	119.729	103.007	12.166
1700	19.865	129.167	112.692	27.805	119.718	101.554	10.943
1800	19.866	130.413	113.632	29.791	119.707	100.146	9.740
1900	19.866	131.527	114.532	31.779	119.697	98.784	8.736
2000	19.867	132.576	115.394	33.764	119.687	97.477	7.832
2100	19.867	133.585	116.221	35.751	119.678	96.216	7.015
2200	19.868	134.559	117.016	37.738	119.669	95.003	6.273
2300	19.868	135.053	117.791	39.725	119.662	93.834	5.595
2400	19.868	135.898	118.518	41.711	119.654	92.712	4.974
2500	19.869	136.709	119.210	43.698	119.647	91.636	4.403
2600	19.869	137.489	119.917	45.685	119.640	90.606	3.876
2700	19.869	138.238	120.557	47.672	119.633	89.624	3.394
2800	19.869	138.961	121.226	49.659	119.626	88.691	2.934
2900	19.869	139.658	121.849	51.644	119.620	87.804	2.512
3000	19.870	140.332	122.454	53.633	119.613	86.961	2.119
3100	19.870	140.983	123.041	55.620	119.606	86.167	1.760
3200	19.870	141.614	123.612	57.607	119.600	85.424	1.434
3300	19.870	142.226	124.167	59.594	119.594	84.734	1.079
3400	19.870	142.819	124.707	61.581	119.588	84.098	.773
3500	19.870	143.395	125.233	63.568	119.582	83.514	.484
3600	19.870	143.955	125.745	65.555	119.576	82.980	.211
3700	19.870	144.499	126.244	67.542	119.570	82.497	.000
3800	19.870	145.029	126.732	69.529	119.564	82.064	-.293
3900	19.870	145.545	127.208	71.516	119.558	81.681	-.526
4000	19.870	146.048	127.687	73.503	119.552	81.348	-.748
4100	19.871	146.539	128.157	75.490	119.546	81.064	-.960
4200	19.871	147.018	128.617	77.477	119.540	80.829	1.162
4300	19.871	147.485	129.065	79.464	119.534	80.644	1.356
4400	19.871	147.942	129.501	81.451	119.528	80.509	1.541
4500	19.871	148.388	129.927	83.438	119.522	80.424	1.719
4600	19.871	148.825	130.355	85.425	119.516	80.389	1.890
4700	19.871	149.253	130.783	87.412	119.510	80.404	2.056
4800	19.871	149.671	131.206	89.399	119.504	80.469	2.212
4900	19.871	150.081	131.624	91.387	119.498	80.584	2.365
5000	19.871	150.482	132.037	93.374	119.492	80.749	2.513
5100	19.871	150.876	132.447	95.361	119.486	80.964	2.654
5200	19.871	151.261	132.851	97.348	119.480	81.229	2.795
5300	19.871	151.640	133.248	99.335	119.474	81.544	2.929
5400	19.871	152.011	133.638	101.322	119.468	81.909	3.060
5500	19.871	152.376	134.024	103.309	119.462	82.324	3.187
5600	19.871	152.734	134.407	105.296	119.456	82.789	3.311
5700	19.871	153.086	134.786	107.283	119.450	83.304	3.432
5800	19.871	153.431	135.162	109.270	119.444	83.869	3.551
5900	19.871	153.771	135.534	111.258	119.438	84.484	3.666
6000	19.871	154.105	135.901	113.245	119.432	85.149	3.780

Dec. 31, 1961 June 30, 1967

POTASSIUM IODIDE, DIMERIC (K_2I_2) (IDEAL GAS)

Point Group (D_{2h})

$S^\circ_{298.15} = [94.61 \text{ gibbs/mol}]$

Ground State Quantum Weight = [1]

$\Delta H^\circ_0 = -99.5 \pm 1 \text{ kcal/mol}$

$\Delta H^\circ_{298.15} = -100.9 \pm 1 \text{ kcal/mol}$

Vibrational Frequencies and Degeneracies

ω , cm^{-1}	ω , cm^{-1}
[90] (1)	[80] (1)
[60] (1)	[105] (1)
[110] (1)	[120] (1)

Bond Distance: K-I = [3.29] Å

Bond Angles: K-I-K = [75°] I-K-I = [105°]

Product of the Moments of Inertia: $I_{A-B-C} = [5.041 \times 10^{-11}] \text{ g}^2 \text{ cm}^6$

$\sigma = [4]$

Heat of Formation

The chemical equilibrium for the reaction $K_2I_2(g) = 2KI(g)$ has been studied by S. Datz, ORNL-2933, Oak Ridge, Tenn., 1960, and S. Datz, W. T. Smith, Jr. and E. H. Taylor, J. Chem. Phys. 34, 598 (1961). They measured the temperature dependence of the molecular weight of $KI(g)$ which was determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume. Based on the reported P-V-T measurements, the enthalpy change of the reaction at 298°K is evaluated by the second and third law methods. The results are given in the table below.

R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956), determined the molecular composition of KI vapor by measurement of the velocity distribution of the molecules in the beam produced as the vapor effused through a small slit in a source. The analysis was based on an assumption that the velocity distribution within the oven is Maxwellian and that the vapor effuses through the ideal slit of kinetic theory. The velocity distributions of potassium and thallium atomic beams were found to be in excellent agreement with the theoretical distributions, so the determination of the molecular composition of KI beams was tried. Using the derived equilibrium constants, we calculate the enthalpy change of the dissociation reaction by the second and third law methods. The results are presented in the following table.

The value of $\Delta H^\circ_{298}(K_2I_2, g)$ is adopted as $-100.9 \pm 1 \text{ kcal/mol}$.

Investigator	Temperature, °K	No. of Points	ΔH°_{298} , kcal/mol	Drift, eu	ΔH°_{298} , kcal/mol
Datz	1228-1395	10	40.0840.82	40.66	-100.86
	1292-1408	6	41.3741.91	41.01	-101.01
Miller-Kusch	816-921	10	54.6222.46	36.28	-98.78

Heat Capacity

The molecular structure and bond distance and angles were estimated by J. Berkowitz, J. Chem. Phys. 29, 1386 (1958). The vibrational frequencies are estimated by comparison with those calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960), and adjusted to give good agreement between second and third law evaluations of the equilibrium data. The three principal moments of inertia are: $I_A = 5.194 \times 10^{-39}$, $I_B = 2.866 \times 10^{-37}$ and $I_C = 3.386 \times 10^{-37} \text{ g cm}^2$.

I_2K_2

Lithium Iodide, Dimeric (Li_2I_2)
(Ideal Gas) $\text{GFW} = 267.6868$

I_2Li_2

$\text{OPW} = 267.6868$

(IDEAL GAS)

LITHIUM IODIDE, DIMERIC (Li_2I_2)

Point Group D_{2h}
 $S_{298.15}^\circ = [79.0] \text{ g/bbs/mol}$
Ground State Quantum Weight = 1
 $\Delta H_f^\circ = -85.3 \pm 4 \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = -86.5 \pm 4 \text{ kcal/mol}$

Vibrational Frequencies and Degeneracies

ω , cm^{-1}	ω , cm^{-1}
[166](1)	[310](1)
[160](1)	248 (1)
[383](1)	375 (1)

Bond Distance: $\text{Li-I} = 2.54 \text{ \AA}$ $\text{Li-Li} = 2.71 \text{ \AA}$
Bond Angle: $\text{I-Li-I} = 116^\circ \pm 4^\circ$
Product of the Moments of Inertia: $I_A I_B I_C = 1.63429 \times 10^{-112} \text{ g}^3 \text{ cm}^6$

$\sigma = 4$

Heat of Formation

This was obtained from the heat of formation of the crystal and the heat of sublimation of the dimer, which derivation has been given in the LiI(g) table.

Heat Capacity and Entropy

J. Berkowitz, J. Chem. Phys. 29, 1366 (1958), 32, 1519 (1960), has calculated the molecular structure and vibrational frequencies based on an ionic model. The planar rhombic structure, proposed by Berkowitz, has been confirmed by the lack of polarity in electric deflection by A. Büchler, J. L. Stauffer and W. Klemperer, J. Am. Chem. Soc. 85, 4544 (1964). The selected bond distances and angle were obtained from the electron diffraction studies of monomer-dimer vapor by P. A. Akishin and N. G. Rambidi, Z. Physik Chem. 213, 111 (1960). The bond distances ($\text{Li-Li} = 2.712 \text{ \AA}$ and $\text{I-I} = 4.520 \text{ \AA}$) calculated by Berkowitz are in good agreement with those from Akishin and Rambidi. The three principal moments of inertia are $I_A = 4.2152 \times 10^{-39}$, $I_B = 194.8074 \times 10^{-39}$ and $I_C = 199.0226 \times 10^{-39} \text{ g cm}^2$.

S. H. Bauer, T. Ito and R. F. Porter, J. Chem. Phys. 33, 685 (1960), have estimated six vibrational frequencies (501, 501, 148, 200, 294, 360 cm^{-1}) for $\text{Li}_2\text{I}_2(\text{g})$ in the electron diffraction studies of the $\text{Li}_2\text{Cl}_2(\text{g})$. W. Klemperer and W. O. Norris, J. Chem. Phys. 33, 1071 (1961), have observed two fundamental vibrational frequencies (248 and 375 cm^{-1}) in the infrared spectrum and tentatively assigned them as E_{2u} and E_{3u} modes; these have been adopted in the table below. The remaining four vibrational frequencies were obtained from J. Berkowitz, loc. cit., because his model and derivation are self-consistent.

T, °K	C_p°	$-\frac{G^\circ - H_{298}^\circ}{T}$, g/bbs/mol	$H^\circ - H_{298}^\circ$, kcal/mol	ΔH_f°	ΔG_f°	Log Kp
0	.0000	INFINITE	-	85.263	85.263	INFINITE
100	12.2445	91.6719	4.127	-	85.263	196.004
200	21.4579	85.9077	3.193	-	85.296	174.553
300	28.1175	78.9977	.000	-	86.500	71.565
400	18.1193	79.1109	.034	-	86.512	-
500	18.8777	84.4449	1.891	-	91.069	-
600	19.2219	86.702	3.798	-	103.521	-
700	19.4112	92.225	82.674	5.730	-	-
800	19.5311	95.227	84.256	7.678	-	-
900	19.610	97.640	85.796	9.615	-	-
1000	19.664	100.153	87.265	11.569	-	-
1100	19.703	102.227	88.659	13.568	-	-
1200	19.732	104.106	89.980	15.539	-	-
1300	19.754	105.824	91.229	17.514	-	-
1400	19.771	107.406	92.414	19.490	-	-
1500	19.785	108.872	93.536	21.468	-	-
1600	19.796	110.237	94.606	23.447	-	-
1700	19.803	111.515	95.623	25.427	-	-
1800	19.813	112.716	96.594	27.408	-	-
1900	19.819	113.849	97.521	29.390	-	-
2000	19.825	114.920	98.409	31.372	-	-
2100	19.829	115.937	99.260	33.354	-	-
2200	19.833	116.905	100.078	35.338	-	-
2300	19.836	117.828	100.864	37.321	-	-
2400	19.839	118.709	101.620	39.305	-	-
2500	19.842	119.554	102.350	41.289	-	-
2600	19.844	120.364	103.055	43.273	-	-
2700	19.846	121.142	103.735	45.258	-	-
2800	19.848	121.891	104.384	47.243	-	-
2900	19.850	122.613	105.002	49.227	-	-
3000	19.851	123.310	105.650	51.212	-	-
3100	19.853	123.981	106.230	53.198	-	-
3200	19.854	124.634	106.833	55.183	-	-
3300	19.855	125.264	107.399	57.168	-	-
3400	19.856	125.875	107.950	59.154	-	-
3500	19.857	126.468	108.486	61.140	-	-
3600	19.858	127.044	109.008	63.125	-	-
3700	19.858	127.603	109.516	65.111	-	-
3800	19.859	128.147	110.013	67.097	-	-
3900	19.860	128.677	110.497	69.083	-	-
4000	19.861	129.193	110.970	71.069	-	-
4100	19.862	129.695	111.432	73.055	-	-
4200	19.862	130.186	111.883	75.041	-	-
4300	19.863	130.664	112.325	77.027	-	-
4400	19.863	131.132	112.757	79.014	-	-
4500	19.863	131.588	113.179	81.000	-	-
4600	19.863	132.035	113.593	82.986	-	-
4700	19.864	132.471	113.999	84.973	-	-
4800	19.864	132.899	114.397	86.959	-	-
4900	19.864	133.317	114.787	88.945	-	-
5000	19.865	133.726	115.169	90.932	-	-
5100	19.865	134.128	115.544	92.918	-	-
5200	19.865	134.521	115.912	94.905	-	-
5300	19.865	134.907	116.274	96.891	-	-
5400	19.866	135.285	116.629	98.878	-	-
5500	19.866	135.657	116.978	100.864	-	-
5600	19.866	136.021	117.321	102.851	-	-
5700	19.866	136.379	117.656	104.838	-	-
5800	19.866	136.731	117.990	106.824	-	-
5900	19.867	137.076	118.316	108.811	-	-
6000	19.867	137.416	118.637	110.798	-	-
	137.750	118.952	112.784	112.784	-	-

Sept. 30, 1961; June 30, 1966

I_2Li_2

Lead Diiodide (PbI₂)

(Crystal) Mol. Wt. = 461.03

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0	10,000	INFINITE	0	41,705	41,705	INFINITE
100	19,080	22,390	3,569	41,778	41,778	6.0385
200	19,050	34,595	1,816	41,806	41,571	45,425
298	19,518	41,869	0	41,855	41,446	30,379
300	19,935	41,886	0.05	41,856	41,443	30,190
400	21,760	48,000	1,000	41,868	41,455	22,406
500	20,290	51,984	3,961	55,950	39,055	11,070
600	20,420	53,129	45,703	55,482	35,710	13,010
700	21,290	58,974	8,121	56,146	32,274	10,076
800	21,760	61,848	10,274	55,615	28,868	7,894
900	22,420	64,388	12,416	55,384	25,594	6,215
1000	22,700	66,804	14,720	54,398	22,356	4,886
1100	23,170	68,900	17,013	53,711	19,185	3,812
1200	23,440	71,026	19,354	52,970	16,078	2,928
1300	23,710	72,937	21,741	52,178	13,035	2,191
1400	24,000	74,681	24,166	51,340	10,057	1,570
1500	24,050	76,251	26,657	50,456	7,1157	1,040
1600	24,520	78,084	29,186	49,528	4,278	.584
1700	24,990	79,866	31,761	48,558	1,479	.190
1800	25,460	81,584	34,384	47,566	1,260	.153
1900	25,910	83,244	37,054	46,546	1,040	.118
2000	27,400	83,981	39,770	45,400	8,568	.086
2100	27,870	85,329	42,533	44,216	10,693	1,113
2200	28,300	86,636	45,344	43,000	15,300	1,520
2300	28,810	87,807	48,201	41,761	19,851	1,886
2400	29,260	88,943	51,106	40,508	24,347	2,217
2500	29,760	90,347	54,057	39,249	28,783	2,516

Lead Diiodide (PbI₂) (crystal)

Mol. Wt. = 461.03

ΔH_f^o 298.15 = -41.86 ± 0.06 kcal. mole⁻¹

S_{298.15}^o = 41.869 cal. deg.⁻¹ mole⁻¹

ΔH_f^o 298.15 = 41.70 ± 0.10 kcal. mole⁻¹

T_m = 680°K.

ΔH_m^o = 3.87 kcal. mole⁻¹

Heat of Formation. Calculated from the data reported by H. Braune and F. Koref, Z. anorg. Chem., 87, 175 (1914) and R. H. Gerke, J. Am. Chem. Soc., 44, 1664 (1922).

Heat Capacity, Entropy, and Melting Data. Cp (10° to 298.15°K.) obtained from Edgar F. Westrum, Jr., University of Michigan, Ann Arbor, Michigan, private communication, May, 1951. Above 298.15°K., Cp given by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) was used. The two heat capacity curves were joined smoothly at 298.15°K. by graphical extrapolation. T_m and ΔH_m^o reported by W. Blanc and G. Petit, Compt. rend., 248, 1305 (1959).

Heat of Sublimation. Calculated from vapor pressure data of K. Jellinek and A. Rudat, Z. Physik. Chem., A143, 55 (1929) and B. Gredner and K. Jellinek, Z. Physik. Chem., A165, 97 (1933).

INTERIM TABLE

Mol. Wt. = 461.03

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0						
100	16.920	42.786	.000	- 40.637	- 40.501	29.687
200	18.915	42.703	.015	- 40.638	- 40.500	29.503
300	19.915	42.603	.035	- 40.532	- 40.312	22.024
400	20.915	42.503	.055	- 40.444	- 40.224	16.750
500	21.915	42.403	.075	- 40.368	- 40.148	12.461
600	22.915	42.303	.095	- 40.300	- 40.080	8.108
700	23.915	42.203	.115	- 40.240	- 40.020	6.401
800	24.915	42.103	.135	- 40.188	- 39.968	5.435
900	25.915	42.003	.155	- 40.144	- 39.924	4.314
1000	26.915	41.903	.175	- 40.108	- 39.888	3.169
1100	27.915	41.803	.195	- 40.078	- 39.858	2.071
1200	28.915	41.703	.215	- 40.052	- 39.832	1.009
1300	29.915	41.603	.235	- 40.030	- 39.810	0.000
1400	30.915	41.503	.255	- 40.012	- 39.792	- .972
1500	31.915	41.403	.275	- 40.000	- 39.780	- .654
1600	32.915	41.303	.295	- 40.000	- 39.780	- .021
1700	33.915	41.203	.315	- 40.000	- 39.780	.247
1800	34.915	41.103	.335	- 40.000	- 39.780	.466
1900	35.915	41.003	.355	- 40.000	- 39.780	.654
2000	36.915	40.903	.375	- 40.000	- 39.780	.821
2100	37.915	40.803	.395	- 40.000	- 39.780	.972
2200	38.915	40.703	.415	- 40.000	- 39.780	1.109
2300	39.915	40.603	.435	- 40.000	- 39.780	1.247
2400	40.915	40.503	.455	- 40.000	- 39.780	1.379
2500	41.915	40.403	.475	- 40.000	- 39.780	1.509
2600	42.915	40.303	.495	- 40.000	- 39.780	1.639
2700	43.915	40.203	.515	- 40.000	- 39.780	1.769
2800	44.915	40.103	.535	- 40.000	- 39.780	1.899
2900	45.915	40.003	.555	- 40.000	- 39.780	2.029
3000	46.915	39.903	.575	- 40.000	- 39.780	2.159

March 31, 1962

Lead Diiodide (PbI₂) (Liquid)

Mol. Wt. = 461.03

ΔH_f^o 238.15 = [-10.637] kcal. mole⁻¹S°_{298.15} = [42.786] cal. deg.⁻¹ mole⁻¹T_m = 690°K.ΔH_m^o = 3.07 kcal. mole⁻¹T_b = 1135°K.ΔH_v^o = 26.99 ± 0.10 kcal. mole⁻¹

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy, and Melting Data. C_p obtained from K.K. Kelley, U. S. Bur. Mines Bull. 584 (1956). T_m and ΔH_m^o reported by M. Blanc and G. Petit, Compt. rend. 248, 1305-6 (1959).

A glass transition temperature of 454°K. is assumed.

Vaporization Phenomena. T_b and ΔH_v^o calculated from ΔH_f^o 238.15

and free energy functions for condensed and gaseous states.

Lead Diiodide (PbI₂)

(Ideal Gas) Mol. Wt. = 461.03

INTERIM TABLE

T, °K.	C _p ^o	S ^o	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _f
0	12.900	105.905	23.493	11.124	17.901	21.893	6.349
100	12.902	105.915	93.737	12.514	18.111	22.285	4.051
200	13.903	107.326	94.632	13.294	18.316	22.581	3.796
300	13.905	108.317	97.194	14.695	18.729	23.207	3.361
400	13.906	109.215	97.918	18.075	18.940	23.498	3.209
500	13.906	110.058	98.407	19.466	19.154	23.776	3.056
600	13.907	110.853	98.786	20.857	19.374	24.043	2.919
700	13.908	111.604	99.078	22.249	19.593	24.299	2.795
800	13.908	112.318	100.499	23.638	19.833	24.539	2.681
900	13.908	112.997	101.078	25.029	20.091	24.761	2.576
1000	13.908	113.644	101.635	26.420	20.367	24.967	2.476
1100	13.908	114.262	102.179	27.811	20.667	25.158	2.380
1200	13.909	114.854	102.706	29.202	20.981	25.335	2.287
1300	13.909	115.422	103.185	30.592	21.305	25.500	2.197
1400	13.909	115.967	103.616	31.983	21.647	25.654	2.110
1500	13.909	116.494	104.000	33.374	22.005	25.798	2.026
1600	13.910	116.999	104.331	34.765	22.378	25.933	1.944
1700	13.910	117.484	104.616	36.156	22.765	26.060	1.863
1800	13.910	117.958	104.852	37.547	23.165	26.180	1.783
1900	13.910	118.414	105.053	38.938	23.578	26.295	1.704
2000	13.910	118.855	105.252	40.329	23.999	26.406	1.625
2100	13.910	119.283	105.441	41.720	24.427	26.513	1.546
2200	13.910	119.698	105.619	43.111	24.861	26.617	1.467
2300	13.910	120.102	105.787	44.502	25.300	26.718	1.388
2400	13.910	120.494	105.946	45.893	25.744	26.816	1.309
2500	13.910	120.875	106.095	47.284	26.193	26.911	1.230
2600	13.910	121.246	106.237	48.675	26.646	27.004	1.151
2700	13.910	121.608	106.374	49.966	27.103	27.094	1.072
2800	13.910	121.959	106.505	51.257	27.565	27.181	0.993
2900	13.910	122.303	106.631	52.548	28.030	27.265	0.914
3000	13.910	122.638	106.752	53.839	28.498	27.347	0.835
3100	13.910	122.965	106.868	55.130	28.968	27.427	0.756
3200	13.910	123.285	106.979	56.421	29.440	27.505	0.677
3300	13.910	123.598	107.085	57.712	29.913	27.582	0.598
3400	13.910	123.903	107.187	59.003	30.387	27.657	0.519
3500	13.910	124.202	107.285	60.294	30.862	27.730	0.440
3600	13.910	124.494	107.378	61.585	31.337	27.802	0.361
3700	13.910	124.781	107.466	62.876	31.812	27.872	0.282
3800	13.910	125.064	107.550	64.167	32.287	27.941	0.203
3900	13.910	125.342	107.629	65.458	32.762	28.009	0.124
4000	13.910	125.615	107.704	66.749	33.237	28.076	0.045
4100	13.910	125.883	107.775	68.040	33.712	28.142	-0.034
4200	13.910	126.146	107.842	69.331	34.187	28.207	-0.113
4300	13.910	126.404	107.905	70.622	34.662	28.271	-0.192
4400	13.910	126.657	107.965	71.913	35.137	28.334	-0.271
4500	13.910	126.905	108.021	73.204	35.612	28.396	-0.350
4600	13.910	127.148	108.074	74.495	36.087	28.457	-0.429
4700	13.910	127.386	108.124	75.786	36.562	28.517	-0.508
4800	13.910	127.619	108.171	77.077	37.037	28.576	-0.587
4900	13.910	127.847	108.215	78.368	37.512	28.635	-0.666
5000	13.910	128.070	108.256	79.659	37.987	28.693	-0.745
5100	13.910	128.288	108.293	80.950	38.462	28.751	-0.824
5200	13.910	128.501	108.327	82.241	38.937	28.808	-0.903
5300	13.910	128.709	108.358	83.532	39.412	28.865	-0.982
5400	13.910	128.912	108.386	84.823	39.887	28.921	-1.061
5500	13.910	129.110	108.411	86.114	40.362	28.977	-1.140
5600	13.910	129.303	108.433	87.405	40.837	29.032	-1.219
5700	13.910	129.491	108.452	88.696	41.312	29.087	-1.298
5800	13.910	129.674	108.469	89.987	41.787	29.142	-1.377
5900	13.910	129.852	108.483	91.278	42.262	29.196	-1.456
6000	13.910	129.999	108.495	92.569	42.737	29.250	-1.535

Nurell 31, 1962

Lead Diiodide (PbI₂) (Ideal Gas)

Mol. Wt. = 461.03
 $\Delta H_f^\circ 298.15 = -0.16 \pm 0.12 \text{ kcal. mole}^{-1}$
 $S^\circ_{298.15} = [85.911] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Point Group C_{2v}

Vibrational Levels and Multiplicities

ω , cm.⁻¹
 [100] (1)
 [40] (1)
 [160] (1)

Pb-I distance = 2.79 ± 0.02 Å IPBI angle = 95° σ = 2
 $I_A = 67.294 \times 10^{-39} \text{ g. cm.}^2$ $I_B = 178.298 \times 10^{-39} \text{ g. cm.}^2$
 $I_C = I_A + I_B = 245.592 \times 10^{-39}$

Heat of Formation. Calculated from $\Delta H_f^\circ 298.15$ and $\Delta H_f^\circ 298.15$ for PbI₂(c).

Heat Capacity and Entropy. Molecular dimensions obtained from L. E. Sutton (ed.), "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958. Vibrational frequencies estimated by comparison with the corresponding values for HgI₂(g).

TITANIUM DIIODIDE (TiI₂) (CRYSTAL)

GFW = 301.7088

 $\Delta H_f^\circ = \text{unknown}$ $\Delta H_f^\circ_{298.15} = -63.6 \pm 3.0 \text{ kcal/mol}$ $\Delta H_s^\circ = [51.80] \text{ kcal/mol}$ $S^\circ_{298.15} = [29.3 \pm 3.0] \text{ gibbs/mol}$ $T_m = [1358.2]^\circ\text{K}$ Titanium Diiodide (TiI₂)

GFW = 301.7088

(Crystal)

T, °K	Cp°	S°	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔHf°	ΔGf°	Log Kp
0									
100									
200									
298	20.609	29.300	29.300	29.300	+000	-	63.600	- 61.876	45.356
300	20.612	29.426	29.300	29.300	+038	-	63.597	- 61.865	45.068
400	20.766	35.361	30.111	30.111	2.108	-	67.317	- 61.173	33.423
500	20.960	40.038	31.647	31.647	4.194	-	77.399	- 58.690	25.653
600	21.134	43.874	33.374	33.374	6.300	-	76.937	- 55.001	20.034
700	21.298	47.064	36.400	36.400	8.400	-	75.800	- 47.876	15.454
800	21.442	50.002	36.800	36.800	10.562	-	75.790	- 47.876	11.079
900	21.656	52.543	36.411	36.411	12.719	-	75.274	- 44.418	10.766
1000	21.630	54.633	39.940	39.940	14.693	-	74.769	- 41.014	8.964
1100	22.004	56.922	41.391	41.391	17.085	-	74.273	- 37.664	7.483
1200	22.094	58.452	44.072	44.072	21.520	-	74.122	- 30.978	5.208
1300	22.132	60.624	45.315	45.315	23.765	-	73.516	- 27.682	4.321
1400	22.526	62.289	46.489	46.489	24.025	-	72.916	- 24.430	3.559
1500	22.700	63.649	46.489	46.489	24.025	-	72.916	- 24.430	3.559
1600	22.874	65.320	47.630	47.630	28.304	-	72.314	- 21.214	2.898
1700	23.000	66.000	48.000	48.000	30.000	-	71.000	- 18.000	2.000
1800	23.222	68.034	49.749	49.749	32.510	-	71.125	- 14.900	1.409
1900	23.396	69.294	50.744	50.744	35.245	-	70.540	- 11.793	1.356
2000	23.570	70.499	51.702	51.702	37.593	-	74.410	- 6.563	.936

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

Heat of Formation

The heat of formation of TiI₂(c) is calculated from the heat of reaction for the process 2TiI₂(c) = Ti(c) + TiI₄(g), and the heat of formation of TiI₄(c). Vapor pressure data for this reaction were reported by Herczog and Pidgeon (1) over the temperature range 750° to 902°K. Second and third law analyses of these data give values for ΔH°_{298} of 60.5 ± 0.8 and 60.85 kcal/mol respectively, the third law drift being $0.4 \pm 1.0 \text{ eu}$. The third law ΔH°_{298} is used to obtain the adopted value of ΔH°_{298} .

Heat Capacity and Entropy

The estimated heat capacity is that reported by Kelley (2). The value of $S^\circ_{298.15}$ is estimated from that of TiCl₂(c) and the difference between ionic entropy contributions of Cl⁻ and I⁻.

Heat of Sublimation

The heat of sublimation of TiI₂(c) is taken as the difference in the heats of formation of TiI₂(c) and TiI₂(g) at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta G^\circ = 0$ for the reaction TiI₂(c) = TiI₂(g).

References

1. A. Herczog and L. M. Pidgeon, Can. J. Chem., **34**, 1687 (1956).
2. K. K. Kelley, U. S. Bur. Mines Bull. 584, 1961.

GFW = 301.7088

(IDEAL GAS)

Point Group [D_{2h}] $\Delta H_f^\circ = [-4.1 \pm 8.0] \text{ kcal/mol}$ $S_{298.15}^\circ = [77.3 \pm 4] \text{ gibbs/mol}$ $\Delta H_f^\circ = [-4.7 \pm 8.0] \text{ kcal/mol}$

Ground State Quantum Weight = [3]

Electronic Levels and Quantum Weights

 $\epsilon_i, \text{ cm}^{-1}$ g_i

[3]

[6]

[17000]

[22000]

[15]

Vibrational Frequencies and Degeneracies

 $\omega, \text{ cm}^{-1}$

[134] (1)

[92] (2)

[290] (1)

Bond Distance: Ti-I = [2.7] Å

Bond Angle: I-Ti-I = [180°]

Rotational Constant: $B_0 = [0.00811] \text{ cm}^{-1}$ $\sigma = 2$

Heat of Formation

The heat of formation of $\text{TiI}_2(\text{g})$ is calculated from that of $\text{TiI}_2(\text{c})$ and the heat of vaporization. Vapor pressure data over the temperature range 750°K to 902°K have been reported by Herzog and Pidgeon (1). Second and third law analyses of these data give values for ΔH_{298}° of 51.9 and 59.9 kcal/mol, respectively. The third law drift for these data is 8.3 ± 1.1 eu, with one point rejected due to failure of a statistical test. The adopted value of ΔH_{298}° is calculated from the third law heat of vaporization.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $\text{TiCl}_2(\text{g})$, $\text{TiCl}_4(\text{g})$, $\text{TiBr}_2(\text{g})$, $\text{TiBr}_4(\text{g})$ and $\text{TiI}_4(\text{g})$. The vibrational frequencies are estimated from a valence force field model. The force constant k is estimated as 1.0 millidynes/Å and the constant K_0/l^2 is assumed to be 0.05 millidynes/Å.

The electronic levels are assumed to be the same as $\text{TiCl}_2(\text{g})$. The levels of TiCl_2 are estimated by assuming they correspond to the inverted states of $\text{NiCl}_2(\text{g})$ (2). The linear configuration is adopted, since experimental evidence indicates that other transition metal dihalides are linear (3, 4, 5, 6).

References

1. A. Herzog and L. M. Pidgeon, Can. J. Chem., **34**, 1687 (1956).
2. C. W. DeKock and D. M. Gruen, J. Chem. Phys., **44**, 4387 (1966).
3. R. A. Berg and O. Sinanoglu, J. Chem. Phys., **32**, 1082 (1960).
4. J. T. Houghen, G. E. Leroi and T. C. James, J. Chem. Phys., **34**, 1670 (1961).
5. G. E. Leroi, T. C. James, J. T. Houghen, and W. Klemperer, J. Chem. Phys., **35**, 2879 (1962).
6. A. Buchlar, J. L. Stauffer and W. Klemperer, J. Chem. Phys., **40**, 3471 (1964).

Titanium Diiodide (TiI_2)

GFW = 301.7088

(Ideal Gas)

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	3.708	4.102	4.102	INFINITE
100	12.418	42.404	89.839	2.743	4.000	4.000	16.764
200	14.027	71.635	76.648	1.403	4.294	13.070	14.282
298	14.476	77.335	77.335	0.000	4.700	17.297	12.619
300	14.481	77.425	77.335	0.027	4.708	17.375	12.656
400	14.659	81.618	77.906	1.485	9.040	21.391	11.687
500	14.745	84.900	78.988	2.956	19.738	23.461	10.255
600	14.793	87.593	80.205	4.433	19.424	24.189	8.814
700	14.822	89.875	82.627	5.911	19.224	24.520	7.780
800	14.843	91.856	84.610	7.397	20.056	25.423	7.000
900	14.861	93.605	86.736	8.882	20.211	26.310	6.389
1000	14.880	95.172	88.803	10.369	20.393	26.979	5.896
1100	14.905	96.591	90.811	11.858	20.600	27.427	5.480
1200	14.939	97.889	92.664	13.350	20.826	27.710	5.139
1300	14.983	99.087	94.467	14.846	21.074	27.950	4.833
1400	15.037	100.189	96.222	16.341	22.036	28.272	4.570
1500	15.102	101.239	97.936	17.854	22.187	29.785	4.340
1600	15.177	102.216	99.611	19.368	22.350	30.284	4.137
1700	15.260	103.126	101.252	20.882	22.520	30.769	3.954
1800	15.348	104.013	102.757	22.397	22.696	31.256	3.795
1900	15.440	104.845	104.235	23.959	22.924	31.725	3.649
2000	15.535	105.640	105.685	25.508	27.595	32.030	3.500
2100	15.631	106.400	107.051	27.066	27.808	32.244	3.356
2200	15.730	107.126	108.346	28.559	28.000	32.374	3.216
2300	15.818	107.830	109.569	30.011	28.210	32.449	3.102
2400	15.907	108.505	110.726	31.428	28.438	32.487	2.990
2500	15.992	109.156	111.816	32.813	28.680	32.497	2.886
2600	16.074	109.785	112.840	34.166	28.935	33.194	2.790
2700	16.152	110.390	113.809	35.497	29.204	33.521	2.700
2800	16.223	110.982	114.723	36.826	29.486	33.821	2.616
2900	16.291	111.553	115.591	38.152	29.782	34.097	2.538
3000	16.355	112.106	116.414	39.474	29.934	34.327	2.464
3100	16.415	112.643	117.193	40.793	29.540	34.509	2.395
3200	16.471	113.164	117.946	42.109	29.620	34.648	2.324
3300	16.524	113.673	118.667	43.423	29.694	34.748	2.260
3400	16.574	114.167	119.356	44.731	29.954	34.811	2.210
3500	16.621	114.648	120.028	46.036	30.085	34.848	2.155
3600	16.666	115.117	120.680	47.336	131.834	34.771	2.087
3700	16.709	115.576	121.314	48.632	132.041	34.655	2.022
3800	16.750	116.020	121.932	49.924	132.204	34.500	1.965
3900	16.788	116.456	122.535	51.212	132.338	34.317	1.915
4000	16.826	116.881	123.124	52.496	132.445	34.102	1.869
4100	16.862	117.297	123.700	53.776	132.525	33.861	1.826
4200	16.897	117.704	124.264	55.052	132.580	33.600	1.786
4300	16.931	118.102	124.816	56.324	132.612	33.324	1.748
4400	16.964	118.492	125.357	57.592	132.624	33.037	1.712
4500	16.996	118.873	125.886	58.856	132.618	32.740	1.678
4600	17.026	119.247	126.404	60.116	132.596	32.434	1.645
4700	17.055	119.614	126.911	61.372	132.560	32.119	1.613
4800	17.085	119.973	127.407	62.624	132.511	31.800	1.582
4900	17.113	120.326	127.893	63.872	132.450	31.478	1.552
5000	17.140	120.672	128.369	65.116	132.378	31.154	1.523
5100	17.166	121.011	128.836	66.356	132.296	30.828	1.494
5200	17.191	121.345	129.294	67.592	132.204	30.500	1.466
5300	17.215	121.672	129.743	68.824	132.102	30.170	1.439
5400	17.237	121.994	130.184	70.052	131.990	29.838	1.413
5500	17.259	122.311	130.617	71.276	131.868	29.504	1.388
5600	17.279	122.622	131.044	72.496	131.736	29.168	1.363
5700	17.298	122.926	131.466	73.712	131.594	28.830	1.339
5800	17.315	123.229	131.884	74.924	131.442	28.482	1.315
5900	17.332	123.525	132.299	76.132	131.280	28.134	1.292
6000	17.347	123.817	132.707	77.336	131.108	27.786	1.269

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

Zirconium Diodide (ZrI_2)
(Crystal) Mol. Wt. = 345.04

INTERIM TABLE

T, °K.	C_p	S° cal. mole ⁻¹ deg. ⁻¹	$-(S^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f kcal. mole ⁻¹	ΔF°_f	Log K _f
0							
100	22.500	35.900		.000	- 62.000	- 61.652	45.190
200	24.550	36.039		.042	- 61.993	- 61.649	44.909
300	26.710	36.168		.234	- 61.764	- 61.454	33.575
400	28.910	36.292		.467	- 61.409	- 59.515	26.013
500	31.150	36.411		.734	- 60.928	- 56.403	20.568
600	33.430	36.525		1.035	- 60.315	- 53.407	15.874
700	35.750	36.635		1.368	- 59.568	- 50.510	11.583
800	38.110	36.741		1.732	- 58.684	- 47.703	9.829
900	40.510	36.843		2.127	- 57.657	- 44.974	8.408
1000	42.950	36.941		2.552	- 56.484	- 42.321	7.229
1100	45.430	37.035		3.007	- 55.167	- 39.752	6.232
1200	47.950	37.125		3.492	- 53.706	- 37.272	5.388
1300	50.510	37.211		4.007	- 52.101	- 34.878	4.665
1400	53.110	37.293		4.552	- 50.353	- 32.571	4.039
1500	55.750	37.371		5.127	- 48.464	- 30.356	3.514
1600	58.430	37.445		5.732	- 46.436	- 28.222	3.089
1700	61.150	37.515		6.367	- 44.269	- 26.166	2.759
1800	63.910	37.581		7.032	- 41.964	- 24.186	2.500
1900	66.710	37.643		7.727	- 39.521	- 22.255	2.213
2000	69.550	37.701		8.452	- 36.936	- 20.285	

June 30, 1962

I_2Zr

Zirconium Diodide (ZrI_2) (Crystal)

Mol. Wt. = 345.04

ΔH°_f 289.15 = [-62] kcal. mole⁻¹

$S^\circ_{298.15}$ = [35.8] cal. deg.⁻¹ mole⁻¹

T_m = [700]°K.

ΔH°_m = [6] kcal. mole⁻¹

T_b = [1300]°K.

ΔH°_v = [27] kcal. mole⁻¹

Heat of Formation. Estimated from a consideration of ΔH°_f $ZrI_4(c)$ and of the disproportionation data given by R. F. Rolsten, "Iodide Metals and Metal Iodides", John Wiley and Sons, Inc., New York, (1961).

Heat Capacity and Entropy. Heat capacity estimated by comparison to the other zirconium halides and titanium halides. Entropy estimated from additive constants.

Melting and Vaporization. ΔH°_m was estimated. T_m , T_b , and ΔH°_v from L. Brewer, National Nuclear Energy Series, Div. IV, 195, paper 7, McGraw-Hill Book Co., Inc., New York, 1950.

I_2Zr

Zirconium Diiodide (ZrI₂)
(Liquid) Mol. Wt. = 345.04

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f ° kcal. mole ⁻¹	ΔF _f ° kcal. mole ⁻¹	Log K _p
0						
100						
200						
298	22,500	44,494	.000	55,945	58,199	42,659
300	22,550	44,633	.042	55,978	58,212	42,406
400	22,710	51,262	2,346	58,481	58,877	32,167
500	22,910	56,351	4,827	69,394	57,797	23,282
600	23,090	60,545	6,928	68,694	55,544	20,231
700	23,290	64,095	9,231	68,015	53,407	16,673
800	23,570	67,320	11,648	67,237	51,370	14,033
900	27,460	70,429	14,290	66,244	49,444	12,006
1000	29,540	73,429	17,140	65,053	47,638	10,411
1100	31,620	76,342	20,198	63,672	45,964	9,132
1200	34,700	79,183	23,464	61,053	44,374	8,081
1300	35,780	81,962	26,938	61,262	42,869	7,210
1400	37,870	84,690	30,620	59,274	41,549	6,486
1500	39,950	87,374	34,511	57,084	40,359	5,880
1600	42,030	90,019	38,610	54,694	39,317	5,370
1700	44,110	92,629	42,917	52,106	38,437	4,941
1800	46,170	95,209	47,432	49,317	37,711	4,579
1900	48,240	97,763	52,156	46,328	37,147	4,273
2000	50,360	100,292	57,088	43,140	36,746	4,015

Zirconium Diiodide (ZrI₂) (Liquid)

Mol. Wt. = 345.04

ΔH_f° 298.15 = [-56] kcal. mole⁻¹

S° 298.15 = [44.5] cal. deg.⁻¹ mole⁻¹

T_m = [700]°K.

ΔH_m° = [6] kcal. mole⁻¹

T_b = [1300]°K.

ΔH_v° = [27] kcal. mole⁻¹

Heat of Formation. Based upon the ΔH_f° ZrI₂(c) and the estimated functions of both crystal and liquid.

Heat Capacity and Entropy. Entropy based upon the estimated values for C_p(c), ΔH_m°, and C_p(l).

Melting and Vaporization. ΔH_m° was estimated. T_m, T_b, and ΔH_v° from L. Brewer, National Nuclear Energy Series, Div. IV, 199, paper 7, McGraw-Hill Book Co., Inc., 1950.

I₂Zr

I₂Zr

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	12.000	47.000	INFINITE	3.660	15.117	INFINITE
100	12.023	47.063	1.332	3.660	15.117	21.203
200	12.046	47.125	5.332	3.660	15.117	21.577
298	12.061	47.180	8.380	3.660	15.117	21.577
300	12.063	47.182	8.380	3.660	15.117	21.577
400	12.071	47.196	1.389	3.660	15.117	21.505
500	12.077	47.207	2.760	3.660	15.117	21.505
600	12.082	47.216	4.144	3.660	15.117	13.526
700	12.086	47.223	5.550	3.660	15.117	11.687
800	12.089	47.228	6.937	3.660	15.117	10.647
900	12.091	47.231	8.325	3.660	15.117	9.675
1000	12.092	47.232	9.714	3.660	15.117	8.691
1100	12.093	47.233	11.103	3.660	15.117	7.692
1200	12.094	47.233	12.493	3.660	15.117	6.688
1300	12.094	47.233	13.882	3.660	15.117	5.680
1400	12.094	47.233	15.271	3.660	15.117	4.668
1500	12.094	47.233	16.660	3.660	15.117	3.652
1600	12.093	47.232	18.050	3.660	15.117	2.637
1700	12.092	47.231	19.443	3.660	15.117	1.621
1800	12.090	47.229	20.833	3.660	15.117	0.605
1900	12.088	47.226	22.224	3.660	15.117	-0.410
2000	12.086	47.223	23.614	3.660	15.117	-1.424
2100	12.083	47.219	25.005	3.660	15.117	-2.438
2200	12.079	47.214	26.396	3.660	15.117	-3.452
2300	12.074	47.208	27.786	3.660	15.117	-4.466
2400	12.069	47.201	29.177	3.660	15.117	-5.480
2500	12.063	47.193	30.568	3.660	15.117	-6.494
2600	12.056	47.184	31.958	3.660	15.117	-7.508
2700	12.048	47.174	33.349	3.660	15.117	-8.522
2800	12.039	47.163	34.740	3.660	15.117	-9.536
2900	12.029	47.151	36.131	3.660	15.117	-10.550
3000	12.018	47.138	37.522	3.660	15.117	-11.564
3100	12.006	47.124	38.913	3.660	15.117	-12.578
3200	11.993	47.109	40.303	3.660	15.117	-13.592
3300	11.979	47.093	41.694	3.660	15.117	-14.606
3400	11.964	47.076	43.085	3.660	15.117	-15.620
3500	11.948	47.058	44.476	3.660	15.117	-16.634
3600	11.931	47.039	45.867	3.660	15.117	-17.648
3700	11.913	47.019	47.258	3.660	15.117	-18.662
3800	11.894	46.998	48.649	3.660	15.117	-19.676
3900	11.874	46.976	50.040	3.660	15.117	-20.690
4000	11.853	46.953	51.431	3.660	15.117	-21.704
4100	11.831	46.929	52.822	3.660	15.117	-22.718
4200	11.808	46.904	54.213	3.660	15.117	-23.732
4300	11.784	46.878	55.604	3.660	15.117	-24.746
4400	11.759	46.851	56.995	3.660	15.117	-25.760
4500	11.733	46.823	58.386	3.660	15.117	-26.774
4600	11.706	46.794	59.777	3.660	15.117	-27.788
4700	11.678	46.764	61.168	3.660	15.117	-28.802
4800	11.649	46.733	62.558	3.660	15.117	-29.816
4900	11.619	46.701	63.950	3.660	15.117	-30.830
5000	11.588	46.668	65.341	3.660	15.117	-31.844
5100	11.556	46.634	66.732	3.660	15.117	-32.858
5200	11.523	46.600	68.123	3.660	15.117	-33.872
5300	11.489	46.565	69.513	3.660	15.117	-34.886
5400	11.454	46.529	70.904	3.660	15.117	-35.900
5500	11.418	46.492	72.295	3.660	15.117	-36.914
5600	11.381	46.454	73.686	3.660	15.117	-37.928
5700	11.343	46.416	75.078	3.660	15.117	-38.942
5800	11.304	46.377	76.469	3.660	15.117	-39.956
5900	11.265	46.337	77.861	3.660	15.117	-40.970
6000	11.225	46.296	79.252	3.660	15.117	-41.984

June 30, 1962

Zirconium Dioxide (ZrI₂)

(Ideal Gas)

Mol. Wt. = 345.04

ΔH°_f 298.15 = [-16] kcal. mole⁻¹S°_{298.15} = [82.4] cal. deg.⁻¹ mole⁻¹Point group C_{2v}

Vibrational Levels and Multiplicities

ω, cm. ⁻¹	(60) (1)	(120) (1)	(210) (1)

rZr-I = [2.66 Å] Δ I-Zr-I = 120° σ = 2
 Product of Moments of Inertia I_AI_BI_C = 1.0716 X 10⁻¹¹ g.³ cm.⁶

Heat of Formation. Based upon the estimated value of the ΔH°_f for the crystal and the appropriate crystal and gas functions.

Heat Capacity and Entropy. Molecular constants were all estimated by comparison to similar molecules of zirconium and titanium.

TITANIUM TRIIODIDE (TiI₃) (CRYSTAL) GFW = 428.6132

ΔHf° = unknown

ΔHf°_{298.15} = [-77 ±5] kcal/mol

ΔHs° = [35.4] kcal/mol

S°_{298.15} = [46.0 ± 2.0] gibbs/mol

Ts = [1000]°K

Heat of Formation

The heat of formation of TiI₃(c) is calculated from the free energy of formation at 623°K combined with the increment ΔGf°₆₂₃ - ΔGf°_{298.15} of TiI₂(c), TiI₃(c) and TiI₄(g). The free energy of formation, ΔGf°_{298.15}, is estimated such that ΔGr°_{298.15} = 0 for the process 2TiI₃(c) = TiI₂(c) + TiI₄(g). This assumption is based on the observations of Herczeg and Pidgeon (1) and Fast (2).

Heat Capacity and Entropy

The heat capacities of TiI₃(c) and the value of S°_{298.15} estimated by Kelley (3) have been adopted.

Heat of Sublimation

The heat of sublimation of TiI₃(c) is taken as the difference in the heats of formation of TiI₃(c) and TiI₃(g) at the sublimation temperature. The sublimation temperature is estimated as the point at which ΔGr° = 0 for the process TiI₃(c) = TiI₃(g).

References

1. A. Herczeg and L. M. Pidgeon, Can. J. Chem., 34, 1687 (1956).
2. J. P. Fast, Rec. Trav. Chim., 58, 174 (1939).
3. K. K. Kelley, U. S. Bur. Mines Bull. 584, 1960; U. S. Bur. Mines Bull. 592, 1961.

Titanium Triiodide (TiI₃) (Crystal)

GFW = 428.6132

T, °K	gibbs/mol		kcal/mol		Log Kp
	Cp°	S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔG°	
0					
100					
200					
298	27.909	46.000	.000	76.117	55.795
300	27.912	46.001	.052	74.995	55.487
400	28.086	47.097	2.852	82.571	51.331
500	28.260	48.174	5.669	87.665	31.687
600	28.434	49.240	8.504	94.861	24.600
700	28.608	50.306	11.356	96.044	19.579
800	28.782	51.372	14.225	95.831	12.646
900	28.956	52.438	17.112	93.431	5.894
1000	29.130	53.504	20.016	93.654	10.683
1100	29.304	54.570	22.938	92.866	6.829
1200	29.478	55.636	25.877	93.062	7.291
1300	29.652	56.702	28.834	92.163	5.993
1400	29.826	57.768	31.800	90.161	3.681
1500	30.000	58.834	34.799	90.430	3.945

Titanium Triiodide (TiI₃) (Ideal Gas) GFW = 428.6132

TITANIUM TRIIODIDE (TiI₃)

(IDEAL GAS)

GFW = 428.6132

Point Group [C_{3v}] $\Delta H_f^\circ = [-34.5 \pm 0.0] \text{ kcal/mol}$ $S_{298.15}^\circ = [91.3 \pm 3] \text{ gibbs/mol}$ $\Delta H_f^\circ = [-35.9 \pm 0.0] \text{ kcal/mol}$

Ground State Quantum Weight = [2]

GFW = 428.6132

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i	$\epsilon_i, \text{cm}^{-1}$	g_i
0 [2]	4000 [2]		
600 [2]	10000 [2]		
1500 [2]			

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}	ω_i, cm^{-1}
[341] (1)	[363] (2)
[123] (1)	[74] (2)

Bond Distance: Ti-I = [2.7] Å

Bond Angle: I-Ti-I = [100°]

 $\sigma = 3$ Product of the Moments of Inertia: $I_A I_B I_C = [1.3 \times 10^{-110}] \text{ g cm}^6$

Heat of Formation

The heat of formation, ΔH_f° , of TiI₃(g) is estimated from the average Ti-I bond energy. The bond energy is estimated from the corresponding quantities for TiBn₃(g), TiBn₃(g), and TiI₄(g).

Heat Capacity and Entropy

The interatomic distance is estimated from those of TiI₄, TiCl₄, and TiCl₃. The pyramidal bond angle is estimated by assuming that TiI₃(g) is similar to the group V trihalides. The principal moments of inertia are $I_A = I_B = 1.9 \times 10^{-37} \text{ g cm}^2$ and $I_C = 3.6 \times 10^{-37} \text{ g cm}^2$. The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti³⁺ reported by C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log Kp
0	13.986	72.986	107.175	-4.525	-34.562	INFINITE
100	17.598	83.501	93.015	-1.823	-35.292	48.354
200	19.311	91.294	91.294	-0.000	-35.900	35.567
300	19.322	91.518	91.294	-0.316	-35.911	35.403
400	20.082	97.092	92.643	2.011	-42.312	23.702
500	20.420	101.415	93.237	4.039	-56.215	23.418
600	20.569	105.393	95.204	6.089	-58.176	19.179
700	20.627	108.529	98.866	8.150	-58.150	16.152
800	20.641	111.284	103.216	10.217	-58.148	13.683
900	20.625	113.689	107.549	12.284	-58.148	11.704
1000	20.625	115.689	107.549	14.350	-58.148	10.704
1100	20.612	117.454	107.943	16.402	-58.132	9.546
1200	20.599	119.487	108.261	18.463	-58.132	8.573
1300	20.586	121.295	108.509	20.522	-58.132	7.741
1400	20.572	122.884	108.684	22.584	-58.132	7.009
1500	20.562	124.239	107.915	24.637	-58.132	6.409
1600	20.551	125.566	108.083	26.692	-58.132	5.866
1700	20.541	126.812	108.261	28.747	-58.132	5.387
1800	20.530	127.986	108.461	30.801	-58.132	4.961
1900	20.520	129.091	108.684	32.854	-58.132	4.586
2000	20.512	130.148	108.925	34.905	-58.132	4.216
2100	20.503	131.168	109.180	36.956	-58.132	3.860
2200	20.495	132.152	109.450	39.005	-58.132	3.573
2300	20.486	133.103	109.722	41.055	-58.132	3.292
2400	20.477	134.021	109.991	43.105	-58.132	3.024
2500	20.469	134.921	110.259	45.151	-58.132	2.795
2600	20.464	135.823	110.527	47.198	-58.132	2.570
2700	20.459	136.726	110.792	49.245	-58.132	2.350
2800	20.454	137.629	111.056	51.291	-58.132	2.139
2900	20.449	138.531	111.321	53.332	-58.132	1.934
3000	20.445	139.432	111.586	55.376	-58.132	1.734
3100	20.441	139.771	121.166	57.426	-66.722	1.677
3200	20.437	140.100	121.759	59.471	-66.932	1.530
3300	20.433	140.428	122.352	61.515	-67.145	1.392
3400	20.428	141.002	122.959	63.561	-67.357	1.261
3500	20.424	142.177	123.587	65.608	-67.570	1.137
3600	20.420	142.737	124.230	67.654	-67.782	1.023
3700	20.416	143.297	124.886	69.699	-67.994	0.918
3800	20.412	143.857	125.548	71.745	-68.206	0.822
3900	20.408	144.417	126.210	73.791	-68.418	0.734
4000	20.404	144.977	126.872	75.837	-68.630	0.652
4100	20.403	145.532	127.534	77.881	-68.842	0.575
4200	20.399	146.087	128.196	79.925	-69.054	0.502
4300	20.395	146.642	128.858	81.969	-69.266	0.434
4400	20.391	147.197	129.520	84.013	-69.478	0.371
4500	20.388	147.752	130.182	86.057	-69.690	0.312
4600	20.384	148.307	130.844	88.101	-69.902	0.258
4700	20.381	148.862	131.506	90.145	-70.114	0.209
4800	20.378	149.417	132.168	92.189	-70.326	0.165
4900	20.375	150.000	132.830	94.233	-70.538	0.125
5000	20.372	150.583	133.492	96.277	-70.750	0.088
5100	20.369	151.166	134.154	98.321	-70.962	0.052
5200	20.366	151.749	134.816	100.365	-71.174	0.018
5300	20.363	152.332	135.478	102.409	-71.386	0.000
5400	20.360	152.915	136.140	104.453	-71.598	0.000
5500	20.357	153.498	136.802	106.497	-71.810	0.000
5600	20.354	154.081	137.464	108.541	-72.022	0.000
5700	20.351	154.664	138.126	110.585	-72.234	0.000
5800	20.348	155.247	138.788	112.629	-72.446	0.000
5900	20.345	155.830	139.450	114.673	-72.658	0.000
6000	20.342	156.413	140.112	116.717	-72.870	0.000

June 30, 1964; Dec. 31, 1964

Zirconium Triiodide (ZrI₃)

(Crystal) Mol. Wt. = 471.950

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔG _f ⁰	Log K _p
0	∞	∞	∞	∞	94.774	94.774	INFINITE
100	19.925	24.059	59.939	4.288	94.727	94.727	207.016
200	23.501	29.627	51.152	4.446	94.680	94.680	164.382
298	24.631	30.897	48.697	4.600	94.636	94.636	99.186
300	24.632	49.051	48.897	0.046	94.636	94.636	68.756
400	25.300	56.267	49.878	2.556	94.602	94.602	51.336
500	25.400	61.923	51.742	5.091	94.575	94.575	39.676
600	25.500	66.584	53.837	7.636	94.549	94.549	31.221
700	25.550	70.499	55.944	10.189	94.523	94.523	25.207
800	25.600	73.914	57.981	12.746	94.497	94.497	20.715
900	25.650	76.932	59.922	15.309	94.471	94.471	17.235
1000	25.680	79.636	61.761	17.875	94.445	94.445	14.462
1100	25.700	82.085	63.499	20.444	94.419	94.419	12.203
1200	25.720	84.322	65.142	23.015	94.393	94.393	10.319
1300	25.740	86.381	66.698	25.588	94.367	94.367	8.724
1400	25.750	88.289	68.173	28.163	94.341	94.341	7.363
1500	25.760	90.066	69.574	30.738	94.315	94.315	6.187
1600	25.770	91.729	70.907	33.315	94.289	94.289	5.162
1700	25.780	93.291	72.178	35.892	94.263	94.263	4.261
1800	25.790	94.765	73.393	38.471	94.237	94.237	3.463
1900	25.800	96.160	74.554	41.050	94.211	94.211	2.751
2000	25.810	97.484	75.668	43.631	94.185	94.185	2.113

ZIRCONIUM TRIIODIDE (ZrI₃)

(CRYSTAL)

MOL. WT. = 471.950

$$\Delta H_f^0 = [-95] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = [-95] \text{ kcal. mole}^{-1}$$

$$\Delta H_g^0 \text{ 298.15} = [42] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = [48.90] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$T_a = [970]^{\circ}\text{K.}$$

$$T_d = [1000]^{\circ}\text{K.}$$

Heat of Formation.

E. M. Larsen and J. J. Leddy, *J. Am. Chem. Soc.* **79**, 5983 (1956), studied the reaction $\text{Zr(c)} + 3\text{ZrI}_3(\text{g}) = 4\text{ZrI}_3(\text{c})$ in the temperature range 475 to 975°K. and pressure range 5 to 15 atm. They present a plot of the fractional reaction, at a number of temperatures, as a function of reaction time; however, they express doubt concerning the attainment of thermodynamic equilibrium.

The free energy function change for this reaction was calculated at 100° intervals from 500 to 1100°K. At each temperature the equilibrium constant was assumed to be 1, and ΔH_f^0 298 accordingly calculated. These values and the heat of formation of $\text{ZrI}_3(\text{g})$ [see ZrI_4 table] were used to compute a series of values for the heat of formation of $\text{ZrI}_3(\text{c})$ at 298.15°K. The following table gives representative values at four temperatures.

T(°K.)	K _p	ΔH _r 298	ΔH _f 298.15 [ZrI ₃ (c)]
500	1	-86.0 kcal. mole ⁻¹	-80.2 kcal. mole ⁻¹
700	1	-90.3 kcal. mole ⁻¹	-86.2 kcal. mole ⁻¹
900	1	-113.5 kcal. mole ⁻¹	-92.1 kcal. mole ⁻¹
1100	1	-135.9 kcal. mole ⁻¹	-97.7 kcal. mole ⁻¹

If one assumes an initial pressure of from 5 to 10 atm. for ZrI_4 and stoichiometric amounts of reactants, then, on the basis of zirconium, the reaction must proceed to the extent of 80 to 90% for the pressure of ZrI_4 to attain a value of 1 atm. and hence an equilibrium constant of 1. The data of Larsen and Leddy indicate that the reaction proceeds to the extent of 86% at 975°K. From this it was assumed that at around 1000°K. the equilibrium constant attains a value of 1 giving -95 kcal. mole⁻¹ for the heat of formation of ZrI_3 at 298.15°K.

Their data was subjected to a second law calculation but the results are of doubtful value in view of the uncertainty in the attainment of thermodynamic equilibrium at the lower temperatures. The limits of error assigned to the heat of formation are ± 15 kcal. mole⁻¹ corresponding to a temperature spread of $\pm 500^{\circ}$ in the above table.

Heat Capacity and Entropy.

The heat capacity was estimated in the same manner as for $\text{ZrBr}_3(\text{c})$ [see $\text{ZrBr}_3(\text{c})$ table]. The values $\theta_p = 60^{\circ}\text{K.}$ and $\theta_g = 115^{\circ}\text{K.}$ were taken to be the same as those estimated for $\text{ZrI}_4(\text{c})$. The internal contribution was obtained from the estimated ZrI_3 vibrational frequencies and the anharmonicity factor, "a", was taken to be 2.5×10^{-3} . The specific heat above 300°K. was obtained by graphical extrapolation.

For the above estimation, it was assumed that the crystalline lattice is made up of ZrI_3 molecules. However, E. Holze [see R. F. Rolsten, "Iodide Metals and Metal Iodides", John Wiley & Sons, Inc., New York, 1961, page 46] came to the conclusion that crystalline ZrI_3 is composed of a chain lattice of $(\text{ZrI}_3)_n$ units. The results of an analysis for a crystalline lattice composed of Zr_2I_6 units would probably not differ significantly from that for a crystalline lattice composed of ZrI_3 units since both are approaching the classical harmonic heat capacity of 12R calories per formula weight of ZrI_3 at relatively low temperatures.

Until more quantitative information becomes available, it is felt that the above analysis gives a fair approximation to the heat capacity of ZrI_3 .

Temperature of Disproportionation.

As described in the "Heat of Formation" section, this was assumed to be $1000^{\circ} \pm 500^{\circ}\text{K.}$

Liquid Phase.

It is assumed that the liquid phase is thermodynamically unstable under ordinary conditions.

Sublimation Data.

The heat of sublimation at 298.15°K. was obtained from the difference in the heats of formation of the gas and solid at 298.15°K. The sublimation point was obtained from the free energy crossover between gas and solid.

T, K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	cal. mole ⁻¹	ΔF°	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	16.291	77.199	4.876	51.828	51.828	51.828	INFINITE
200	18.704	87.442	5.000	51.909	56.905	124.359	
300	19.317	95.047	5.000	52.419	61.709	67.429	
400	19.557	100.762	5.000	53.011	66.229	48.246	
500	19.669	105.139	5.000	53.631	70.334	38.427	
600	19.730	108.731	5.000	54.281	73.531	31.264	
700	19.768	111.776	5.000	54.959	75.852	25.766	
800	19.792	114.417	5.000	55.659	77.258	21.494	
900	19.809	116.749	5.000	56.374	77.741	18.880	
1000	19.821	118.837	5.000	57.099	78.202	16.579	
1100	19.830	120.727	5.000	57.828	78.642	14.735	
1200	19.837	122.452	5.000	58.561	79.064	13.224	
1300	19.842	124.040	5.000	59.299	79.471	11.954	
1400	19.846	125.511	5.000	60.041	79.864	10.870	
1500	19.850	126.880	5.000	60.787	80.244	9.940	
1600	19.852	128.161	5.000	61.538	80.611	9.132	
1700	19.855	129.365	5.000	62.293	80.966	8.423	
1800	19.857	130.500	5.000	63.051	81.311	7.797	
1900	19.858	131.574	5.000	63.803	81.646	7.237	
2000	19.860	132.592	5.000	64.559	81.971	6.736	
2100	19.861	133.561	5.000	65.318	82.287	6.284	
2200	19.862	134.485	5.000	66.079	82.594	5.874	
2300	19.863	135.368	5.000	66.841	82.892	5.499	
2400	19.864	136.213	5.000	67.603	83.181	5.119	
2500	19.864	137.024	5.000	68.366	83.461	4.785	
2600	19.865	137.803	5.000	69.130	83.733	4.476	
2700	19.866	138.553	5.000	69.894	84.000	4.191	
2800	19.866	139.276	5.000	70.659	84.261	3.928	
2900	19.866	139.973	5.000	71.424	84.518	3.687	
3000	19.867	140.646	5.000	72.189	84.771	3.467	
3100	19.867	141.298	5.000	72.944	85.020	3.231	
3200	19.868	141.928	5.000	73.689	85.266	3.028	
3300	19.868	142.540	5.000	74.424	85.509	2.858	
3400	19.868	143.133	5.000	75.149	85.749	2.688	
3500	19.868	143.709	5.000	75.864	85.986	2.527	
3600	19.869	144.269	5.000	76.569	86.220	2.376	
3700	19.869	144.813	5.000	77.264	86.450	2.216	
3800	19.869	145.343	5.000	77.949	86.676	2.072	
3900	19.869	145.859	5.000	78.624	86.900	1.938	
4000	19.869	146.362	5.000	79.289	87.121	1.804	
4100	19.870	146.853	5.000	79.944	87.339	1.660	
4200	19.870	147.331	5.000	80.589	87.554	1.521	
4300	19.870	147.796	5.000	81.224	87.766	1.384	
4400	19.870	148.256	5.000	81.849	87.976	1.250	
4500	19.870	148.702	5.000	82.464	88.181	1.119	
4600	19.870	149.139	5.000	83.069	88.382	1.000	
4700	19.870	149.566	5.000	83.664	88.579	0.882	
4800	19.870	149.985	5.000	84.249	88.771	0.750	
4900	19.870	150.394	5.000	84.824	88.959	0.635	
5000	19.871	150.796	5.000	85.389	89.144	0.535	
5100	19.871	151.189	5.000	85.944	89.324	0.439	
5200	19.871	151.575	5.000	86.489	89.500	0.349	
5300	19.871	151.954	5.000	87.024	89.671	0.264	
5400	19.871	152.325	5.000	87.549	89.838	0.184	
5500	19.871	152.690	5.000	88.064	89.999	0.109	
5600	19.871	153.048	5.000	88.569	90.156	0.039	
5700	19.871	153.400	5.000	89.064	90.309	0.000	
5800	19.871	153.745	5.000	89.549	90.459	-0.049	
5900	19.871	154.085	5.000	90.024	90.606	-0.109	
6000	19.871	154.419	5.000	90.489	90.750	-0.169	

June 30, 1964

Point Group = [C_{3v}]S°_{298.15} = [95.05] cal. mole⁻¹ deg.⁻¹

Ground State Quantum Weight = [2]

ΔH°_{f, 0} = [-52] kcal. mole⁻¹ΔH°_{f, 298.15} = [-53] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	[95] (1)	[89] (1)	[220] (2)	[65] (2)
----------------------	----------	----------	-----------	----------

Bond Distance: Zr-I = [2.59] Å

Bond Angle: I-Zr-I = [101]°

Product of the Moments of Inertia: I_AI_BI_C = [1.1545 X 10⁻¹¹⁰] gm.³ cm.⁶Heat of Formation: -53 kcal. mole⁻¹

Heat of Formation.

The heats of formation, from the gaseous atoms, of the gaseous zirconium tetrahalides were computed from data issued in these tables. The zirconium-halide bond energy, taken as 1/4 of this heat of formation, was found to be linear with internuclear separation. From gaseous titanium tri- and tetrachloride, it was found that the bond energy of the trichloride was around 7 kcal. mole⁻¹ greater than that for titanium tetrachloride. This amount was added to the bond energy of zirconium tetrachloride to get that of zirconium trichloride which, when used with its estimated internuclear distance, was found to lie almost exactly on the bond energy versus internuclear distance curve for the tetrahalides. The bond energy for each of the gaseous trihalides of zirconium was determined from this curve and their estimated bond distances.

For zirconium triiodide, the heat of formation from the gaseous atoms was -275 kcal. mole⁻¹ and from the elements in their standard state, -53 kcal. mole⁻¹.

Heat Capacity and Entropy.

The measured internuclear distances for the triiodides of phosphorus, arsenic, and antimony were plotted as a function of the atomic weight of these elements and a smooth curve was drawn through the points. The bond distance in ZrI₃ was taken from this plot. The bond angle was assumed to be 101°. The individual moments of inertia are: I_A = I_B = 1.8520 X 10⁻⁵⁷ gm.² cm.², I_C = 3.3661 X 10⁻⁵⁷ gm.² cm.².

Force constants for ZrI₃ were estimated from those of the triiodides of phosphorus and arsenic. These were used in a valence force field calculation giving ω₁ = 195, ω₂ = 88, ω₃ = 181, and ω₄ = 65 cm.⁻¹. For the fluorides and chlorides of P, As, and Sb, ω₁ is greater than ω₃ but there appears to be a reversal as one goes to the bromides and iodides with ω₃ becoming greater than ω₁. An empirical correlation procedure for ZrI₃ gave ω₁ = 195, ω₂ = 90, ω₃ = 220, and ω₄ = 65 cm.⁻¹ in which ω₃ > ω₁. Since ω₃ > ω₁ for PI₃ and AsI₃, the correlation value for ω₃ was used to represent this frequency in ZrI₃.

Lead Tetraiodide (PbI₄)
(Ideal Gas) Mol. Wt. = 714.85 **INTERIM TABLE**

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	22.757	84.703	133.594	0.949	6.603	0.949	INFINITE	INFINITE
200	24.923	101.355	113.728	0.889	4.889	0.889	3.492	8.505
298	25.410	111.416	111.416	0.861	4.000	0.861	9.136	9.126
300	25.415	111.573	111.416	0.857	3.947	0.857	12.524	9.123
400	25.596	118.913	112.416	0.857	2.599	0.857	16.181	8.840
500	25.681	124.634	114.308	0.857	1.563	0.857	16.003	6.995
600	25.737	129.321	116.431	0.857	0.825	0.857	13.210	4.812
700	25.756	133.249	118.523	0.857	0.316	0.857	10.468	3.144
800	25.774	136.730	120.624	0.857	0.065	0.857	7.273	1.987
900	25.787	139.766	122.585	0.857	0.009	0.857	4.316	1.068
1000	25.796	142.484	124.442	0.857	0.000	0.857	1.364	0.298
1100	25.802	144.943	126.195	0.857	0.000	0.857	0.000	0.000
1200	25.808	147.168	127.853	0.857	0.000	0.857	0.000	0.000
1300	25.812	149.254	129.420	0.857	0.000	0.857	0.000	0.000
1400	25.815	151.167	130.906	0.857	0.000	0.857	0.000	0.000
1500	25.817	152.948	132.317	0.857	0.000	0.857	0.000	0.000
1600	25.819	154.614	133.658	0.857	0.000	0.857	0.000	0.000
1700	25.821	156.179	134.939	0.857	0.000	0.857	0.000	0.000
1800	25.823	157.655	136.160	0.857	0.000	0.857	0.000	0.000
1900	25.824	159.052	137.328	0.857	0.000	0.857	0.000	0.000
2000	25.825	160.376	138.448	0.857	0.000	0.857	0.000	0.000
2100	25.826	161.636	139.522	0.857	0.000	0.857	0.000	0.000
2200	25.827	162.838	140.552	0.857	0.000	0.857	0.000	0.000
2300	25.827	163.986	141.549	0.857	0.000	0.857	0.000	0.000
2400	25.828	165.085	142.507	0.857	0.000	0.857	0.000	0.000
2500	25.828	166.139	143.431	0.857	0.000	0.857	0.000	0.000
2600	25.829	167.152	144.324	0.857	0.000	0.857	0.000	0.000
2700	25.829	168.127	145.184	0.857	0.000	0.857	0.000	0.000
2800	25.830	169.066	146.024	0.857	0.000	0.857	0.000	0.000
2900	25.830	169.973	146.834	0.857	0.000	0.857	0.000	0.000
3000	25.830	170.849	147.620	0.857	0.000	0.857	0.000	0.000
3100	25.831	171.695	148.393	0.857	0.000	0.857	0.000	0.000
3200	25.831	172.515	149.144	0.857	0.000	0.857	0.000	0.000
3300	25.831	173.310	149.884	0.857	0.000	0.857	0.000	0.000
3400	25.831	174.081	150.547	0.857	0.000	0.857	0.000	0.000
3500	25.831	174.830	151.230	0.857	0.000	0.857	0.000	0.000
3600	25.832	175.558	151.896	0.857	0.000	0.857	0.000	0.000
3700	25.832	176.265	152.544	0.857	0.000	0.857	0.000	0.000
3800	25.832	176.955	153.178	0.857	0.000	0.857	0.000	0.000
3900	25.832	177.626	153.797	0.857	0.000	0.857	0.000	0.000
4000	25.832	178.280	154.400	0.857	0.000	0.857	0.000	0.000
4100	25.832	178.917	154.991	0.857	0.000	0.857	0.000	0.000
4200	25.832	179.538	155.564	0.857	0.000	0.857	0.000	0.000
4300	25.832	180.148	156.132	0.857	0.000	0.857	0.000	0.000
4400	25.833	180.742	156.685	0.857	0.000	0.857	0.000	0.000
4500	25.833	181.322	157.226	0.857	0.000	0.857	0.000	0.000
4600	25.833	181.890	157.756	0.857	0.000	0.857	0.000	0.000
4700	25.833	182.445	158.275	0.857	0.000	0.857	0.000	0.000
4800	25.833	182.989	158.785	0.857	0.000	0.857	0.000	0.000
4900	25.833	183.522	159.284	0.857	0.000	0.857	0.000	0.000
5000	25.833	184.044	159.774	0.857	0.000	0.857	0.000	0.000
5100	25.833	184.556	160.255	0.857	0.000	0.857	0.000	0.000
5200	25.833	185.057	160.725	0.857	0.000	0.857	0.000	0.000
5300	25.833	185.549	161.191	0.857	0.000	0.857	0.000	0.000
5400	25.833	186.032	161.647	0.857	0.000	0.857	0.000	0.000
5500	25.833	186.506	162.094	0.857	0.000	0.857	0.000	0.000
5600	25.833	186.971	162.534	0.857	0.000	0.857	0.000	0.000
5700	25.833	187.428	162.963	0.857	0.000	0.857	0.000	0.000
5800	25.833	187.878	163.393	0.857	0.000	0.857	0.000	0.000
5900	25.833	188.320	163.811	0.857	0.000	0.857	0.000	0.000
6000	25.834	188.754	164.224	0.857	0.000	0.857	0.000	0.000

June 30, 1962

Lead Tetraiodide (PbI₄) (Ideal Gas)

Mol. Wt. = 714.85

ΔH_f⁰ 298.15 = [-0.4] kcal. mole⁻¹

S_{298.15} = 111.4 cal. deg.⁻¹ mole⁻¹

Point Group T_d

Vibrational Levels and Multiplicities

ω, cm.⁻¹

137 (1)

37 (2)

168 (3)

48 (3)

Pb-I distance = 2.77 Å I-Pb-I angle = 109° 28'

I_AB₃C = 8.0044 X 10⁻¹¹⁰ g.³ cm.⁶ σ = 12

Heat of Formation. ΔH_f⁰ 298.15 was estimated by comparison with the value of ΔH_f⁰ 298.15 for PbI₂(g).

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagarajan, Bull. Soc. Chim. Belg., 71, 119 (1962).

TITANIUM TETRAIODIDE (TiI₄)

GFW = 555.5176

(CRYSTAL)

Titanium Tetraiodide (TiI₄)
(Crystal) GFW = 555.5176

$$\Delta H_f^\circ = -89.3 \pm 2.0 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = -89.8 \pm 2.0 \text{ kcal/mol}$$

$$\Delta H^\circ = 2.37 \pm 0.15 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 4.74 \pm 0.15 \text{ kcal/mol}$$

$$S^\circ_{298.15} = 58.8 \pm 1.6 \text{ gibbs/mol}$$

$$T_t = 379^\circ\text{K}$$

$$T_m = 428^\circ\text{K}$$

Heat of Formation

The heat of formation of TiI₄(c) was measured by Johnson et al. (1), based on the heats of hydrolysis of TiBr₄(c) and TiI₄(c) in sulfuric acid. These data result in a heat of reaction of -57.88 kcal/mol for the process TiI₄(c) + 2Br₂(l) = TiBr₄(c) + 2I₂(c), when recalculated with revised values of ΔH_f° for HBr(aq) and HI(aq) (2). Combination of ΔH_f° with auxiliary JANAF data gives the adopted value of ΔH_f° .

Heat Capacity and Entropy

King et al. (3) reported the heat capacity and enthalpy of TiI₄(c) over the temperature range 51° to 428°K. The value of S°_{298} is calculated from these data based on $S^\circ_{51} = 14.62$ eu. The value of $H^\circ_{51} - H^\circ_0$ is calculated to be 0.356 kcal/mol from a Debye-Einstein extrapolation of the measured heat capacities.

Transition Data

A first order transition was observed by King et al. (2) at 379°K. They reported the measured value of 2.37 kcal/mol, noting that this value had an uncertainty of 0.15 kcal/mol due to hysteresis in the transition.

Melting Data

The melting temperature and heat of melting were reported by King et al. (2). The large uncertainty on ΔH_m° is due to the uncertainty and close proximity of the transition at 379°K.

References

1. W. H. Johnson, A. A. Gilliland, and E. J. Prosen, J. Res. Natl. Bur. Std., **63A**, 161 (1959).
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. E. G. King, W. M. Waller, A. U. Christensen and K. K. Kalley, U. S. Bur. Minas RI 5799, 1961.

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	∞	∞	INFINITE	-6.948	-89.305	-89.305	INFINITE
100	24.041	26.695	84.359	-5.566	-89.404	-89.295	195.066
200	26.525	27.130	61.536	-2.681	-89.627	-89.611	97.212
298	30.026	28.831	56.831	∞	-89.600	-89.605	64.949
300	30.102	29.017	56.432	-0.056	-89.603	-89.597	64.883
400	35.400	34.583	60.393	5.174	-85.195	-86.041	48.103
500	35.400	42.682	64.050	9.216	-115.297	-88.372	36.679
600	35.400	66.937	67.676	12.756	-114.217	-76.291	26.517
700	35.400	94.394	71.113	16.296	-113.161	-72.387	22.600
800	35.400	121.851	74.327	19.836	-112.133	-66.631	16.203
900	35.400	149.308	77.377	23.376	-111.126	-60.881	12.126
1000	35.400	176.765	80.104	26.916	-110.171	-55.066	
1100	35.400	204.222	82.706	30.456	-109.234	-50.062	9.946
1200	35.400	231.679	85.144	33.996	-108.264	-44.666	6.138
1300	35.400	259.136	87.454	37.536	-107.266	-39.345	2.674
1400	35.400	286.593	89.641	41.076	-106.246	-34.024	
1500	35.400	314.050	91.629	44.616	-106.100	-28.600	0.209

Titanium Tetraiodide (TiI₄)

(Liquid) GFW = 555.5176

TITANIUM TETRAIODIDE (TiI₄)

(LIQUID)

GFW = 555.5176

 $\Delta H_f^\circ = \text{unknown}$ $\Delta H_f^\circ_{298.15} = -83.25 \text{ kcal/mol}$ $\Delta H_m^\circ = 4.74 \pm 0.15 \text{ kcal/mol}$ $\Delta H_v^\circ = 13.50 \pm 0.5 \text{ kcal/mol}$ $S^\circ_{298.15} = 74.532 \text{ gibbs/mol}$ $T_m = 428^\circ \text{K}$ $T_b = 652.6^\circ \text{K}$

Heat of Formation

The heat of formation of $\text{TiI}_4(l)$ is calculated from the heat of melting, ΔH_m° , the heat of formation of $\text{TiI}_4(c)$, and the values of $H_{428}^\circ - H_{298.15}^\circ$ for both crystal and liquid.

Heat Capacity and Entropy

King et al. (1) reported the enthalpy of $\text{TiI}_4(l)$ above the melting temperature. The heat capacity derived from these data is constant. The entropy, S°_{298} , of $\text{TiI}_4(l)$ is calculated from ΔS_m° and the values of $S^\circ_{428} - S^\circ_{298.15}$ of both crystal and liquid.

Melting Data

The melting temperature and heat of melting were reported by King et al. (1).

Vaporization Data

The boiling temperature, T_b , is taken as the point at which $K_p = 1$ for the reaction $\text{TiI}_4(l) = \text{TiI}_4(g)$. The heat of vaporization is calculated as the difference between ΔH_f° of the liquid and gas at the boiling temperature. The vapor pressure data are discussed in the table for $\text{TiI}_4(g)$.

Reference

1. E. G. King, W. W. Weller, A. U. Christensen, and K. K. Kelley, U. S. Bur. Mines RI 5799, 1961.

T, °K	C _p ^o	gibbs/mol		kcal/mol		Log K _p
		$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	
0						
100						
200						
298	37.400	74.532	0.000	83.250	86.736	63.579
300	37.400	74.763	0.069	83.240	86.757	63.202
400	37.400	85.522	3.809	90.462	87.733	57.915
500	37.400	93.888	7.549	110.414	85.102	37.733
600	37.400	100.687	81.871	109.134	80.258	29.234
700	37.400	106.452	81.982	107.874	75.545	23.566
800	37.400	111.446	87.984	106.650	71.008	19.399
900	37.400	115.851	90.841	105.454	66.628	16.179
1000	37.400	119.791	93.542	104.288	62.374	13.632
1100	37.400	123.356	96.093	103.151	58.238	11.571
1200	37.400	126.610	98.503	102.041	54.166	9.865
1300	37.400	129.604	100.781	101.773	50.147	8.430
1400	37.400	132.376	102.940	100.586	46.220	7.215
1500	37.400	134.956	104.990	99.417	42.361	6.175

TITANIUM TETRAIODIDE (TiI₄)

(IDEAL GAS)

GFW = 555.5176

Titanium Tetraiodide (TiI₄)

(Ideal Gas) GFW = 555.5176

Point Group T_d

$$\Delta H_f^\circ = -65.0 \pm 2 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 103.40 \pm 2 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = -66.27 \pm 2 \text{ kcal/mol}$$

Ground State Quantum Weight = 1

(IDEAL GAS)

GFW = 555.5176

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
[175] (1)	[280] (3)
(55) (2)	[69] (3)

Bond Distance: Ti-I = [2.5] Å

Bond Angle: I-Ti-I = [109°28']

 $\sigma = 12$ Product of the Moments of Inertia: $I_A I_B I_C = [4.33 \times 10^{-110}] \text{ g cm}^6$

Heat of Formation

The heat of formation of TiI₄(g) is calculated from that of TiI₄(l) and the heat of vaporization of the liquid. Blocher and Campbell (1) reported vapor pressure data for TiI₄(l) over the temperature range 473° to 655°K. Second and third law analyses of these data give values for ΔH_f° of 17.2 ± 0.1 and 16.98 kcal/mol , respectively, the third law drift being $-0.4 \pm 0.2 \text{ eu}$. The adopted value of ΔH_f° is based on the third law heat of vaporization.

Heat Capacity and Entropy

The interatomic distances are estimated from those of TiBr₄(c), TiBr₄(g) and TiI₄(c) (2). The tetrahedral model is assumed by analogy with TiCl₄(g) and TiBr₄(g). The principal moments of inertia are: $I_A = I_B = I_C = 3.51 \times 10^{-37} \text{ g cm}^2$. The vibrational frequencies of TiI₄(g) have been estimated by Ushanova et al. (3). The given estimates are based on their predictions and valence force field calculations.

References

1. J. M. Blocher, Jr. and I. E. Campbell, *J. Am. Chem. Soc.*, **69**, 2100 (1947).
2. O. Hasoel and H. Kringstand, *Z. Phys. Chem.*, **131**, 274 (1932).
3. N. I. Ushanova, I. N. Godnev and I. V. Orlova, *Opt. Spektrosk.*, **5**, 567 (1958).

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔH°	ΔG°	Log Kp
0	+0.00	+0.00	INFINITE	-	-	-	-	INFINITE
100	20.496	78.168	124.839	-6.169	-64.979	-64.979	-	152.488
200	23.946	93.703	105.734	-2.466	-65.069	-65.069	-	81.159
298	24.917	103.479	103.479	+0.000	-66.270	-66.270	-	57.459
300	24.928	103.633	103.679	-0.066	-66.283	-66.283	-	57.159
400	25.309	110.864	104.462	2.560	-74.731	-74.731	-	44.879
500	25.493	116.533	106.330	5.102	-81.982	-81.982	-	35.834
600	25.595	121.191	108.430	7.687	-85.766	-85.766	-	28.953
700	25.658	125.142	110.543	10.219	-85.768	-85.768	-	23.871
800	25.727	131.599	114.534	15.159	-85.652	-85.652	-	19.234
900	25.747	134.311	116.378	17.932	-85.625	-85.625	-	14.912
1000	25.762	136.766	118.122	20.508	-85.652	-85.652	-	13.012
1200	25.773	139.008	119.770	23.085	-86.645	-86.645	-	11.421
1400	25.786	142.982	123.810	28.562	-86.590	-86.590	-	10.067
1600	25.795	148.761	124.215	30.820	-86.546	-86.546	-	7.902
1800	25.799	146.426	125.551	33.400	-86.577	-86.577	-	7.02
2000	25.803	147.990	126.826	35.980	-86.612	-86.612	-	6.247
2200	25.809	150.861	129.207	41.181	-86.755	-86.755	-	5.336
2400	25.811	152.185	130.323	43.722	-101.312	-101.312	-	4.365
2600	25.813	153.444	131.395	46.303	-101.423	-101.423	-	3.837
2800	25.817	154.685	132.424	48.885	-101.537	-101.537	-	3.358
3000	25.818	156.091	133.371	51.468	-101.648	-101.648	-	2.916
3200	25.820	157.645	134.241	54.051	-101.772	-101.772	-	2.516
3400	25.822	159.278	135.038	56.630	-101.894	-101.894	-	2.145
3600	25.824	160.958	135.768	59.212	-102.018	-102.018	-	1.802
3800	25.825	162.672	136.438	61.794	-102.146	-102.146	-	1.484
4000	25.826	164.324	137.056	64.376	-102.270	-102.270	-	1.193
4200	25.827	165.985	137.624	66.959	-102.407	-102.407	-	0.913
4400	25.828	167.661	138.146	69.541	-102.543	-102.543	-	0.656
4600	25.829	169.329	138.624	72.123	-102.681	-102.681	-	0.415
4800	25.830	170.983	139.056	74.706	-102.820	-102.820	-	0.189
5000	25.831	172.624	139.438	77.289	-102.960	-102.960	-	0.000
5200	25.832	174.258	139.770	79.871	-103.100	-103.100	-	0.225
5400	25.833	175.885	140.056	82.453	-103.257	-103.257	-	0.454
5600	25.834	177.508	140.294	85.036	-103.424	-103.424	-	0.680
5800	25.835	179.124	140.496	87.619	-103.596	-103.596	-	0.906
6000	25.836	180.734	140.662	90.202	-103.772	-103.772	-	1.132
6200	25.837	182.338	140.796	92.785	-103.952	-103.952	-	1.358
6400	25.838	183.937	140.896	95.367	-104.136	-104.136	-	1.584
6600	25.839	185.532	140.964	97.950	-104.324	-104.324	-	1.810
6800	25.840	187.124	141.000	100.532	-104.516	-104.516	-	2.036
7000	25.841	188.712	141.016	103.115	-104.712	-104.712	-	2.262
7200	25.842	190.296	141.016	105.698	-104.912	-104.912	-	2.488
7400	25.843	191.876	141.000	108.281	-105.116	-105.116	-	2.714
7600	25.844	193.452	140.964	110.864	-105.324	-105.324	-	2.940
7800	25.845	195.024	140.912	113.447	-105.536	-105.536	-	3.166
8000	25.846	196.592	140.840	116.030	-105.752	-105.752	-	3.392
8200	25.847	198.156	140.748	118.613	-105.972	-105.972	-	3.618
8400	25.848	199.716	140.636	121.196	-106.196	-106.196	-	3.844
8600	25.849	201.272	140.504	123.779	-106.424	-106.424	-	4.070
8800	25.850	202.824	140.352	126.362	-106.656	-106.656	-	4.296
9000	25.851	204.372	140.190	128.945	-106.892	-106.892	-	4.522
9200	25.852	205.916	140.016	131.528	-107.132	-107.132	-	4.748
9400	25.853	207.456	139.832	134.111	-107.376	-107.376	-	4.974
9600	25.854	208.992	139.636	136.694	-107.624	-107.624	-	5.200
9800	25.855	210.524	139.424	139.277	-107.876	-107.876	-	5.426
10000	25.856	212.052	139.196	141.860	-108.132	-108.132	-	5.652
10200	25.857	213.576	138.952	144.443	-108.392	-108.392	-	5.878
10400	25.858	215.096	138.696	147.026	-108.656	-108.656	-	6.104
10600	25.859	216.612	138.424	149.609	-108.924	-108.924	-	6.330
10800	25.860	218.124	138.136	152.192	-109.196	-109.196	-	6.556
11000	25.861	219.632	137.832	154.775	-109.472	-109.472	-	6.782
11200	25.862	221.136	137.512	157.358	-109.752	-109.752	-	7.008
11400	25.863	222.636	137.176	159.941	-110.036	-110.036	-	7.234
11600	25.864	224.132	136.824	162.524	-110.324	-110.324	-	7.460
11800	25.865	225.624	136.456	165.107	-110.616	-110.616	-	7.686
12000	25.866	227.112	136.072	167.690	-110.912	-110.912	-	7.912
12200	25.867	228.596	135.672	170.273	-111.212	-111.212	-	8.138
12400	25.868	230.076	135.256	172.856	-111.516	-111.516	-	8.364
12600	25.869	231.552	134.824	175.439	-111.824	-111.824	-	8.590
12800	25.870	233.024	134.376	178.022	-112.136	-112.136	-	8.816
13000	25.871	234.492	133.912	180.605	-112.452	-112.452	-	9.042
13200	25.872	235.956	133.432	183.188	-112.772	-112.772	-	9.268
13400	25.873	237.416	132.936	185.771	-113.096	-113.096	-	9.494
13600	25.874	238.872	132.424	188.354	-113.424	-113.424	-	9.720
13800	25.875	240.324	131.896	190.937	-113.756	-113.756	-	9.946
14000	25.876	241.772	131.352	193.520	-114.092	-114.092	-	10.172
14200	25.877	243.216	130.792	196.103	-114.432	-114.432	-	10.398
14400	25.878	244.656	130.216	198.686	-114.776	-114.776	-	10.624
14600	25.879	246.092	129.624	201.269	-115.124	-115.124	-	10.850
14800	25.880	247.524	129.016	203.852	-115.476	-115.476	-	11.076
15000	25.881	248.952	128.392	206.435	-115.832	-115.832	-	11.302
15200	25.882	250.376	127.752	209.018	-116.192	-116.192	-	11.528
15400	25.883	251.796	127.096	211.601	-116.556	-116.556	-	11.754
15600	25.884	253.212	126.424	214.184	-116.924	-116.924	-	11.980
15800	25.885	254.624	125.736	216.767	-117.296	-117.296	-	12.206
16000	25.886	256.032	125.032	219.350	-117.672	-117.672	-	12.432
16200	25.887	257.436	124.312	221.933	-118.052	-118.052	-	12.658
16400	25.888	258.836	123.576	224.516	-118.436	-118.436	-	12.884
16600	25.889	260.232	122.824	227.099	-118.824	-118.824	-	13.110
16800	25.890	261.624	122.056	229.682	-119.216	-119.216	-	13.336
17000	25.891	263.012	121.272	232.265	-119.612	-119.612	-	13.562
17200	25.892	264.396	120.472	234.848	-120.012	-120.012	-	13.788
17400	25.893	265.776	119.656	237.431	-120.416	-120.416	-	14.014
17600	25.894	267.152	118.824	240.014	-120.824	-120.824	-	14.240
17800	25.895	268.524	117.976	242.597	-121.236	-121.236	-	14.466
18000	25.896	269.892	117.112	245.180	-121.652	-121.652	-	14.692
18200	25.897	271.256	116.232	247.763	-122.072	-122.072	-	14.918
18400	25.898	272.616	115.336	250.346	-122.496	-122.496	-	15.144
18600	25.899	273.972	114.424	252.929	-122.924	-122.924	-	15.370
18800	25.900	275.324	113.496	255.512	-123.356	-123.356	-	15.596
19000	25.901	276.672	112.552	258.095	-123.792	-123.792	-	15.822
19200	25.902	278.016	111.592	260.678	-124.232	-124.232	-	16.048
19400	25.903	279.356	110.616	263.261	-124.676	-124.676	-	16.274
19600	25.904	280.692	109.624	265.844	-125.124	-125.124	-	16.500

Zirconium Tetraiodide (ZrI₄)

(Crystal) Mol. Wt. = 598.86

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	INFINITE
100	24.645	31.267	86.777	-115.414	-115.414	252.128
200	28.426	49.842	144.085	-115.496	-115.370	182.869
298	29.543	61.442	0.000	-115.500	-115.500	84.207
300	29.556	61.595	0.055	-115.904	-114.875	83.682
400	30.170	70.188	3.043	-123.895	-114.221	62.404
500	30.550	76.966	6.804	-144.574	-109.846	48.011
600	30.810	82.561	9.150	-144.003	-102.956	37.500
700	30.990	87.325	12.241	-143.435	-96.160	30.021
800	31.100	91.471	15.346	-142.870	-89.443	24.434
900	31.180	95.139	18.460	-142.309	-82.800	20.106
1000	31.220	98.426	21.580	-141.753	-76.216	16.656
1100	31.250	101.403	24.704	-141.213	-69.690	13.845
1200	31.260	104.123	27.830	-141.643	-63.163	11.503
1300	31.270	106.625	30.956	-141.109	-56.644	9.522
1400	31.280	108.943	34.084	-140.587	-50.167	7.831
1500	31.290	111.102	37.212	-140.073	-43.729	6.371

ZIRCONIUM TETRAIODIDE (ZrI₄)

(CRYSTAL)

MOL. WT. = 598.86

$$\Delta H_f^o = [-115.4] \pm 1.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o 298.15 = -115.9 \pm 0.8 \text{ kcal. mole}^{-1}$$

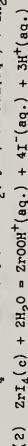
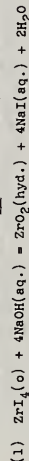
$$\Delta H_g^o 298.15 = 31.0 \pm 0.7 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = [61.4] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$T_g = 704^\circ\text{K.}$$

Heat of Formation.

A. G. Turnbull, J. Phys. Chem. **65**, 1652 (1961), measured the heat of reaction for the following reactions:



Turnbull used the same procedure to calculate the heat of formation of zirconium tetraiodide as he did for zirconium tetrabromide [see ZrBr₄ table]. The heat of formation of the solid zirconium tetraiodide from reaction (1) was -115.6 ± 0.8 kcal. mole⁻¹ and from reaction (2) was -116.3 ± 0.8 kcal. mole⁻¹. An average of these was taken as the heat of formation of the tetraiodide.

Heat Capacity and Entropy.

The heat capacity from 0 to 300°K. was calculated in the same manner as for ZrBr₄(c) [see ZrBr₄(c) table]. The values, $\bar{C}_p^o$ = 60°K. and $\bar{C}_p^o$ = 115°K. were used in the analysis. The value, $\bar{C}_p^o$ = 1.5 X 10⁻³, was obtained from a consideration of the sublimation calculations [see below]. The heat capacity above 300°K. represents a graphical extrapolation.

Melting.

T_m = 772°K. was reported by O. Rahlfs and W. Fischer, Z. anorg. allgem. Chem. **211**, 349 (1933).

Sublimation Data.

Vapor pressure measurements have been reported by Rahlfs and Fischer (loc. cit.). Four values of "a" were used to compute the thermodynamic functions of the solid. That value of "a" was chosen which gave agreement between 2nd and 3rd law values for the heat of sublimation. The sublimation results for the four values of "a" are given in the following table.

"a"	ΔH _g (298) [3rd law]	ΔH _g (298) [2nd law]
3.0 X 10 ⁻³	29.99 kcal. mole ⁻¹	31.65 kcal. mole ⁻¹
2.5 X 10 ⁻³	30.39 kcal. mole ⁻¹	31.34 kcal. mole ⁻¹
2.0 X 10 ⁻³	30.76 kcal. mole ⁻¹	31.17 kcal. mole ⁻¹
1.5 X 10 ⁻³	31.02 kcal. mole ⁻¹	31.04 kcal. mole ⁻¹

A temperature dependent third law heat of sublimation at 298°K. was obtained for "a" = 3.0 X 10⁻³; this temperature trend decreased for smaller values of "a" and there was essentially no temperature dependence for "a" = 1.5 X 10⁻³. Various high temperature extrapolations were not used since, by experience with ZrBr₄(c), they produced insignificant changes in the heat values. The heat of sublimation was taken to be 31.0 kcal. mole⁻¹ since the entire analysis was conducted to obtain 2nd and 3rd law agreement.

From experience with a number of other compounds, that were found to be amenable to the theoretical treatment used here, the value "a" = 1.5 X 10⁻³ appears to be rather low, but no further analysis was deemed practical since all parameters for the gas and solid are estimated.

The sublimation point obtained from the free energy crossover of solid and gas was 703°K. The value reported by Rahlfs and Fischer (loc. cit.), was 704°K. The sublimation point was taken as 704°K.

Since the sublimation point is lower than the melting point, the liquid phase is thermodynamically unstable under ordinary conditions.

Zirconium Tetraiodide (ZrI₄)
(Ideal Gas) Mol. Wt. = 598.86

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	-0.000	INFINITE	6.430	83.605	83.605	INFINITE
100	21.256	40.985	128.418	83.605	83.605	INFINITE
200	24.265	106.900	106.900	83.605	83.605	101.802
298	25.090	106.775	106.775	83.605	83.605	101.802
300	25.099	106.930	106.930	83.605	83.605	101.802
400	25.411	114.200	107.765	83.605	83.605	101.802
500	25.560	119.668	106.681	83.605	83.605	101.802
600	25.663	124.556	111.750	83.605	83.605	101.802
700	25.726	128.513	113.569	83.605	83.605	101.802
800	25.766	131.938	115.519	83.605	83.605	101.802
900	25.789	134.978	117.671	83.605	83.605	101.802
1000	25.799	137.691	119.770	83.605	83.605	101.802
1100	25.777	140.188	121.847	83.605	83.605	101.802
1200	25.726	142.391	123.119	83.605	83.605	101.802
1300	25.703	144.455	124.681	83.605	83.605	101.802
1400	25.709	146.387	126.163	83.605	83.605	101.802
1500	25.803	148.187	127.570	83.605	83.605	101.802
1600	25.807	149.857	128.909	83.605	83.605	101.802
1700	25.810	151.377	130.185	83.605	83.605	101.802
1800	25.813	152.852	131.403	83.605	83.605	101.802
1900	25.815	154.288	132.569	83.605	83.605	101.802
2000	25.817	155.572	133.687	83.605	83.605	101.802
2100	25.819	156.832	134.759	83.605	83.605	101.802
2200	25.821	158.033	135.790	83.605	83.605	101.802
2300	25.821	159.181	136.782	83.605	83.605	101.802
2400	25.822	160.280	137.738	83.605	83.605	101.802
2500	25.823	161.334	138.661	83.605	83.605	101.802
2600	25.824	162.347	139.553	83.605	83.605	101.802
2700	25.825	163.321	140.415	83.605	83.605	101.802
2800	25.825	164.260	141.250	83.605	83.605	101.802
2900	25.826	165.167	142.059	83.605	83.605	101.802
3000	25.827	166.042	142.834	83.605	83.605	101.802
3100	25.827	166.889	143.576	83.605	83.605	101.802
3200	25.828	167.709	144.293	83.605	83.605	101.802
3300	25.828	168.504	144.987	83.605	83.605	101.802
3400	25.829	169.275	145.658	83.605	83.605	101.802
3500	25.829	170.024	146.306	83.605	83.605	101.802
3600	25.829	170.751	146.934	83.605	83.605	101.802
3700	25.829	171.459	147.543	83.605	83.605	101.802
3800	25.829	172.148	148.136	83.605	83.605	101.802
3900	25.830	172.819	148.714	83.605	83.605	101.802
4000	25.830	173.473	149.277	83.605	83.605	101.802
4100	25.830	174.110	149.827	83.605	83.605	101.802
4200	25.830	174.733	150.364	83.605	83.605	101.802
4300	25.831	175.341	150.889	83.605	83.605	101.802
4400	25.831	175.935	151.403	83.605	83.605	101.802
4500	25.831	176.515	151.907	83.605	83.605	101.802
4600	25.831	177.083	152.402	83.605	83.605	101.802
4700	25.831	177.638	152.889	83.605	83.605	101.802
4800	25.831	178.182	153.367	83.605	83.605	101.802
4900	25.831	178.715	153.836	83.605	83.605	101.802
5000	25.832	179.237	154.296	83.605	83.605	101.802
5100	25.832	179.745	154.747	83.605	83.605	101.802
5200	25.832	180.250	155.190	83.605	83.605	101.802
5300	25.832	180.742	155.625	83.605	83.605	101.802
5400	25.832	181.225	156.053	83.605	83.605	101.802
5500	25.832	181.699	156.475	83.605	83.605	101.802
5600	25.832	182.168	156.892	83.605	83.605	101.802
5700	25.832	182.621	157.305	83.605	83.605	101.802
5800	25.832	183.071	157.714	83.605	83.605	101.802
5900	25.832	183.517	158.120	83.605	83.605	101.802
6000	25.832	183.946	158.523	83.605	83.605	101.802

Mar. 31, 1962; June 30, 1964

ZIRCONIUM TETRAIODIDE (ZrI₄)
(IDEAL GAS)

MOL. WT. = 598.86

ΔH_f⁰ = [-83.6] ± 1.7 kcal. mole⁻¹
ΔH_f⁰ 298 = -84.9 ± 1.5 kcal. mole⁻¹

Point Group = D_{2d}
S₂₉₈ = [106.78] cal. mole⁻¹ deg.⁻¹
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	(146) (1)	(45) (2)	(237) (3)	(58) (3)

Q = [12]

Bond Distance: Zr-I = [2.68] Å
Bond Angle: I-Zr-I = [109° 28']

Product of the Moments of Inertia: I_AI_BI_C = [6.5718 × 10⁻¹¹⁰] gm.³ cm.⁶

Heat of Formation

Calculated from the heats of formation and sublimation for the crystal at 298.15°K. (see crystal table for details).

Heat Capacity and Entropy

The interatomic distance was obtained from an involved correlation of the interatomic distances and covalent radii of the tetrahalides of Pb, Si, Ti, Ge, and Sn. I. N. Godnev, A. M. Aleksandrovskaya, and I. V. Regina, Optics and Spectroscopy 7, 172 (1959), estimated the interatomic distance and report 2.67 Å as the Zr-I distance. The I-Zr-I angle was taken as the tetrahedral angle. The three principal moments of inertia are: I_A = I_B = I_C = 4.0355 × 10⁻³⁷ gm. cm.².

The fundamental vibrational frequencies are estimated. The product of ω₁ and ω₂ versus internuclear distance for the tetrahalides of Pb, Ti, Ge, and Sn was found to be approximately constant. Using the estimated Zr-I interatomic distance a value of 147 cm.⁻¹ was obtained for ω₁. Plots of ω₁ and ω₂ versus internuclear distance for these molecules were constructed and smooth curves drawn through the points. Values of ω₁ and ω₂ for ZrI₄ were read off from these plots; they were 146 cm.⁻¹ and 44 cm.⁻¹ respectively. Using ω₁ = 146 cm.⁻¹ and ω₂ = 45 cm.⁻¹, ω₃ = 237 cm.⁻¹ and ω₄ = 58 cm.⁻¹ were obtained from a valence force field calculation. Godnev, Aleksandrovskaya, and Regina (loc. cit.) estimated the vibrational frequencies and reported ω₁ = 152 cm.⁻¹, ω₂ = 44 cm.⁻¹, ω₃ = 211 cm.⁻¹ and ω₄ = 55 cm.⁻¹.

Potassium (K)

(Reference State) Mol. Wt. = 39.100

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(°K.-H ₂₉₈ °)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	0.000	INFINITE	1.693	.000	.000	.000
100	5.887	4.509	1.279	.000	.000	.000
200	9.856	14.785	0.000	.000	.000	.000
298	15.457	15.457	.000	.000	.000	.000
300	15.457	15.457	.013	.000	.000	.000
400	7.598	19.332	1.327	.000	.000	.000
500	7.336	20.990	1.651	.000	.000	.000
600	7.203	22.315	2.794	.000	.000	.000
700	7.124	23.419	3.512	.000	.000	.000
800	7.112	24.389	4.224	.000	.000	.000
900	7.155	25.208	4.936	.000	.000	.000
1000	7.256	25.967	5.657	.000	.000	.000
1100	4.945	26.782	21.788	25.294	.000	.000
1200	4.948	25.215	21.722	25.791	.000	.000
1300	4.969	45.612	25.391	26.288	.000	.000
1400	4.970	45.981	26.449	26.785	.000	.000
1500	4.972	46.324	27.136	27.282	.000	.000
1600	4.974	46.645	28.283	27.779	.000	.000
1700	4.980	46.944	30.313	28.277	.000	.000
1800	4.984	47.231	31.245	28.775	.000	.000
1900	4.994	47.501	32.094	29.275	.000	.000
2000	5.013	47.758	32.870	29.775	.000	.000
2100	5.033	48.003	34.585	30.277	.000	.000
2200	5.057	48.238	34.246	30.782	.000	.000
2300	5.087	48.463	34.859	31.289	.000	.000
2400	5.122	48.680	35.431	31.799	.000	.000
2500	5.164	48.890	35.965	32.314	.000	.000
2600	5.213	49.094	36.464	32.832	.000	.000
2700	5.270	49.291	36.937	33.356	.000	.000
2800	5.334	49.484	37.382	33.887	.000	.000
2900	5.407	49.673	37.802	34.424	.000	.000
3000	5.489	49.857	38.201	34.968	.000	.000
3100	5.582	50.039	38.580	35.522	.000	.000
3200	5.682	50.218	38.941	36.089	.000	.000
3300	5.802	50.394	39.285	36.659	.000	.000
3400	5.932	50.569	39.615	37.246	.000	.000
3500	6.079	50.743	39.930	37.846	.000	.000
3600	6.242	50.917	40.233	38.462	.000	.000
3700	6.422	51.090	40.523	39.094	.000	.000
3800	6.630	51.264	40.804	39.748	.000	.000
3900	6.858	51.439	41.075	40.422	.000	.000
4000	7.111	51.616	41.336	41.120	.000	.000
4100	7.392	51.795	41.590	41.845	.000	.000
4200	7.701	51.977	41.834	42.600	.000	.000
4300	8.041	52.162	42.072	43.386	.000	.000
4400	8.412	52.351	42.304	44.209	.000	.000
4500	8.815	52.545	42.529	45.070	.000	.000
4600	9.250	52.743	42.740	45.973	.000	.000
4700	9.717	52.947	42.944	46.921	.000	.000
4800	10.215	53.157	43.174	47.917	.000	.000
4900	10.741	53.373	43.380	48.945	.000	.000
5000	11.294	53.595	43.582	50.066	.000	.000
5100	11.871	53.825	43.781	51.224	.000	.000
5200	12.467	54.066	43.977	52.418	.000	.000
5300	13.079	54.304	44.169	53.718	.000	.000
5400	13.701	54.554	44.359	55.057	.000	.000
5500	14.327	54.811	44.546	56.459	.000	.000
5600	14.953	55.075	44.722	57.923	.000	.000
5700	15.572	55.344	44.912	59.459	.000	.000
5800	16.178	55.621	45.098	61.037	.000	.000
5900	16.745	55.903	45.279	62.684	.000	.000
6000	17.326	56.190	45.458	64.389	.000	.000

December 31, 1961

K

MOL. WT. = 39.100

(REFERENCE STATE)

POTASSIUM (K)

0°K. to 336.35°K. Crystal
336.35°K. to 1043.7°K. Liquid
1043.7°K. to 6000°K. Ideal Monatomic Gas

Heat of Formation.

Zero by definition.

Heat Capacity of Crystal.

Low temperature heat capacity measurements have been reported by L. M. Roberts [Proc. Phys. Soc. (London) 70B, 744-52 (1957)] (1.5°-20°K.), by C. A. Krier, R. S. Craig, and W. E. Wallace [J. Phys. Chem. 61, 522 (1957)] (12°-320°K.), by T. M. Dauphinee, D. L. Martin, and H. Preston-Thomas [Proc. Roy. Soc. (London), A253, 214 (1955)] (20°-350°K.), by F. Simon and M. Zeidler [Z. physikal. Chem. 123, 383 (1926)] (15°-300°K.), and by E. D. Eastman and W. H. Rodabaugh [J. Am. Chem. Soc. 40, 489 (1918)] (70°-230°K.). A smooth curve was drawn through a large scale plot of the data, giving the most weight to the first three references. Above 300°K. the heat capacity data were adjusted to join smoothly with the heat content measurements of T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis [J. Am. Chem. Soc. 74, 2472 (1952)].

Heat Capacity of Liquid and Heat of Melting.

The heat of melting and liquid heat capacity are from the heat content measurements of T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis (loc. cit.).

Heat of Sublimation, Ideal Gas Functions.

See tables for K(g) and K₂(g) for details.

K

T, °K.	C_p°	S°	$-(H^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _f
0							
100	1.816	17.078	17.078	.000	.546	.063	.066
200	1.819	17.332	17.332	.014	.547	.066	.066
300	1.824	17.590	17.590	.028	.547	.066	.066
400	1.836	17.854	17.854	.042	.547	.066	.066
500	1.856	18.124	18.124	.056	.547	.066	.066
600	1.884	18.400	18.400	.070	.547	.066	.066
700	1.920	18.682	18.682	.084	.547	.066	.066
800	1.964	18.970	18.970	.098	.547	.066	.066
900	2.016	19.264	19.264	.112	.547	.066	.066
1000	2.076	19.564	19.564	.126	.547	.066	.066
1100	2.144	19.870	19.870	.140	.547	.066	.066
1200	2.220	20.182	20.182	.154	.547	.066	.066
1300	2.304	20.500	20.500	.168	.547	.066	.066
1400	2.396	20.824	20.824	.182	.547	.066	.066
1500	2.496	21.154	21.154	.196	.547	.066	.066
1600	2.604	21.490	21.490	.210	.547	.066	.066
1700	2.720	21.832	21.832	.224	.547	.066	.066
1800	2.844	22.180	22.180	.238	.547	.066	.066
1900	2.976	22.534	22.534	.252	.547	.066	.066
2000	3.116	22.894	22.894	.266	.547	.066	.066

POTASSIUM (K)

(LIQUID)

MOL. WT. = 39.100

$$\Delta H_f^\circ 298 = 0.546 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = 0.558 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^\circ = 18.38 \text{ kcal. per formula weight}$$

$$T_m = 336.35^\circ \text{K.}$$

$$T_b = 1037^\circ \text{K.}$$

Heat of Formation.

Back calculated from the heat of melting and the heat contents of solid and liquid at the melting point.

Heat of Melting and Heat Capacity.

The heat of melting, melting point, and liquid heat capacity were measured by T. B. Douglas, A. P. Ball, D. C. Ginnings, and W. D. Davis [J. Am. Chem. Soc. 74, 2472 (1952)]. The heat capacity curve was extrapolated back to 298°K. and up to 2000°K. in a reasonable manner.

Entropy.

Back calculated from the entropy of the liquid at the melting point and the extrapolated heat capacity from the melting point to 298°K.

Vaporization.

Potassium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1037°K. The vapor composition at this temperature is 94.5 mole % monatomic and 5.5 mole % diatomic gas. The heat of vaporization of 39.1 grams of liquid potassium to this equilibrium mixture is 18.38 kcal. See also tables for K(g) and K₂(g).

Potassium, Monatomic (K)

(Ideal Gas) Mol. Wt. = 39.100

T. °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	Log K _p
0	.000	INFINITE	INFINITE	21.522	INFINITE
100	4.869	32.714	.984	21.605	41.991
200	4.868	36.313	.466	21.461	18.331
298	4.868	38.297	.000	21.310	10.629
300	4.868	38.297	.000	21.306	10.532
400	4.868	37.757	.506	20.489	6.731
500	4.868	36.865	1.003	20.243	4.504
600	4.868	36.272	1.500	20.014	3.038
700	4.868	35.637	1.996	19.794	2.002
800	4.868	35.000	2.493	19.579	1.233
900	4.868	34.366	2.990	19.364	.642
1000	4.868	33.732	3.487	19.140	.174
1100	4.868	33.098	3.984	18.916	.000
1200	4.868	32.464	4.481	18.692	.000
1300	4.868	31.830	4.978	18.468	.000
1400	4.868	31.196	5.475	18.244	.000
1500	4.868	30.562	5.972	18.020	.000
1600	4.868	29.928	6.469	17.796	.000
1700	4.868	29.294	6.966	17.572	.000
1800	4.868	28.660	7.463	17.348	.000
1900	4.868	28.026	7.960	17.124	.000
2000	4.868	27.392	8.457	16.900	.000
2100	4.868	26.758	8.954	16.676	.000
2200	4.868	26.124	9.451	16.452	.000
2300	4.868	25.490	9.948	16.228	.000
2400	4.868	24.856	10.445	16.004	.000
2500	4.868	24.222	10.942	15.780	.000
2600	4.868	23.588	11.439	15.556	.000
2700	4.868	22.954	11.936	15.332	.000
2800	4.868	22.320	12.433	15.108	.000
2900	4.868	21.686	12.930	14.884	.000
3000	4.868	21.052	13.427	14.660	.000
3100	4.868	20.418	13.924	14.436	.000
3200	4.868	19.784	14.421	14.212	.000
3300	4.868	19.150	14.918	13.988	.000
3400	4.868	18.516	15.415	13.764	.000
3500	4.868	17.882	15.912	13.540	.000
3600	4.868	17.248	16.409	13.316	.000
3700	4.868	16.614	16.906	13.092	.000
3800	4.868	15.980	17.403	12.868	.000
3900	4.868	15.346	17.900	12.644	.000
4000	4.868	14.712	18.397	12.420	.000
4100	4.868	14.078	18.894	12.196	.000
4200	4.868	13.444	19.391	11.972	.000
4300	4.868	12.810	19.888	11.748	.000
4400	4.868	12.176	20.385	11.524	.000
4500	4.868	11.542	20.882	11.300	.000
4600	4.868	10.908	21.379	11.076	.000
4700	4.868	10.274	21.876	10.852	.000
4800	4.868	9.640	22.373	10.628	.000
4900	4.868	9.006	22.870	10.404	.000
5000	4.868	8.372	23.367	10.180	.000
5100	4.868	7.738	23.864	9.956	.000
5200	4.868	7.104	24.361	9.732	.000
5300	4.868	6.470	24.858	9.508	.000
5400	4.868	5.836	25.355	9.284	.000
5500	4.868	5.202	25.852	9.060	.000
5600	4.868	4.568	26.349	8.836	.000
5700	4.868	3.934	26.846	8.612	.000
5800	4.868	3.300	27.343	8.388	.000
5900	4.868	2.666	27.840	8.164	.000
6000	4.868	2.032	28.337	7.940	.000

POTASSIUM, MONATOMIC (K)

(IDEAL GAS)

MOL. WT. = 39.100

$$\Delta H_f^o = 21.522 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 21.31 \pm 0.20 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 38.297 \text{ cal. mole}^{-1} \text{ deg}^{-1}$$

$$\text{Ground State} = {}^2S_{1/2}$$

$$\Delta H_f^o = 21.522 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 38.297 \text{ cal. mole}^{-1} \text{ deg}^{-1}$$

Electronic Levels and Multiplicities

$\bar{\epsilon}$, cm. ⁻¹	g_1	$\bar{\epsilon}$, cm. ⁻¹	g_1	$\bar{\epsilon}$, cm. ⁻¹	g_1
0.00	2	28999.27	2	33185.5	32
12985.17	2	29007.71	4	33578.5	32
13042.88	4	30185.44	10	33815.6	18
21026.58	2	30274.26	2	34059.8	24
21537.00	4	30614.08	32	34335.7	12
21534.70	6	31072.15	6	34472.3	6
24701.43	2	31072.90	12	34568.3	12
24720.17	4	31696.00	10	34662.3	12
27398.14	4	31785.37	2	34753.8	24
27397.10	6	31958.70	54	34859.4	54
27450.69	2	32229.20	6	34985.0	276
28127.85	14	32691.70	26		

Thermodynamic Functions.

Thermodynamic functions were calculated using electronic levels and multiplicities from P. Rieberg [Arkiv. Fysik 10, 583 (1956)] and C. E. Moore [Nat. Bur. Standards Circ. 467 (1949)]. Higher levels were averaged. The results are in excellent agreement with W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards 55, 83 (1955)].

Heat of Formation.

Evans, Munson, and Wagman (loc. cit.) have reviewed the vapor pressure data on potassium. Their calculations were revised slightly for the changes made in the functions for the condensed state. In addition, the recent data of M. M. Makansi, M. Madan, W. A. Selke, and C. P. Bonilla [J. Phys. Chem. 60, 138 (1956)] were considered in selecting the heat of sublimation of 21.31 ± 0.20 kcal. mole⁻¹. A review of the properties of potassium vapor using imperfect gas theory to establish the dimer dissociation energy has recently been published by R. J. Thorn and G. H. Minnow [J. Phys. Chem. 65, 1297 (1961)]. Although the imperfect gas treatment appears to be favored by the experimental data available, this could not be unequivocally established. Unpublished vapor pressure data cited by Thorn and Minnow are in agreement with the values selected here, assuming ideal gas behavior.

Potassium Unipositive Ion (K^+)
(Ideal Gas) At. Wt. = 39.100

K^+

POTASSIUM UNIPosITIVE ION (K^+) (IDEAL GAS) AT. WT. = 39.100

Ground State Configuration $1s^2$
 $\Delta H_f^\circ = 36.919$ cal. deg. $^{-1}$ mole $^{-1}$
 $\Delta H_f^\circ = 121.627$ kcal. mole $^{-1}$
 $\Delta H_f^\circ = 122.696$ kcal. mole $^{-1}$

Electronic Levels and Multiplicities

ϵ , cm. $^{-1}$	g
0	1
167978	52
187837	36
217452	65

Heat of Formation.

The heat of formation at 0°K. was obtained from that of the ideal monatomic potassium gas by adding the enthalpy of ionization, calculated from the ionization limit given by C. E. Moore "Atomic Energy Levels", Natl. Bur. Standards Circ. 467 (1949). This was converted to 298°K. by using the formation equation $K(\text{ref. state}) - e^-(\text{ref. state}) = K^+(\text{monatomic gas})$, thus K^+ involves the difference in enthalpies of two reference states as well as its own enthalpy.

Heat Capacity and Entropy.

These were calculated using the electronic energy levels tabulated above, taken from C. E. Moore, loc. cit.

K^+

Mar. 31, 1965

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	ΔH _f °	ΔF _f °	Log K _p
0					
100	4.968	36.919	0.000	115.010	- 84.301
200	4.968	36.919	0.000	115.010	- 84.301
298	4.968	36.919	0.000	115.010	- 84.301
300	4.968	36.919	0.000	115.010	- 84.301
400	4.968	37.114	0.000	115.010	- 84.301
500	4.968	37.482	1.003	109.804	- 47.993
600	4.968	37.894	1.500	107.174	- 39.036
700	4.968	38.357	2.093	104.468	- 30.079
800	4.968	38.766	2.690	101.781	- 21.077
900	4.968	39.086	3.287	99.031	- 12.074
1000	4.968	39.445	3.887	96.248	- 2.074
1100	4.968	39.783	3.984	94.463	- 18.767
1200	4.968	40.106	4.077	92.687	- 15.016
1300	4.968	40.423	4.171	90.912	- 11.265
1400	4.968	40.693	4.265	89.137	- 7.514
1500	4.968	40.965	4.359	87.362	- 3.763
1600	4.968	41.224	4.453	85.587	- 0.012
1700	4.968	41.471	4.547	83.812	- 3.763
1800	4.968	41.718	4.641	82.037	- 7.514
1900	4.968	41.932	4.735	80.262	- 11.265
2000	4.968	42.148	4.829	78.487	- 15.016
2100	4.968	42.355	4.923	76.712	- 18.767
2200	4.968	42.561	5.017	74.937	- 22.518
2300	4.968	42.768	5.111	73.162	- 26.269
2400	4.968	42.970	5.205	71.387	- 29.020
2500	4.968	43.168	5.299	69.612	- 32.771
2600	4.968	43.366	5.393	67.837	- 36.522
2700	4.968	43.561	5.487	66.062	- 40.273
2800	4.968	43.756	5.581	64.287	- 44.024
2900	4.968	43.946	5.675	62.512	- 47.775
3000	4.968	44.135	5.769	60.737	- 51.526
3100	4.968	44.324	5.863	58.962	- 55.277
3200	4.968	44.513	5.957	57.187	- 59.028
3300	4.968	44.702	6.051	55.412	- 62.779
3400	4.968	44.891	6.145	53.637	- 66.530
3500	4.968	45.080	6.239	51.862	- 70.281
3600	4.968	45.269	6.333	50.087	- 74.032
3700	4.968	45.458	6.427	48.312	- 77.783
3800	4.968	45.647	6.521	46.537	- 81.534
3900	4.968	45.836	6.615	44.762	- 85.285
4000	4.968	46.025	6.709	42.987	- 89.036
4100	4.968	46.214	6.803	41.212	- 92.787
4200	4.968	46.403	6.897	39.437	- 96.538
4300	4.968	46.592	6.991	37.662	- 100.289
4400	4.968	46.781	7.085	35.887	- 104.040
4500	4.968	46.970	7.179	34.112	- 107.791
4600	4.968	47.159	7.273	32.337	- 111.542
4700	4.968	47.348	7.367	30.562	- 115.293
4800	4.968	47.537	7.461	28.787	- 119.044
4900	4.968	47.726	7.555	27.012	- 122.795
5000	4.968	47.915	7.649	25.237	- 126.546
5100	4.968	48.104	7.743	23.462	- 130.297
5200	4.968	48.293	7.837	21.687	- 134.048
5300	4.968	48.482	7.931	19.912	- 137.799
5400	4.968	48.671	8.025	18.137	- 141.550
5500	4.968	48.860	8.119	16.362	- 145.301
5600	4.968	49.049	8.213	14.587	- 149.052
5700	4.968	49.238	8.307	12.812	- 152.803
5800	4.968	49.427	8.401	11.037	- 156.554
5900	4.968	49.616	8.495	9.262	- 160.305
6000	4.968	49.805	8.589	7.487	- 164.056

Potassium Monoxide (KO)
(Ideal Gas)

GFW = 55.1014

T, °K	Cp*	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔG°	Log Kp
0	-0.000	INFINITE	-	2.310	17.420	17.420	INFINITE
100	7.309	44.130	44.207	1.404	17.362	15.469	-33.908
200	7.425	45.502	45.639	0.827	17.174	13.652	-14.919
298	7.450	45.863	46.000	0.000	17.000	11.960	-8.767
300	7.450	45.863	46.000	0.016	16.984	11.929	-8.600
400	7.471	46.320	46.457	0.987	16.198	10.385	-5.672
500	7.496	46.783	46.920	1.971	15.074	8.953	-3.013
600	7.526	47.250	47.387	2.965	13.764	7.569	-2.757
700	7.561	47.720	47.857	3.964	12.304	6.219	-1.942
800	7.599	48.190	48.327	4.964	10.744	4.893	-1.338
900	7.639	48.660	48.797	5.964	9.144	3.593	-0.850
1000	7.680	49.130	49.264	6.964	7.544	2.333	-0.510
1100	7.722	49.600	49.737	7.964	5.944	1.112	-0.420
1200	7.765	50.070	50.207	8.964	4.344	0.269	-0.400
1300	7.809	50.540	50.677	9.964	2.744	-0.577	-0.717
1400	7.854	51.010	51.147	10.964	1.144	-1.421	-1.165
1500	7.900	51.480	51.617	11.964	-0.464	-2.317	-1.680
1600	7.947	51.950	52.087	12.964	-1.864	-3.257	-2.257
1700	7.995	52.420	52.557	13.964	-3.264	-4.237	-2.887
1800	8.044	52.890	53.027	14.964	-4.664	-5.257	-3.567
1900	8.094	53.360	53.497	15.964	-6.064	-6.317	-4.287
2000	8.145	53.830	53.967	16.964	-7.464	-7.417	-5.047
2100	8.197	54.300	54.437	17.964	-8.864	-8.547	-5.847
2200	8.250	54.770	54.907	18.964	-10.264	-9.707	-6.687
2300	8.304	55.240	55.377	19.964	-11.664	-10.897	-7.567
2400	8.359	55.710	55.847	20.964	-13.064	-12.117	-8.487
2500	8.415	56.180	56.317	21.964	-14.464	-13.357	-9.447
2600	8.472	56.650	56.787	22.964	-15.864	-14.627	-10.447
2700	8.530	57.120	57.257	23.964	-17.264	-15.927	-11.487
2800	8.589	57.590	57.727	24.964	-18.664	-17.257	-12.567
2900	8.649	58.060	58.197	25.964	-20.064	-18.617	-13.687
3000	8.710	58.530	58.667	26.964	-21.464	-19.997	-14.847
3100	8.772	59.000	59.137	27.964	-22.864	-21.407	-16.047
3200	8.835	59.470	59.607	28.964	-24.264	-22.847	-17.287
3300	8.899	59.940	59.977	29.964	-25.664	-24.317	-18.567
3400	8.964	60.410	60.447	30.964	-27.064	-25.817	-19.887
3500	9.030	60.880	60.917	31.964	-28.464	-27.337	-21.247
3600	9.096	61.350	61.387	32.964	-29.864	-28.877	-22.647
3700	9.163	61.820	61.857	33.964	-31.264	-30.437	-24.087
3800	9.231	62.290	62.327	34.964	-32.664	-32.017	-25.567
3900	9.300	62.760	62.797	35.964	-34.064	-33.617	-27.087
4000	9.370	63.230	63.267	36.964	-35.464	-35.237	-28.647
4100	9.440	63.700	63.737	37.964	-36.864	-36.877	-30.247
4200	9.511	64.170	64.207	38.964	-38.264	-38.537	-31.887
4300	9.583	64.640	64.677	39.964	-39.664	-40.217	-33.567
4400	9.656	65.110	65.147	40.964	-41.064	-41.917	-35.287
4500	9.730	65.580	65.617	41.964	-42.464	-43.637	-37.047
4600	9.805	66.050	66.087	42.964	-43.864	-45.377	-38.847
4700	9.881	66.520	66.557	43.964	-45.264	-47.137	-40.687
4800	9.958	66.990	67.027	44.964	-46.664	-48.917	-42.567
4900	10.036	67.460	67.497	45.964	-48.064	-50.717	-44.487
5000	10.115	67.930	67.967	46.964	-49.464	-52.537	-46.447
5100	10.195	68.400	68.437	47.964	-50.864	-54.377	-48.447
5200	10.276	68.870	68.907	48.964	-52.264	-56.237	-50.487
5300	10.358	69.340	69.377	49.964	-53.664	-58.117	-52.567
5400	10.441	69.810	69.847	50.964	-55.064	-60.017	-54.687
5500	10.525	70.280	70.317	51.964	-56.464	-61.937	-56.847
5600	10.610	70.750	70.787	52.964	-57.864	-63.877	-59.047
5700	10.696	71.220	71.257	53.964	-59.264	-65.837	-61.287
5800	10.783	71.690	71.727	54.964	-60.664	-67.817	-63.567
5900	10.871	72.160	72.197	55.964	-62.064	-69.817	-65.887
6000	10.960	72.630	72.667	56.964	-63.464	-71.837	-68.247
6100	11.050	73.100	73.137	57.964	-64.864	-73.877	-70.647
6200	11.141	73.570	73.607	58.964	-66.264	-75.937	-73.087
6300	11.233	74.040	74.077	59.964	-67.664	-78.017	-75.567
6400	11.326	74.510	74.547	60.964	-69.064	-80.117	-78.087
6500	11.420	74.980	75.017	61.964	-70.464	-82.237	-80.647
6600	11.515	75.450	75.487	62.964	-71.864	-84.377	-83.247
6700	11.611	75.920	75.957	63.964	-73.264	-86.537	-85.887
6800	11.708	76.390	76.427	64.964	-74.664	-88.717	-88.567
6900	11.806	76.860	76.897	65.964	-76.064	-90.917	-91.287
7000	11.905	77.330	77.367	66.964	-77.464	-93.137	-94.047
7100	12.005	77.800	77.837	67.964	-78.864	-95.377	-96.847
7200	12.106	78.270	78.307	68.964	-80.264	-97.637	-99.687
7300	12.208	78.740	78.777	69.964	-81.664	-99.917	-102.567
7400	12.311	79.210	79.247	70.964	-83.064	-102.217	-105.487
7500	12.415	79.680	79.717	71.964	-84.464	-104.537	-108.447
7600	12.520	80.150	80.187	72.964	-85.864	-106.877	-111.447
7700	12.626	80.620	80.657	73.964	-87.264	-109.237	-114.487
7800	12.733	81.090	81.127	74.964	-88.664	-111.617	-117.567
7900	12.841	81.560	81.597	75.964	-90.064	-114.017	-120.687
8000	12.950	82.030	82.067	76.964	-91.464	-116.437	-123.847
8100	13.060	82.500	82.537	77.964	-92.864	-118.877	-127.047
8200	13.171	82.970	83.007	78.964	-94.264	-121.337	-130.287
8300	13.283	83.440	83.477	79.964	-95.664	-123.817	-133.567
8400	13.396	83.910	83.947	80.964	-97.064	-126.317	-136.887
8500	13.510	84.380	84.417	81.964	-98.464	-128.837	-140.247
8600	13.625	84.850	84.887	82.964	-99.864	-131.377	-143.647
8700	13.741	85.320	85.357	83.964	-101.264	-133.937	-147.087
8800	13.858	85.790	85.827	84.964	-102.664	-136.517	-150.567
8900	13.976	86.260	86.297	85.964	-104.064	-139.117	-154.087
9000	14.095	86.730	86.767	86.964	-105.464	-141.737	-157.647
9100	14.215	87.200	87.237	87.964	-106.864	-144.377	-161.247
9200	14.336	87.670	87.707	88.964	-108.264	-147.037	-164.887
9300	14.458	88.140	88.177	89.964	-109.664	-149.717	-168.567
9400	14.581	88.610	88.647	90.964	-111.064	-152.417	-172.287
9500	14.705	89.080	89.117	91.964	-112.464	-155.137	-176.047
9600	14.830	89.550	89.587	92.964	-113.864	-157.877	-179.847
9700	14.956	90.020	90.057	93.964	-115.264	-160.637	-183.687
9800	15.083	90.490	90.527	94.964	-116.664	-163.417	-187.567
9900	15.211	90.960	90.997	95.964	-118.064	-166.217	-191.487
10000	15.340	91.430	91.467	96.964	-119.464	-169.037	-195.447

Dec. 31, 1962; Dec. 31, 1967

POTASSIUM MONOXIDE (KO)

(IDEAL GAS)

GFW = 55.1014

Ground State Configuration [2]
S^{298.15} = [56.9 ± 0.5] gibbs/mol

ΔH_f⁰ = [17.4 ± 10] kcal/mol

ΔH_f²⁹⁸ = [17.0 ± 10] kcal/mol

Electronic Levels and Quantum Weights

$$\frac{e_i, \text{ cm}^{-1}}{0} = \frac{g_i}{[4]}$$

ω_e = [350] cm⁻¹
ω_ex_e = [2.2] cm⁻¹
B_e = [0.3068] cm⁻¹
α_e = [0.0027] cm⁻¹

σ = 1
r_e = [2.2] Å

Heat of Formation

Brewer and Margrave (1) suggested that the ΔH_f⁰ value for KO(g) from the gaseous ions can be taken as the mean of the corresponding ΔH_f⁰ values for the alkali fluoride and chloride with a maximum uncertainty of 10 kcal/mol. We obtain the values ΔH_f⁰ = -137.84 and -117.7 kcal/mol for the reactions K⁺(g) + F⁻(g) = KF(g) and K⁺(g) + Cl⁻(g) = KCl(g), respectively. Assuming ΔH_f⁰ = -127.83 kcal/mol for the reaction K⁺(g) + O⁻(g) = KO(g), we calculate ΔH_f⁰ (KO, g) = 19.0 kcal/mol with the JANAF auxiliary values for the gaseous ions.

Based on the assumption that D₀(KO) = 1/2(D₀(K₂) + D₀(O₂)), or ΔH_f⁰ = 64.9 kcal/mol for the reaction KO(g) = K(g) + O(g), we evaluate ΔH_f⁰(KO, g) = 15.6 kcal/mol or ΔH_f²⁹⁸(KO, g) = 15.2 kcal/mol.

According to Somayajulu (2), in a sequence of similar diatomic molecules, k_rv_e/D₀ = constant, where k_r = force constant, r_e = equilibrium bond distance and D₀ = dissociation energy. Using r_e = 1.62 Å, D₀ = 77.9 kcal/mol for LiO(g), r_e = 2.2 Å and k_r(KO)/r_e(LiO) = 0.3015, we calculate D₀ = 55 kcal/mol for KO(g), yielding ΔH_f²⁹⁸(KO, g) = 26.1 kcal/mol. The value k_r is derived from the relation k_r = 4π²ν²μ where ν is the vibrational frequency of the diatomic molecule and μ is the reduced mass. The value of ΔH_f²⁹⁸(KO, g) is tentatively adopted as 17 ± 10 kcal/mol.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that for the OH(g) molecule, which has the same number of valence electrons. The values of ω_e and ω_ex_e are estimated by comparison with those for LiF(g) and KF(g). The bond distance is estimated from those for HO(g), HF(g) and KF(g). B_e and α_e are derived from r_e, ω_e and ω_ex_e by the method suggested by Herzberg (3).

References

1. L. Brewer and J. Margrave, J. Phys. Chem. **59**, 421 (1955).
2. G. R. Somayajulu, J. Chem. Phys. **32**, 1541 (1960).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

Potassium Monoxide Uninegative Ion (K⁰⁻)
(Ideal Gas) GFW = 55.10195

T, °K	C _p ^o	S ^o	-(G°-H°)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0							
100							
200	8.577	54.062	54.062	.000	- 31.000	- 35.719	26.192
298							
300	8.592	54.115	54.062	.016	- 33.013	- 35.734	26.032
400	8.685	54.585	54.062	.516	- 35.116	- 35.735	25.812
500	8.765	54.995	54.048	1.268	- 35.032	- 35.737	16.116
600	8.854	55.211	55.777	2.560	- 35.741	- 37.171	13.540
700	9.009	56.159	61.596	3.559	- 36.443	- 37.353	11.682
800	9.251	57.502	67.228	4.465	- 37.149	- 37.434	10.227
900	9.495	59.160	73.984	5.369	- 37.877	- 37.429	8.089
1000	9.719	61.029	80.829	6.279	- 38.575	- 37.383	6.161
1100	9.919	63.070	88.161	7.193	- 39.218	- 37.361	7.165
1200	10.177	65.497	95.739	8.109	- 39.720	- 37.344	6.217
1300	10.403	67.232	102.988	9.024	- 40.123	- 37.326	5.300
1400	10.603	69.209	110.309	9.949	- 40.452	- 37.311	4.465
1500	10.784	71.371	117.653	10.874	- 40.732	- 37.301	4.052
1600	10.948	73.700	125.056	11.800	- 41.000	- 37.295	3.501
1700	11.097	76.118	132.526	12.729	- 41.245	- 37.295	3.011
1800	11.236	78.626	140.065	13.661	- 41.472	- 37.295	2.572
1900	11.367	81.221	147.670	14.594	- 41.683	- 37.295	2.176
2000	11.491	83.896	155.346	15.530	- 41.877	- 37.295	1.816
2100	11.609	86.659	163.096	16.469	- 42.057	- 37.295	1.488
2200	11.721	89.506	170.921	17.410	- 42.223	- 37.295	1.198
2300	11.828	92.436	178.821	18.353	- 42.377	- 37.295	.911
2400	11.931	95.450	186.796	19.300	- 42.520	- 37.295	.665
2500	12.030	98.549	194.846	20.245	- 42.653	- 37.295	.418
2600	12.125	101.724	202.971	21.195	- 42.777	- 37.295	.197
2700	12.217	104.974	211.174	22.147	- 42.892	- 37.295	.008
2800	12.306	108.300	219.456	23.102	- 42.998	- 37.295	.201
2900	12.392	111.704	227.819	24.059	- 43.095	- 37.295	.382
3000	12.475	115.187	236.264	25.017	- 43.183	- 37.295	.553
3100	12.556	118.740	244.792	25.976	- 43.263	- 37.295	.713
3200	12.634	122.364	253.304	26.937	- 43.336	- 37.295	.865
3300	12.709	126.060	261.799	27.897	- 43.402	- 37.295	1.009
3400	12.782	129.828	270.278	28.856	- 43.461	- 37.295	1.145
3500	12.853	133.669	278.743	29.815	- 43.515	- 37.295	1.275
3600	12.922	137.583	287.196	30.774	- 43.565	- 37.295	1.399
3700	12.989	141.570	295.638	31.731	- 43.612	- 37.295	1.518
3800	13.054	145.630	304.071	32.688	- 43.655	- 37.295	1.630
3900	13.118	149.764	312.494	33.644	- 43.695	- 37.295	1.738
4000	13.181	153.974	320.907	34.599	- 43.732	- 37.295	1.842
4100	13.243	158.259	329.310	35.554	- 43.765	- 37.295	1.942
4200	13.304	162.619	337.704	36.507	- 43.795	- 37.295	2.038
4300	13.364	167.054	346.089	37.460	- 43.822	- 37.295	2.130
4400	13.423	171.564	354.464	38.413	- 43.847	- 37.295	2.219
4500	13.481	176.149	362.830	39.367	- 43.869	- 37.295	2.305
4600	13.538	180.800	371.187	40.320	- 43.888	- 37.295	2.388
4700	13.594	185.517	379.534	41.273	- 43.905	- 37.295	2.469
4800	13.649	190.299	387.872	42.226	- 43.919	- 37.295	2.547
4900	13.703	195.146	396.201	43.179	- 43.931	- 37.295	2.623
5000	13.756	200.059	404.521	44.132	- 43.941	- 37.295	2.697
5100	13.808	205.039	412.834	45.085	- 43.949	- 37.295	2.769
5200	13.859	210.084	421.141	46.038	- 43.955	- 37.295	2.839
5300	13.909	215.194	429.442	46.991	- 43.959	- 37.295	2.908
5400	13.958	220.369	437.738	47.944	- 43.962	- 37.295	2.976
5500	14.006	225.609	446.031	48.897	- 43.964	- 37.295	3.043
5600	14.054	230.914	454.321	49.850	- 43.965	- 37.295	3.104
5700	14.101	236.284	462.607	50.803	- 43.965	- 37.295	3.167
5800	14.147	241.719	470.889	51.756	- 43.965	- 37.295	3.229
5900	14.193	247.219	479.167	52.709	- 43.965	- 37.295	3.290
6000	14.238	252.784	487.442	53.662	- 43.965	- 37.295	3.350

Dec. 31, 1967

(IDEAL GAS)

GFW = 55.10195

Ground State Configuration [1²]

S_{298.15} = [54.1 ± 0.3] gibbs/mol

ΔHf^o = [-33 ± 20] kcal/mol

ΔHf^o_{298.15} = [-33 ± 20] kcal/mol

Electronic Levels and Quantum Weights

$$\frac{g_i}{o} \frac{e_i}{\text{cm}^{-1}}$$

$$\omega_e X_e = [2.3] \text{ cm}^{-1}$$

$$\omega_e = [0.0027] \text{ cm}^{-1}$$

$$\sigma = 1$$

$$r_e = [2.2] \text{ Å}$$

Heat of Formation

The electron affinity (E. A.) of K⁰⁻(g) is unavailable, therefore the value of ΔHf^o₂₉₈(K⁰⁻, g) is estimated. Assuming that the enthalpy change (ΔHf^o) of the reaction (1) K⁰⁻(g) = K(g) + O⁺(g) is approximately the average of the ΔHf^o value for the reaction (2) KO(g) = K(g) + O(g) and (3) KF(g) = K(g) + F(g), we obtain ΔHf^o = 1/2(63.5 + 117.3) = 90.4 kcal/mol for reaction (1). However, we compare the ΔHf^o values for the reactions (4) HO(g) = H(g) + O(g), (5) H⁰⁻(g) = H(g) + O⁺(g), and (6) HF(g) = H(g) + F(g), and find that ΔHf^o for reaction (5) is experimentally determined as 109.7 kcal/mol which is about 8 kcal/mol more negative than the average of ΔHf^o values for reactions (4) and (6). Based on this fact we estimated ΔHf^o = 80 kcal/mol for reaction (1), yielding ΔHf^o₂₉₈(K⁰⁻, g) = -33 kcal/mol. The value of ΔHf^o₂₉₈(K⁰⁻, g) is tentatively adopted as -33 ± 20 kcal/mol. The electronic affinity of KO(g) is derived to be 2.2 ± 0.9 eV. The value of E. A. for HO(g) is determined as 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of KF(g) which is isoelectronic with K⁰⁻(g). The values of ω_e, ω_eX_e, and r_e are estimated by comparison with those for KF(g). The values of B_e and α_e are calculated from r_e, ω_e and ω_eX_e using the method recommended by G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc. New York, 1950. The enthalpy at 0°K is -2.30 kcal/mol.

KO

Potassium, Diatomic (K_2)

(Ideal Gas) Mol. Wt. = 78.200

T, °K.	C _p ^o	S ^o - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	49.923	49.923	31.194	2.566	31.194	INFINITE
200	49.923	49.923	31.159	1.773	27.469	60.904
300	49.923	49.923	31.124	1.080	24.388	76.868
400	49.923	49.923	31.089	0.487	21.902	88.980
500	49.923	49.923	31.054	0.094	19.416	98.240
600	49.923	49.923	31.019	0.001	16.930	105.560
700	49.923	49.923	30.984	0.000	14.444	111.840
800	49.923	49.923	30.949	0.000	11.958	117.080
900	49.923	49.923	30.914	0.000	9.472	121.300
1000	49.923	49.923	30.879	0.000	6.986	124.520
1100	49.923	49.923	30.844	0.000	4.500	126.740
1200	49.923	49.923	30.809	0.000	2.014	128.000
1300	49.923	49.923	30.774	0.000	0.000	128.320
1400	49.923	49.923	30.739	0.000	0.000	127.700
1500	49.923	49.923	30.704	0.000	0.000	127.140
1600	49.923	49.923	30.669	0.000	0.000	126.640
1700	49.923	49.923	30.634	0.000	0.000	126.200
1800	49.923	49.923	30.599	0.000	0.000	125.820
1900	49.923	49.923	30.564	0.000	0.000	125.500
2000	49.923	49.923	30.529	0.000	0.000	125.240
2100	49.923	49.923	30.494	0.000	0.000	125.040
2200	49.923	49.923	30.459	0.000	0.000	124.900
2300	49.923	49.923	30.424	0.000	0.000	124.820
2400	49.923	49.923	30.389	0.000	0.000	124.800
2500	49.923	49.923	30.354	0.000	0.000	124.840
2600	49.923	49.923	30.319	0.000	0.000	124.940
2700	49.923	49.923	30.284	0.000	0.000	125.100
2800	49.923	49.923	30.249	0.000	0.000	125.320
2900	49.923	49.923	30.214	0.000	0.000	125.600
3000	49.923	49.923	30.179	0.000	0.000	125.940
3100	49.923	49.923	30.144	0.000	0.000	126.340
3200	49.923	49.923	30.109	0.000	0.000	126.800
3300	49.923	49.923	30.074	0.000	0.000	127.320
3400	49.923	49.923	30.039	0.000	0.000	127.900
3500	49.923	49.923	30.004	0.000	0.000	128.540
3600	49.923	49.923	29.969	0.000	0.000	129.240
3700	49.923	49.923	29.934	0.000	0.000	130.000
3800	49.923	49.923	29.899	0.000	0.000	130.820
3900	49.923	49.923	29.864	0.000	0.000	131.700
4000	49.923	49.923	29.829	0.000	0.000	132.640
4100	49.923	49.923	29.794	0.000	0.000	133.640
4200	49.923	49.923	29.759	0.000	0.000	134.700
4300	49.923	49.923	29.724	0.000	0.000	135.820
4400	49.923	49.923	29.689	0.000	0.000	137.000
4500	49.923	49.923	29.654	0.000	0.000	138.240
4600	49.923	49.923	29.619	0.000	0.000	139.540
4700	49.923	49.923	29.584	0.000	0.000	140.900
4800	49.923	49.923	29.549	0.000	0.000	142.320
4900	49.923	49.923	29.514	0.000	0.000	143.800
5000	49.923	49.923	29.479	0.000	0.000	145.340
5100	49.923	49.923	29.444	0.000	0.000	146.940
5200	49.923	49.923	29.409	0.000	0.000	148.600
5300	49.923	49.923	29.374	0.000	0.000	150.320
5400	49.923	49.923	29.339	0.000	0.000	152.100
5500	49.923	49.923	29.304	0.000	0.000	153.940
5600	49.923	49.923	29.269	0.000	0.000	155.840
5700	49.923	49.923	29.234	0.000	0.000	157.800
5800	49.923	49.923	29.199	0.000	0.000	159.820
5900	49.923	49.923	29.164	0.000	0.000	161.900
6000	49.923	49.923	29.129	0.000	0.000	164.040

December 31, 1961

POTASSIUM, DIATOMIC (K_2)

(IDEAL GAS)

MOL. WT. = 78.200

$\Delta H_f^o = 31.194$ kcal. mole⁻¹
Ground State = 1Σ

$\Delta H_f^o = 30.374 \pm 0.5$ kcal. mole⁻¹
 $S_{298}^o = 59.666$ cal. mole⁻¹ deg.⁻¹

$\omega_e x_e = 92.64$ cm.⁻¹
 $B_e = 0.05622$ cm.⁻¹

$\omega_e x_e = 0.354$ cm.⁻¹
 $\sigma_e = 0.000219$ cm.⁻¹

$D_0 = 8.3 \times 10^{-8}$ cm.⁻¹
 $\sigma^* = 2$

Thermodynamic Functions.

Spectroscopic data are the same as that selected by W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards 55, 63 (1955)]. The calculated functions are in excellent agreement with their results.

Heat of Formation.

The heat of dissociation selected by Evans, Munson, and Wagman (loc. cit.) was used with the previously adopted heat of sublimation of the monomer to derive the heat of formation.

Dipotassium Monoxide (K_2O)
(Crystal) Mol. Wt. = 94.20

T, °K.	C_p	S°	$-(F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K_p
0						
100						
200						
298	20.000	22.500	22.500	-86.800	-76.986	56.430
300	20.050	22.624	22.500	-86.795	-76.925	56.037
400	21.880	28.683	23.314	-87.168	-73.458	40.134
500	22.530	33.634	24.899	-87.300	-69.946	30.572
600	23.280	37.806	26.711	-86.840	-66.516	24.227
700	24.120	41.456	28.593	-86.257	-63.171	19.722
800	24.950	44.766	30.500	-85.571	-59.811	15.722
900	25.780	47.787	32.453	-84.901	-56.741	13.778
1000	26.610	50.593	34.458	-84.092	-53.656	11.726
1100	27.440	53.224	36.500	-83.095	-49.600	9.637
1200	28.270	55.670	38.582	-81.935	-45.582	7.606
1300	29.100	57.930	40.700	-80.630	-41.591	5.632
1400	30.000	60.000	42.850	-79.180	-37.630	3.700
1500	31.000	62.000	45.000	-77.590	-33.700	1.800
1600	32.000	64.000	47.150	-75.860	-29.800	-0.100
1700	33.000	66.000	49.300	-74.000	-25.900	-2.000
1800	34.000	68.000	51.450	-72.000	-22.000	-3.900
1900	35.000	70.000	53.600	-69.860	-18.100	-5.800
2000	36.000	72.000	55.750	-67.590	-14.200	-7.700

June 30, 1963

K_2O

DIPOTASSIUM MONOXIDE (K_2O)
(CRYSTAL)
MOL. WT. = 94.20
 $\Delta H_f^\circ O = \text{Unknown}$
 $\Delta H_f^\circ 298.15 = -86.8 \pm 0.5 \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [22.5 \pm 1.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_d = 1154^\circ K. (600 \text{ mm Hg})$
Heat of Formation.
 $\Delta H_f^\circ 298.15$ was reported by M. Rengada, Ann. Chim. et phys. [8] 14, 540 (1908), based on the measurements of the heats of solution of K(c) and $K_2O(c)$ in H_2O . The same value of $\Delta H_f^\circ 298.15$ was also given by R. de Forcrand, Compt. rend. 159, 991 (1914).
Heat Capacity and Entropy.
Both C_p and $S_{298.15}^\circ$ were estimated by comparison with those of the $Na_2O(c)$.

Temperature of Decomposition.

T_d was taken from, "Data on Chemicals for Ceramic Use", National Research Council Bulletin 118 (1949).

Dipotassium Dioxide (K₂O₂)

(Crystal) Mol. Wt. = 110.20

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0						
100						
200						
298	23.940	27.000	0.000	-118.500	-102.723	75.294
300	23.940	27.000	0.044	-118.495	-102.624	74.758
400	27.400	29.467	2.467	-118.445	-102.467	70.256
500	27.400	29.467	5.208	-118.387	-91.567	60.066
600	28.450	32.022	8.037	-118.265	-86.279	51.425
700	30.581	34.268	11.000	-117.503	-81.005	43.220
800	32.200	36.486	14.125	-116.585	-75.854	35.721
900	33.706	38.683	17.446	-115.484	-70.819	28.726
1000	35.150	40.864	20.987	-114.154	-65.919	16.426
1100	36.548	42.860	24.649	-150.885	-59.089	11.739
1200	37.992	44.850	28.196	-140.000	-50.825	6.256
1300	39.432	46.777	32.067	-140.080	-42.726	7.183
1400	40.868	48.646	36.189	-140.080	-34.846	8.109
1500	42.300	50.460	40.561	-142.529	-27.004	3.934
1600	43.728	52.224	44.542	-140.099	-19.180	2.647
1700	45.152	53.941	48.866	-137.533	-11.916	1.532
1800	46.572	55.615	53.573	-134.831	-4.603	0.559
1900	47.988	57.249	58.401	-131.098	2.554	-0.294
2000	49.400	58.846	63.170	-126.029	8.561	-1.054

Heat of Formation.

ΔH_f⁰ 298.15 was reported by National Bureau of Standards Report 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds," January 1, 1962. The value was based on the measured decomposition pressure of K₂O₂(c) by M. Centner and M. Blumenthal, IX Congr. IUPAC, 3A, 201 (1955).

Heat Capacity and Entropy.

The heat capacities and S_{298.15} were estimated by comparison with those for Na₂O₂(c), Na₂O(c), and K₂O(c).

Temperature of Melting.

T_m was reported by Centner and Blumenthal, loc. cit.

K₂O₂

DIPOTASSIUM DIOXIDE (K₂O₂) (CRYSTAL) MOL. WT. = 110.20

ΔH_f⁰ 0 = Unknown

S° 298.15 = [27.0 ± 1.5] cal. deg.⁻¹ mole⁻¹ ΔH_f⁰ 298.15 = -118.5 ± 1.0 kcal. mole⁻¹

ΔH_m⁰ = Unknown

T_m = 763°K.

K₂O₂

Lithium (Li)

(Reference State) At. Wt. = 6.940

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	1.91411E-1	-	1.105	.000	.000
100	3.193	1.7290	11.222	.996	.000	.000
200	5.156	4.7422	7.474	.546	.000	.000
298	5.887	6.954	.000	.000	.000	.000
300	5.896	6.990	6.954	.011	.000	.000
400	6.509	8.784	7.183	.832	.000	.000
500	7.200	11.115	7.014	2.050	.000	.000
600	7.660	13.216	6.610	2.763	.000	.000
700	8.026	14.294	9.387	3.463	.000	.000
800	8.316	15.218	10.024	4.155	.000	.000
900	8.564	16.032	10.648	4.846	.000	.000
1000	8.782	16.759	11.273	5.538	.000	.000
1100	8.980	17.415	11.757	6.224	.000	.000
1200	9.166	18.013	12.253	6.912	.000	.000
1300	9.346	18.562	12.718	7.594	.000	.000
1400	9.516	19.070	13.154	8.263	.000	.000
1500	9.679	19.541	13.558	8.920	.000	.000
1600	9.830	19.981	13.951	9.647	.000	.000
1700	9.971	20.390	15.100	45.374	.000	.000
1800	10.104	20.775	16.591	45.471	.000	.000
1900	10.230	21.144	18.424	45.568	.000	.000
2000	10.349	21.509	19.166	46.866	.000	.000
2100	10.461	21.872	20.287	47.165	.000	.000
2200	10.567	22.233	21.318	47.465	.000	.000
2300	10.667	22.592	22.269	48.305	.000	.000
2400	10.762	22.949	23.150	48.464	.000	.000
2500	10.852	23.304	23.968	49.372	.000	.000
2600	10.937	23.657	24.732	49.878	.000	.000
2700	11.018	24.007	25.446	50.367	.000	.000
2800	11.094	24.354	26.115	50.898	.000	.000
2900	11.166	24.698	26.745	51.414	.000	.000
3000	11.234	25.039	27.339	51.932	.000	.000
3100	11.298	25.377	27.900	52.456	.000	.000
3200	11.358	25.712	28.432	52.983	.000	.000
3300	11.415	26.044	28.936	53.516	.000	.000
3400	11.469	26.373	29.415	54.054	.000	.000
3500	11.520	26.699	29.872	54.597	.000	.000
3600	11.569	27.022	30.307	55.147	.000	.000
3700	11.615	27.342	30.723	55.703	.000	.000
3800	11.659	27.659	31.122	56.266	.000	.000
3900	11.701	27.973	31.513	56.836	.000	.000
4000	11.741	28.283	31.899	57.414	.000	.000
4100	11.779	28.589	32.221	58.000	.000	.000
4200	11.815	28.891	32.540	58.595	.000	.000
4300	11.849	29.189	32.846	59.194	.000	.000
4400	11.881	29.484	33.140	59.810	.000	.000
4500	11.912	29.775	33.434	60.433	.000	.000
4600	11.941	30.062	33.727	61.066	.000	.000
4700	11.969	30.346	34.018	61.710	.000	.000
4800	11.995	30.626	34.306	62.366	.000	.000
4900	12.020	30.902	34.592	63.035	.000	.000
5000	12.044	31.175	34.877	63.716	.000	.000
5100	12.067	31.445	35.163	64.412	.000	.000
5200	12.089	31.711	35.453	65.123	.000	.000
5300	12.110	31.974	35.745	65.850	.000	.000
5400	12.130	32.234	36.039	66.593	.000	.000
5500	12.149	32.491	36.334	67.353	.000	.000
5600	12.167	32.745	36.630	68.135	.000	.000
5700	12.184	33.000	36.926	68.935	.000	.000
5800	12.200	33.252	37.221	69.757	.000	.000
5900	12.216	33.501	37.516	70.600	.000	.000
6000	12.231	33.747	37.811	71.467	.000	.000

June 30, 1962

LITHIUM (Li)

(REFERENCE STATE)

AT. WT. = 6.940

O° to 453.69°K
453.69° to 1638°K
1638° to 6000°K

Crystal
Liquid
Ideal Monatomic Gas

See crystal, liquid, and ideal monatomic gas for details.

Li

Lithium (Li)

(Crystal) At. Wt. = 6.940

T, °K.	C_p	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	.000	INFINITE	INFINITE	1.105	.000	.000	INFINITE
100	3.193	1.878	1.878	.546	.000	.000	.000
200	5.193	2.727	2.727	.000	.000	.000	.000
298	5.894	3.494	3.494	.000	.000	.000	.000
300	5.894	3.494	.011	.011	.000	.000	.000
400	7.592	6.990	6.990	.632	.000	.000	.000
500	8.775	10.178	10.178	1.330	.000	.000	.000
600	9.761	11.650	11.650	2.055	.000	.000	.000
700	10.562	12.669	12.669	2.782	.000	.000	.000
800	11.202	13.339	13.339	3.508	.000	.000	.000
900	11.702	13.755	13.755	4.234	.000	.000	.000
1000	12.082	14.039	14.039	4.960	.000	.000	.000
1100	12.352	14.282	14.282	5.686	.000	.000	.000
1200	12.532	14.484	14.484	6.413	.000	.000	.000
1300	12.632	14.655	14.655	7.139	.000	.000	.000
1400	12.662	14.795	14.795	7.865	.000	.000	.000
1500	12.682	14.904	14.904	8.591	.000	.000	.000
1600	12.692	15.000	15.000	9.317	.000	.000	.000
1700	12.692	15.084	15.084	10.044	.000	.000	.000
1800	12.692	15.158	15.158	10.770	.000	.000	.000
1900	12.692	15.222	15.222	11.496	.000	.000	.000
2000	12.692	15.277	15.277	12.222	.000	.000	.000

LITHIUM (Li)

(CRYSTAL)

AT. WT. = 6.940

$$\Delta H_f^\circ 298.15 = 0$$

$$\Delta H_f^\circ 298.15 = 38.41 \pm 0.40 \text{ kcal. mole}^{-1} \text{ (Monatomic gas)}$$

$$\Delta H_f^\circ 298.15 = 50.41 \pm 0.30 \text{ kcal. mole}^{-1} \text{ (Diatomic gas)}$$

$$\Delta H_m^\circ = 0.7171 \pm 0.0037 \text{ kcal. mole}^{-1}$$

$$T_m = 453.69^\circ\text{K}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Heat capacities have been reported by the following authors for the temperature ranges indicated: L. M. Roberts, Proc. Phys. Soc. **70**, 744 (1957), 1.5 to 20°K (Li 99.5% pure); F. Simon and R. C. Swain, Z. Phys. Chem. **B28**, 189 (1935), 18° to 300°K; D. L. Martin, Proc. Roy. Soc. **A251**, 444 (1960), 22° to 300°K (Li 99.95% pure); T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. **77**, 2144 (1955), 298° to 1200°K (Li 99.98% pure). Martin, in a series of determinations, found that C_p depended on the thermal history of the sample; a peak at roughly 107°K was ascribed to a martensitic transformation. There is excellent continuity between the results of Roberts and of Martin, while those of Douglas et al. differ by 1% at 300°K and have been smoothly joined. The values of Simon and Swain were not used as they were 5% lower than Martin's and did not show the peak at 107°K; also their values for Al_2O_3 , reported at the same time, are lower than recent measurements. Heat capacities between 1200°K and the normal boiling point were obtained from the heat content equation given by Douglas et al. between 420° and 300°K.

Melting.

Douglas et al. (loc. cit.) report the triple point to be 186.54°C, which is here adopted as the melting point since the densities of solid and liquid lithium at 180°C are not available for calculating dT_m/dP . The same authors give the heat of melting as 432.3 ± 2.2 abs. joule g^{-1} .

Heat of Sublimation.

Lithium vapor contains an appreciable amount of dimer, whose heat of dissociation has been selected by W. H. Evans, R. Jacobson, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bureau of Standards **55**, 83 (1955), from spectroscopic and molecular beam measurements to be $25.76 \pm 0.10 \text{ kcal. mole}^{-1}$ at 0°K. This heat of dissociation, together with the thermodynamic functions calculated in this work, has been used to find the partial pressures of Li(g) and $\text{Li}_2(\text{g})$ from the measured total vapor pressures. H. Hartmann and R. Schneider, Z. anorg. allgem. Chem. **180**, 275 (1929), report values from 1204° to 1353°K, while M. Mancherat, C. Rendus **268**, 499 (1939), reports effusion measurements from 735° to 915°K. Mancherat's pressures are calculated on the assumption of monatomic vapor and have been recalculated to find the true total pressure. Effusion measurements by L. C. Lewis, Z. Physik **69**, 786 (1931), and A. Bogros, C. Rendus **191**, 560 (1930) and Ann. Phys. **17**, 199 (1932), have been disregarded. Mancherat considers them to be inaccurate because of impurities in the lithium used, and Lewis used a doubtful calibration method. Heats of sublimation to monatomic vapor calculated from the vapor pressures of Hartmann and Schneider and of Mancherat agree to within 2% and the average value has been adopted. The heat of sublimation of the dimer was then calculated using this value.

Lithium (Li)

(Liquid) At. Wt. = 6.940

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔH_v°	ΔF_f°	Log K _P
0						
100	7.441	8.113	0.000	.569	.223	.164
200	7.477	8.159	0.014	.572	.221	.161
300	7.530	8.205	0.042	.575	.218	.158
400	7.591	8.251	0.075	.578	.215	.155
500	7.660	8.300	0.114	.582	.212	.152
600	7.738	8.351	0.159	.587	.209	.149
700	7.825	8.405	0.210	.593	.206	.146
800	7.916	8.463	0.268	.600	.203	.143
900	8.014	8.524	0.334	.608	.200	.140
1000	8.120	8.589	0.408	.617	.197	.137
1100	8.234	8.658	0.490	.628	.194	.134
1200	8.356	8.732	0.580	.640	.191	.131
1300	8.486	8.811	0.678	.654	.188	.128
1400	8.624	8.895	0.785	.670	.185	.125
1500	8.770	8.985	0.900	.688	.182	.122
1600	8.924	9.080	1.024	.708	.179	.119
1700	9.086	9.181	1.157	.730	.176	.116
1800	9.256	9.288	1.300	.754	.173	.113
1900	9.434	9.401	1.453	.780	.170	.110
2000	9.620	9.520	1.617	.808	.167	.107
2100	9.814	9.645	1.792	.838	.164	.104
2200	10.016	9.776	1.978	.870	.161	.101
2300	10.226	9.913	2.176	.904	.158	.098
2400	10.444	10.056	2.386	.940	.155	.095
2500	10.670	10.205	2.608	.978	.152	.092
2600	10.904	10.360	2.842	1.018	.149	.089
2700	11.146	10.521	3.088	1.060	.146	.086
2800	11.396	10.688	3.346	1.104	.143	.083
2900	11.654	10.861	3.616	1.150	.140	.080
3000	11.920	11.040	3.898	1.200	.137	.077
3100	12.194	11.225	4.192	1.252	.134	.074
3200	12.476	11.416	4.498	1.306	.131	.071
3300	12.766	11.613	4.816	1.362	.128	.068
3400	13.064	11.816	5.146	1.420	.125	.065
3500	13.370	12.025	5.488	1.480	.122	.062
3600	13.684	12.240	5.842	1.542	.119	.059
3700	14.006	12.461	6.208	1.606	.116	.056
3800	14.336	12.688	6.586	1.672	.113	.053
3900	14.674	12.921	6.976	1.740	.110	.050
4000	15.020	13.160	7.378	1.810	.107	.047

June 30, 1962

Li

LITHIUM (LI)

(LIQUID)

AT. WT. = 6.940

 $\Delta H_f^\circ 298.15 = 0.569 \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = 8.113 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_m^\circ = 0.7171 \pm 0.0035 \text{ kcal. mole}^{-1}$ $T_m = 453.69^\circ \text{K}$ $T_b = 1620^\circ \text{K (equilibrium mixture)}$ $T_b \text{ (monatomic gas)} = 1639^\circ \text{K}$ $\Delta H_v 1639 = 35.16 \text{ kcal. mole}^{-1}$

Heat of Formation.

Obtained from the heat of fusion by adding $H_{453.69}^\circ - H_{298.15}^\circ$ for the solid and subtracting $H_{1639}^\circ - H_{298.15}^\circ$ for the liquid.

Heat Capacity.

The data of T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. 77, 2144 (1955) were taken and extrapolated below T_m and above 1200°K in a reasonable manner.

Entropy.

Back calculated from the entropy of the liquid at the melting point and the extrapolated heat capacity from the melting point to 298°K .

Vaporization.

Lithium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1620°K ; the vapor pressure of the monatomic gas reaches 1 atm. at 1639°K and the heat of vaporization to monatomic gas is $35.16 \text{ kcal. mole}^{-1}$. See also Li(crystal).

Lithium, Monatomic (Li)

(Ideal Gas) At. Wt. = 6.940

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH°	ΔF°	Log K _p
0	.000	INFINITE	1.481	38.034	INFINITE	
100	4.968	27.716	38.412	35.814	76.272	
200	4.968	31.150	38.466	35.811	36.261	
298	4.968	33.183	38.410	35.802	22.431	
300	4.968	33.174	.009	38.408	30.253	22.257
400	4.968	34.603	1.506	38.424	27.952	15.272
500	4.968	35.712	1.003	37.363	25.464	11.130
600	4.968	36.618	1.500	37.147	23.106	8.416
700	4.968	37.384	2.093	36.943	20.781	6.488
800	4.968	38.047	2.693	36.748	18.485	5.050
900	4.968	38.632	3.310	36.554	16.214	3.937
1000	4.968	39.156	3.887	36.361	13.964	3.052
1100	4.968	39.629	4.424	36.170	11.738	2.331
1200	4.968	40.061	4.941	35.979	9.521	1.734
1300	4.968	40.459	5.427	35.789	7.323	1.231
1400	4.968	40.827	5.874	35.601	5.141	.863
1500	4.968	41.170	6.289	35.415	2.972	.513
1600	4.970	41.491	6.668	35.231	.815	.111
1700	4.971	41.792	7.015	35.050	.000	.000
1800	4.974	42.076	7.331	.000	.000	.000
1900	4.978	42.345	7.620	.000	.000	.000
2000	4.983	42.601	7.888	.000	.000	.000
2100	4.991	42.844	8.137	.000	.000	.000
2200	5.001	43.076	8.366	.000	.000	.000
2300	5.014	43.294	8.576	.000	.000	.000
2400	5.031	43.513	8.769	.000	.000	.000
2500	5.051	43.719	8.947	.000	.000	.000
2600	5.074	43.917	9.106	.000	.000	.000
2700	5.102	44.109	9.249	.000	.000	.000
2800	5.134	44.295	9.379	.000	.000	.000
2900	5.169	44.476	9.491	.000	.000	.000
3000	5.209	44.652	9.584	.000	.000	.000
3100	5.253	44.823	9.659	.000	.000	.000
3200	5.300	44.991	9.716	.000	.000	.000
3300	5.352	45.155	9.757	.000	.000	.000
3400	5.407	45.315	9.784	.000	.000	.000
3500	5.466	45.473	9.798	.000	.000	.000
3600	5.529	45.628	9.798	.000	.000	.000
3700	5.596	45.780	9.786	.000	.000	.000
3800	5.666	45.930	9.758	.000	.000	.000
3900	5.740	46.076	9.714	.000	.000	.000
4000	5.818	46.225	9.656	.000	.000	.000
4100	5.901	46.369	9.582	.000	.000	.000
4200	5.987	46.513	9.497	.000	.000	.000
4300	6.079	46.655	9.400	.000	.000	.000
4400	6.175	46.795	9.291	.000	.000	.000
4500	6.277	46.935	9.169	.000	.000	.000
4600	6.385	47.074	9.038	.000	.000	.000
4700	6.500	47.213	8.898	.000	.000	.000
4800	6.621	47.351	8.750	.000	.000	.000
4900	6.750	47.489	8.595	.000	.000	.000
5000	6.886	47.627	8.436	.000	.000	.000
5100	7.032	47.764	8.272	.000	.000	.000
5200	7.176	47.902	8.104	.000	.000	.000
5300	7.329	48.041	7.932	.000	.000	.000
5400	7.523	48.180	7.756	.000	.000	.000
5500	7.707	48.320	7.576	.000	.000	.000
5600	7.901	48.460	7.392	.000	.000	.000
5700	8.104	48.602	7.204	.000	.000	.000
5800	8.322	48.745	6.999	.000	.000	.000
5900	8.569	48.889	6.779	.000	.000	.000
6000	8.747	49.034	6.548	.000	.000	.000

LITHIUM, MONATOMIC (Li)

(IDEAL GAS)

AT. WT. = 6.940

ΔH° = 38.034 kcal. mole⁻¹ΔH° = 38.034 kcal. mole⁻¹Ground State Configuration 2s¹/2S°_{298.15} = 33.143 cal. deg. mole⁻¹

Electronic Levels and Multiplicities

E ₁ cm. ⁻¹	E ₁	E ₁ cm. ⁻¹	E ₁
0	2	36596	50
14904	6	38500	2
27205	2	39623	50
30925	6	41756	70
31283	10	42756	52
35012	2	43319	162

Same as the heat of sublimation to the monatomic gas; see notes on Li(crystal).

Heat of Formation.

Heat Capacity and Entropy.

The energy levels have been taken from C. E. Moore, "National Bureau of Standards Circular 467," U. S. Government Printing Office, Washington (1949) p. 9. Closely spaced levels have been averaged and the appropriate multiplicities assigned to the averages.

Li⁺Lithium Unipositive Ion (Li⁺)

(Ideal Gas) At. Wt. = 6.940

LITHIUM UNIPOSITIVE ION (Li⁺) (IDEAL GAS)

AT. WT. = 6.940

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	keal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0							
100	4.968	31.766	31.766	0.000	164.236	155.351	-113.870
200	4.968	31.766	31.766	0.000	164.236	155.295	-113.127
300	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
400	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
500	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
600	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
700	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
800	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
900	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
1000	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
1100	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
1200	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
1300	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
1400	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
1500	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
1600	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
1700	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
1800	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
1900	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
2000	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
2100	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
2200	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
2300	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
2400	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
2500	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
2600	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
2700	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
2800	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
2900	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
3000	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
3100	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
3200	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
3300	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
3400	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
3500	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
3600	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
3700	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
3800	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
3900	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
4000	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
4100	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
4200	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
4300	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
4400	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
4500	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
4600	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
4700	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
4800	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
4900	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
5000	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
5100	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
5200	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
5300	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
5400	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
5500	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
5600	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
5700	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
5800	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
5900	4.968	31.766	31.766	0.000	164.236	155.256	-113.127
6000	4.968	31.766	31.766	0.000	164.236	155.256	-113.127

Mar. 31, 1965

Ground State Configuration ¹S₀
 $\Delta H_f^0 = 162.379 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = 164.236 \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$E, \text{ cm}^{-1}$ g_i

0

1

432008

16

561765

39

582517

61

595039

125

601915

65

Heat of Formation.

The heat of formation at 0°K. was obtained from that of the ideal monatomic lithium gas by adding the enthalpy of ionization, calculated from the ionization limit given by C. E. Moore "Atomic Energy Levels" Natl. Bur. Standards Circ. 467 (1949). This was converted to 298°K. by using the formation equation $\text{Li}(\text{ref. state}) - e^-(\text{ref. state}) = \text{Li}(\text{monatomic gas})$, thus Li^+ involves the difference in enthalpies of two reference states as well as its own enthalpy.

Heat Capacity and Entropy.

These were calculated using the electronic energy levels tabulated above, taken from C. E. Moore loc. cit.

Li⁺

Lithium Nitride (LiN)

(Ideal Gas) GFW = 20.9457

LiN

LITHIUM NITRIDE (LiN) (IDEAL GAS) OFW = 20.9457

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ - (G^\circ - H^\circ_{298})/T}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0	0.000	INFINITE	70.900	70.900	INFINITE
100	6.000	41.800	60.219	60.219	170.736
200	7.326	46.719	50.446	50.446	83.099
298	7.868	47.744	47.000	76.066	54.291
300	7.857	49.793	49.745	74.028	53.929
400	8.241	52.110	50.056	72.063	38.263
500	8.490	53.777	50.661	70.217	30.692
600	8.655	55.241	51.348	68.501	24.951
700	8.772	56.684	52.045	66.817	20.861
800	8.858	58.062	52.725	65.160	17.801
900	8.928	59.109	53.377	63.527	15.427
1000	8.980	60.052	53.998	61.914	13.251
1100	9.026	60.910	54.588	60.319	11.984
1200	9.067	61.698	55.148	58.739	10.698
1300	9.102	62.425	55.680	57.176	9.612
1400	9.135	63.100	56.187	55.628	8.684
1500	9.165	63.732	56.669	54.090	7.881
1600	9.193	64.324	57.129	52.568	7.180
1700	9.220	64.882	57.569	52.033	6.734
1800	9.246	65.410	57.990	51.507	6.437
1900	9.271	65.911	58.394	51.032	6.171
2000	9.295	66.387	58.761	50.602	5.932
2100	9.318	66.841	59.155	50.212	5.715
2200	9.341	67.275	59.514	50.836	5.518
2300	9.364	67.691	59.860	50.476	5.338
2400	9.386	68.090	60.195	50.136	5.173
2500	9.408	68.473	60.519	49.817	5.022
2600	9.430	68.843	60.829	49.522	4.881
2700	9.451	69.199	61.135	49.252	4.752
2800	9.473	69.543	61.429	49.007	4.632
2900	9.494	69.876	61.713	48.787	4.520
3000	9.515	70.198	62.000	48.590	4.415
3100	9.536	70.510	62.262	48.417	4.317
3200	9.556	70.813	62.524	48.265	4.226
3300	9.577	71.108	62.780	48.131	4.140
3400	9.598	71.394	63.029	48.014	4.059
3500	9.618	71.673	63.272	47.912	3.982
3600	9.639	71.944	63.509	47.824	3.911
3700	9.659	72.208	63.741	47.750	3.843
3800	9.679	72.466	63.967	47.689	3.778
3900	9.700	72.718	64.186	47.638	3.717
4000	9.720	72.963	64.405	47.597	3.660
4100	9.740	73.204	64.616	47.565	3.605
4200	9.760	73.439	64.824	47.538	3.552
4300	9.780	73.669	65.027	47.515	3.502
4400	9.800	73.894	65.226	47.495	3.455
4500	9.821	74.114	65.421	47.478	3.410
4600	9.841	74.330	65.612	47.464	3.367
4700	9.861	74.542	65.800	47.451	3.326
4800	9.881	74.750	65.984	47.440	3.286
4900	9.901	74.954	66.165	47.432	3.246
5000	9.921	75.154	66.343	47.426	3.213
5100	9.941	75.351	66.518	47.423	3.178
5200	9.960	75.544	66.689	47.424	3.145
5300	9.980	75.734	66.858	47.428	3.113
5400	10.000	75.921	67.024	47.434	3.083
5500	10.020	76.104	67.188	47.441	3.054
5600	10.040	76.285	67.349	47.448	3.026
5700	10.060	76.463	67.507	47.456	3.000
5800	10.080	76.638	67.663	47.464	2.974
5900	10.100	76.810	67.816	47.472	2.950
6000	10.120	76.980	67.966	47.480	2.926

Dec. 31, 1960; Sept. 30, 1966; Dec. 31, 1966

Ground State Configuration [3Σ] $\Delta H^\circ_{298.15} = 80 \pm 40 \text{ kcal/mol}$ $\Delta H^\circ_{298.15} = 80 \pm 40 \text{ kcal/mol}$ $S^\circ_{298.15} = [49.7] \text{ gibbs/mol}$

Electronic Levels and Quantum Weights

$$\frac{\epsilon_i, \text{cm}^{-1}}{0} = \frac{E_i}{[3]}$$

$$\omega_{e^*e} = [7] \text{ cm}^{-1}$$

$$\sigma = 1$$

$$\alpha_e = [0.0183] \text{ cm}^{-1}$$

$$r_e = [1.71] \text{ \AA}$$

Heat of Formation.

The adopted $\Delta H^\circ_{298.15}$, $80 \pm 40 \text{ kcal/mol}$, is calculated from the following estimates:

Method	D_0° kcal/mol	$\Delta H^\circ_{298.15}$ kcal/mol
--------	-------------------------	---------------------------------------

76

75

Estimate D_0° from geometric mean for Li_2 and N_2 Estimate from D_0° for series $\text{N}_2(\text{g})$, $\text{CN}(\text{g})$, and $\text{BeN}(\text{g})$ Estimate from D_0° for series $\text{HN}(\text{g})$, $\text{HO}(\text{g})$, $\text{HF}(\text{g})$, $\text{LiF}(\text{g})$ and $\text{LiO}(\text{g})$

J. L. Margrave and P. Sthapitanonda, J. Phys. Chem. 59, 1231 (1955), report estimated dissociation energies in the range 111-178 kcal/mol, based on approximate ionic binding energies calculated from ionic radii for N^- in the range 0.70 to 1.08 $\text{\AA}$.

Heat Capacity and Entropy.

The molecular constants ω_e , r_e and ω_{e^*e} are estimated by comparison with those of CN, CO, BO and LiO. The values of α_e and B_e are calculated from the above constants. The ground state configuration is assumed to be 3Σ by analogy with NH and OH $^+$.

LiN

Point Group C_{2v}
 $S_{298.15}^{\circ} = 58.61$ gibbs/mol
 Ground State Quantum Weight = 1

$$\Delta H_f^{\circ} = [43.5 \pm 10] \text{ kcal/mol}$$

$$\Delta H_{298.15}^{\circ} = [43.0 \pm 10] \text{ kcal/mol}$$

Vibrational Frequencies and Degeneracies

ω , cm^{-1}	
1350 (1)	
330 (1)	
650 (1)	

$$O-N = 1.30 \pm 0.05 \text{ \AA}$$

$$\sigma = 1$$

$$\text{Bond Angle: Li-O-N} = 100 \pm 10^{\circ}$$

$$\text{Product of the Moments of Inertia: } I_A I_B I_C = 2.6523 \times 10^{-116} \text{ g}^3 \text{ cm}^6$$

Heat of Formation

The heat of formation (ΔH_f°) for LiON(g) has not been determined experimentally. The ΔH_{298}° value adopted is calculated from the estimated Li-O and O-N bond energies. The value, $D(\text{Li-O}) = 88$ kcal/mol, is obtained by averaging the bonds in $\text{Li}_2\text{O(g)}$. The value, $D(\text{O-N}) = 69$ kcal/mol, is calculated on the assumption that $D(\text{ClON-O}) = D(\text{N-OH})$. The ΔH_{298}° of LiOH(g) , calculated similarly from bond energies (i.e. $D(\text{Li-O}) = 88$ kcal/mol and $D(\text{O-H}) = 111$ kcal/mol), is 10 kcal/mol more than the measured value. Therefore, we subtract 10 kcal/mol from the ΔH_{298}° of LiON, 53 kcal/mol, estimated from the above bond energies, and arrive at 43 kcal/mol for the adopted value.

Heat Capacity and Entropy

The vibrational frequencies, bond distances and bond angle were obtained from W. L. S. Andrews and G. C. Pimentel, loc. cit. The three principal moments of inertia are: $I_A = 1.2706 \times 10^{-36}$, $I_B = 3.9776 \times 10^{-39}$ and $I_C = 5.2482 \times 10^{-39} \text{ g cm}^2$.

T, K	C_p°	$S^{\circ} - (C_p^{\circ} - H^{\circ}_{298})/T$	$H^{\circ} - H^{\circ}_{298}$	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	-2.701	43.478	43.478	INFINITE
100	8.359	48.573	1.698	43.468	43.468	43.468
200	10.617	58.608	0.000	43.400	43.400	30.587
300	10.633	58.674	0.020	42.906	41.719	30.393
400	11.373	61.839	0.035	42.773	41.328	22.581
500	11.932	64.440	1.284	41.804	41.069	17.951
600	12.351	66.654	3.503	40.945	40.945	16.914
700	12.663	68.583	6.170	41.371	40.855	12.756
800	12.897	70.290	8.748	41.187	40.793	11.144
900	13.075	71.819	11.672	41.009	40.756	9.897
1000	13.212	73.204	14.557	40.833	40.738	8.903
1100	13.319	74.469	17.394	40.658	40.736	8.093
1200	13.404	75.632	20.187	40.482	40.750	7.422
1300	13.473	76.707	22.934	40.306	40.780	6.856
1400	13.529	77.708	25.637	40.129	40.823	6.373
1500	13.575	78.643	28.295	39.951	40.878	5.856
1600	13.613	79.520	30.911	39.773	40.947	5.593
1700	13.645	80.347	33.486	39.586	41.027	5.445
1800	13.672	81.127	36.019	39.393	41.112	5.312
1900	13.696	81.867	38.504	39.196	41.201	5.187
2000	13.716	82.570	40.944	38.996	41.294	5.069
2100	13.733	83.240	43.334	38.793	41.391	4.956
2200	13.749	83.879	45.674	38.586	41.490	4.846
2300	13.762	84.490	47.969	38.376	41.591	4.739
2400	13.774	85.076	50.219	38.163	41.694	4.635
2500	13.784	85.639	52.434	37.947	41.800	4.534
2600	13.793	86.180	54.614	37.728	41.908	4.435
2700	13.802	86.700	56.754	37.504	42.018	4.339
2800	13.810	87.203	58.854	37.276	42.130	4.244
2900	13.816	87.687	60.914	37.044	42.244	4.150
3000	13.822	88.156	62.934	36.808	42.360	4.057
3100	13.828	88.609	64.914	36.568	42.478	3.965
3200	13.833	89.048	66.854	36.324	42.596	3.874
3300	13.837	89.474	68.754	36.076	42.714	3.783
3400	13.841	89.887	70.614	35.824	42.832	3.692
3500	13.845	90.288	72.434	35.568	42.950	3.601
3600	13.849	90.678	74.214	35.308	43.068	3.510
3700	13.852	91.058	75.954	35.044	43.186	3.419
3800	13.855	91.427	77.654	34.776	43.304	3.328
3900	13.858	91.787	79.314	34.504	43.422	3.237
4000	13.860	92.138	80.934	34.228	43.540	3.146
4100	13.863	92.480	82.514	33.948	43.658	3.055
4200	13.865	92.814	84.054	33.664	43.776	2.964
4300	13.867	93.141	85.554	33.376	43.894	2.873
4400	13.869	93.460	87.014	33.084	44.012	2.782
4500	13.871	93.771	88.434	32.788	44.130	2.691
4600	13.872	94.076	89.814	32.488	44.248	2.600
4700	13.874	94.374	91.154	32.184	44.366	2.509
4800	13.875	94.667	92.454	31.876	44.484	2.418
4900	13.877	94.953	93.714	31.564	44.602	2.327
5000	13.878	95.233	94.934	31.248	44.720	2.236
5100	13.879	95.508	96.114	30.928	44.838	2.145
5200	13.880	95.777	97.254	30.604	44.956	2.054
5300	13.882	96.042	98.354	30.276	45.074	1.963
5400	13.883	96.301	99.414	29.944	45.192	1.872
5500	13.884	96.555	100.434	29.608	45.310	1.781
5600	13.885	96.806	101.414	29.268	45.428	1.690
5700	13.885	97.052	102.354	28.924	45.546	1.600
5800	13.886	97.293	103.254	28.576	45.664	1.509
5900	13.887	97.531	104.114	28.224	45.782	1.418
6000	13.888	97.764	104.934	27.868	45.900	1.327

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 45.931

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	0.000	0.000	INFINITE	INFINITE	2.421	23.938	23.938	INFINITE
100	6.160	51.433	60.456	60.456	1.821	23.935	26.259	57.382
200	9.195	57.391	62.176	62.176	1.957	24.436	28.398	31.030
298	10.296	61.270	61.270	0.000	0.000	25.000	30.222	22.152
300	10.315	61.333	61.270	0.019	0.019	25.010	30.254	22.039
400	10.257	62.525	62.525	1.000	1.000	25.000	30.250	14.682
500	11.199	67.026	62.502	62.502	2.262	27.613	33.117	14.475
600	12.415	69.247	63.446	63.446	3.481	28.205	34.161	12.443
700	12.748	71.188	64.416	64.416	4.740	28.741	35.113	10.962
800	12.966	72.906	65.372	65.372	6.027	29.240	35.988	9.831
900	13.123	74.435	66.310	66.310	7.340	29.700	36.802	8.836
1000	13.291	75.840	67.182	67.182	8.658	30.191	37.564	8.029
1100	13.391	77.112	68.028	68.028	9.992	30.660	38.280	7.605
1200	13.469	78.260	68.834	68.834	11.335	31.109	38.953	7.011
1300	13.531	79.361	69.603	69.603	12.685	31.630	39.161	6.247
1400	13.581	80.421	70.341	70.341	14.040	32.128	39.808	5.368
1500	13.622	81.364	71.036	71.036	15.401	32.604	40.436	5.017
1600	13.656	82.164	71.706	71.706	16.765	33.036	41.046	4.514
1700	13.684	82.833	72.347	72.347	18.132	33.493	41.633	3.897
1800	13.708	83.438	72.951	72.951	19.502	33.968	42.199	3.249
1900	13.728	83.981	73.521	73.521	20.872	34.462	42.746	2.581
2000	13.746	84.542	74.118	74.118	22.248	34.904	43.268	2.146
2100	13.761	85.093	74.664	74.664	23.623	35.397	43.777	1.673
2200	13.774	85.554	75.190	75.190	25.000	35.904	44.267	1.242
2300	13.785	86.036	75.698	75.698	26.378	36.416	44.737	0.849
2400	13.795	86.536	76.186	76.186	27.756	36.932	45.186	0.486
2500	13.804	86.936	76.662	76.662	29.137	37.451	45.613	0.156
2600	13.812	87.358	77.121	77.121	30.517	37.966	46.026	0.151
2700	13.819	87.779	77.565	77.565	31.899	38.476	46.426	0.436
2800	13.826	88.192	77.996	77.996	33.281	38.976	46.816	0.701
2900	13.833	88.614	78.414	78.414	34.664	39.476	47.196	0.967
3000	13.837	89.036	78.820	78.820	36.046	39.966	47.571	1.176
3100	13.841	89.458	79.215	79.215	37.431	40.456	47.946	1.394
3200	13.845	89.879	79.600	79.600	38.816	40.946	48.316	1.597
3300	13.849	90.296	79.974	79.974	40.200	41.436	48.686	1.787
3400	13.853	90.714	80.346	80.346	41.586	41.926	49.056	1.967
3500	13.856	91.137	80.709	80.709	42.971	42.416	49.426	2.137
3600	13.859	91.561	81.040	81.040	44.357	42.906	49.796	2.296
3700	13.862	91.974	81.378	81.378	45.743	43.396	50.166	2.450
3800	13.867	92.386	81.706	81.706	47.129	43.886	50.536	2.595
3900	13.871	92.796	82.036	82.036	48.514	44.376	50.906	2.732
4000	13.869	93.206	82.346	82.346	49.902	44.866	51.276	2.863
4100	13.871	93.614	82.655	82.655	51.289	45.356	51.646	2.986
4200	13.873	94.026	82.957	82.957	52.677	45.846	52.016	3.107
4300	13.874	94.436	83.252	83.252	54.064	46.336	52.386	3.222
4400	13.876	94.846	83.546	83.546	55.452	46.826	52.756	3.331
4500	13.878	95.256	83.836	83.836	56.840	47.316	53.126	3.436
4600	13.879	95.661	84.103	84.103	58.227	47.806	53.496	3.537
4700	13.880	96.066	84.375	84.375	59.615	48.296	53.866	3.633
4800	13.882	96.471	84.643	84.643	61.003	48.786	54.236	3.726
4900	13.883	96.876	84.911	84.911	62.391	49.276	54.606	3.816
5000	13.884	97.281	85.163	85.163	63.780	49.766	54.976	3.903
5100	13.885	97.686	85.415	85.415	65.168	50.256	55.346	3.986
5200	13.886	98.091	85.667	85.667	66.557	50.746	55.716	4.067
5300	13.887	98.496	85.919	85.919	67.945	51.236	56.086	4.146
5400	13.888	98.901	86.171	86.171	69.334	51.726	56.456	4.221
5500	13.889	99.306	86.423	86.423	70.723	52.216	56.826	4.295
5600	13.889	99.711	86.675	86.675	72.112	52.706	57.196	4.367
5700	13.890	100.116	86.927	86.927	73.501	53.196	57.566	4.436
5800	13.891	100.521	87.179	87.179	74.890	53.686	57.936	4.504
5900	13.891	100.926	87.431	87.431	76.280	54.176	58.306	4.570
6000	13.892	101.331	87.683	87.683	77.669	54.666	58.676	4.635

June 30, 1961

Lithium Sodium Oxide (LiNaO) (Ideal Gas)

Mol. Wt. = 45.931

 $\Delta H_f^\circ 298.15 = [-25 \pm 30] \text{ kcal. mole}^{-1}$ $\Delta G_f^\circ 298.15 = [61.270] \text{ cal. deg}^{-1} \text{ mole}^{-1}$

Vibrational Levels and Multiplicities

ν , cm ⁻¹	[400] (1)	[1000] (1)	[900] (1)
--------------------------	-----------	------------	-----------

Li-O-Na angle = 105° , O-Li distance = $[1.82] \text{ \AA}$, ONa distance = $[2.21] \text{ \AA}$

Product of moments of inertia, $I_A I_B I_C = [3.179 \times 10^{-115}] \text{ g}^3 \text{ cm}^6$
 $\sigma = 1$

Heat of Formation. Estimated from bond energies derived from heats of formation used in JANAP tables.

Heat Capacity and Entropy. The molecular constants have been estimated by comparison of similar molecules.

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF°	Log K _p
0	.000	INFINITE	INFINITE	2.138	20.105	20.105	INFINITE
100	9.966	50.940	-1.443	20.124	20.124	20.124	-40.045
200	7.522	51.087	-1.736	20.251	16.361	16.361	-17.856
298	7.745	50.945	-1.900	20.251	16.361	16.361	-17.856
300	7.754	50.945	-1.900	20.251	16.361	16.361	-17.856
400	8.142	52.730	-1.810	19.916	12.552	12.552	-10.903
500	8.400	54.577	-1.618	18.961	10.810	10.810	-4.725
600	8.573	56.125	-1.379	18.270	9.204	9.204	-3.352
700	8.694	57.456	-1.141	18.494	7.635	7.635	-2.384
800	8.782	58.623	-0.941	18.777	6.098	6.098	-1.666
900	8.848	59.661	-0.767	18.061	4.589	4.589	-1.114
1000	8.901	60.596	-0.602	17.885	3.104	3.104	-0.678
1100	8.945	61.447	-0.447	17.630	1.660	1.660	-0.326
1200	8.981	62.227	-0.301	17.414	0.195	0.195	-0.036
1300	9.013	62.947	-0.168	17.199	-1.231	-1.231	0.207
1400	9.042	63.614	-0.046	16.985	-2.641	-2.641	0.412
1500	9.067	64.241	0.074	16.772	-4.035	-4.035	0.588
1600	9.091	64.827	0.202	16.561	-5.415	-5.415	0.740
1700	9.113	65.378	0.330	16.354	-6.782	-6.782	0.871
1800	9.133	65.900	0.458	16.152	-8.137	-8.137	0.986
1900	9.153	66.394	0.586	15.954	-9.480	-9.480	1.087
2000	9.172	66.864	0.714	15.762	-10.812	-10.812	1.175
2100	9.190	67.312	0.842	15.577	-12.134	-12.134	1.252
2200	9.207	67.740	0.970	15.399	-13.447	-13.447	1.319
2300	9.224	68.150	1.100	15.224	-14.753	-14.753	1.377
2400	9.241	68.543	1.230	15.052	-16.052	-16.052	1.427
2500	9.257	68.920	1.360	14.884	-17.345	-17.345	1.470
2600	9.273	69.283	1.490	14.721	-18.632	-18.632	1.507
2700	9.289	69.634	1.620	14.562	-19.914	-19.914	1.539
2800	9.305	69.972	1.750	14.407	-21.192	-21.192	1.566
2900	9.320	70.299	1.880	14.256	-22.466	-22.466	1.589
3000	9.335	70.615	2.010	14.108	-23.737	-23.737	1.608
3100	9.350	70.921	2.140	13.964	-25.004	-25.004	1.623
3200	9.365	71.218	2.270	13.824	-26.267	-26.267	1.635
3300	9.380	71.507	2.400	13.688	-27.526	-27.526	1.644
3400	9.395	71.787	2.530	13.556	-28.781	-28.781	1.650
3500	9.410	72.060	2.660	13.428	-30.032	-30.032	1.653
3600	9.424	72.325	2.790	13.303	-31.279	-31.279	1.655
3700	9.439	72.583	2.920	13.181	-32.522	-32.522	1.656
3800	9.453	72.835	3.050	13.062	-33.761	-33.761	1.656
3900	9.468	73.081	3.180	12.946	-35.000	-35.000	1.655
4000	9.482	73.321	3.310	12.833	-36.239	-36.239	1.653
4100	9.497	73.555	3.440	12.723	-37.478	-37.478	1.650
4200	9.511	73.784	3.570	12.616	-38.717	-38.717	1.646
4300	9.525	74.008	3.700	12.512	-39.956	-39.956	1.641
4400	9.540	74.227	3.830	12.410	-41.195	-41.195	1.635
4500	9.554	74.442	3.960	12.310	-42.434	-42.434	1.628
4600	9.568	74.652	4.090	12.212	-43.673	-43.673	1.620
4700	9.582	74.858	4.220	12.116	-44.912	-44.912	1.611
4800	9.596	75.060	4.350	12.022	-46.151	-46.151	1.601
4900	9.610	75.258	4.480	11.930	-47.390	-47.390	1.590
5000	9.624	75.452	4.610	11.840	-48.629	-48.629	1.578
5100	9.639	75.643	4.740	11.752	-49.868	-49.868	1.565
5200	9.653	75.830	4.870	11.666	-51.107	-51.107	1.551
5300	9.667	76.014	5.000	11.582	-52.346	-52.346	1.536
5400	9.681	76.195	5.130	11.500	-53.585	-53.585	1.520
5500	9.695	76.373	5.260	11.419	-54.824	-54.824	1.503
5600	9.709	76.547	5.390	11.340	-56.063	-56.063	1.485
5700	9.723	76.719	5.520	11.262	-57.302	-57.302	1.466
5800	9.737	76.889	5.650	11.186	-58.541	-58.541	1.446
5900	9.751	77.055	5.780	11.112	-59.780	-59.780	1.425
6000	9.765	77.219	5.910	11.040	-61.019	-61.019	1.403

Dec. 31, 1960; Mar. 31, 1961

LITHIUM MONOXIDE (LiO)

(IDEAL GAS)

MOL. WT. = 22.940

Ground State Configuration $[^2\Pi]$
 $\Delta H_f^\circ = 20.1 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 20.1 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 20.1 \pm 5 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{\epsilon_i, \text{ cm}^{-1}}{0} \frac{g_i}{4}$$

$\omega_e x_e = 4.835 \text{ cm}^{-1}$
 $\omega_e = 1.62 \text{ cm}^{-1}$
 $\alpha_e = 0.01288 \text{ cm}^{-1}$

Heat of Formation

D. White, K. S. Sahasrab, D. P. Dever, and D. E. Mann, and M. J. Linevsky, J. Chem. Phys. **39**, 2463 (1963) calculated the heat of formation from their mass spectral data by two different methods.

For the first calculation (a) they combined the slope of the log Π vs $1/T$ curve for LiO^+ with the slope for Li^+ and Li_2O^+ for the reaction $\text{Li}_2\text{O}^+ (\text{g}) \rightarrow \text{Li}^+ (\text{g}) + \text{LiO}^+ (\text{g})$. For the second calculation (b) they assumed a cross section $\sigma_{\text{LiO}^+/\text{Li}_2\text{O}^+} = 1$ and from this they calculated a partial pressure for $\text{LiO}^+ (\text{g})$ at 1500°K and an equilibrium constant for the reaction $\text{Li}_2\text{O}^+ (\text{g}) \rightarrow \text{Li}^+ (\text{g}) + \text{LiO}^+ (\text{g})$. They obtained (a) $\Delta H_f^\circ = 18.3 \text{ kcal. mole}^{-1}$ and (b) $\Delta H_f^\circ = 16.3 \text{ kcal. mole}^{-1}$, and used the average value from the two methods for the heat of formation of $\text{LiO}^+ (\text{g})$. The JANAF heat of formation, $20.1 \pm 5 \text{ kcal. mole}^{-1}$, was obtained in the same way using their data and the present tables i.e. (a) $\Delta H_f^\circ = 22.0 \text{ kcal. mole}^{-1}$ and (b) $\Delta H_f^\circ = 18.3 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy

The molecular constants, $\omega_e x_e$, ω_e , and α_e , were calculated from ω_e and r_e , reported by White et al. The ground state configuration, $^2\Pi$, was estimated by J. S. Gorton, Thiol Chemical Corp., Reaction Motor Division, Denville, N. J., "Thermodynamic Data for Combustion Products", January, 1960, by A. Buchler and J. L. Stauffer, J. Chem. Phys. **39**, 2299 (1963) and by White et al.

Lithium Monoxide Uninegative Ion (LiO⁻)
(Ideal Gas) GFW = 22.93895

T, °K	Cp°	$\frac{\text{gibbs/mol}}{T}$ $S^\circ - (H^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH°	ΔG°	Log Kp
0						
100	7.734	47.593	47.593	-	19.324	14.165
200						
298						
300	7.742	47.641	47.593	-	19.385	14.093
400	8.131	46.925	47.002	-	20.354	11.121
500	8.390	46.769	46.496	-	21.112	9.228
600	8.564	46.315	46.174	-	21.536	7.881
700	8.685	45.645	45.563	-	22.037	6.880
800	8.773	45.810	45.535	-	22.337	6.102
900	8.840	45.848	51.140	-	22.546	5.475
1000	8.893	45.782	51.794	-	22.575	4.956
1100	8.936	45.632	52.378	-	22.462	4.517
1200	8.972	45.411	52.932	-	22.238	4.139
1300	9.004	45.130	53.454	-	22.561	3.810
1400	9.032	45.799	53.959	-	22.540	3.519
1500	9.057	45.423	54.436	-	22.168	3.259
1600	9.080	45.008	54.891	-	22.117	3.025
1700	9.101	45.559	55.324	-	20.556	2.823
1800	9.121	45.080	55.742	-	18.114	2.649
1900	9.141	45.573	56.142	-	15.565	1.900
2000	9.159	46.043	56.525	-	13.150	1.437
2100	9.176	46.490	56.892	-	10.626	1.006
2200	9.193	46.917	57.248	-	8.197	.800
2300	9.210	47.326	57.591	-	5.503	.523
2400	9.226	47.719	57.922	-	2.907	.265
2500	9.242	48.096	58.241	-	.268	.025
2600	9.257	48.458	58.550	-	2.353	.198
2700	9.272	48.800	58.850	-	5.353	.400
2800	9.287	49.145	59.140	-	7.594	.601
2900	9.302	49.472	59.422	-	9.242	.784
3000	9.317	49.787	59.695	-	10.275	.956
3100	9.331	49.993	59.961	-	11.584	1.118
3200	9.346	50.189	60.220	-	12.742	1.278
3300	9.360	50.377	60.472	-	13.514	1.417
3400	9.374	50.557	60.717	-	14.101	1.555
3500	9.389	50.729	60.957	-	14.690	1.686
3600	9.403	50.894	61.190	-	15.286	1.811
3700	9.417	51.051	61.418	-	15.880	1.910
3800	9.430	51.200	61.641	-	16.474	2.004
3900	9.444	51.348	61.854	-	17.067	2.093
4000	9.458	51.497	62.071	-	17.660	2.183
4100	9.472	51.645	62.270	-	18.254	2.267
4200	9.486	51.794	62.463	-	18.848	2.353
4300	9.499	51.943	62.650	-	19.442	2.440
4400	9.513	52.092	62.838	-	20.036	2.528
4500	9.527	52.241	63.029	-	20.630	2.617
4600	9.540	52.390	63.222	-	21.224	2.707
4700	9.554	52.539	63.417	-	21.818	2.798
4800	9.567	52.688	63.612	-	22.412	2.890
4900	9.581	52.837	63.807	-	23.006	2.982
5000	9.594	52.986	64.002	-	23.600	3.075
5100	9.608	53.135	64.197	-	24.194	3.167
5200	9.621	53.284	64.392	-	24.788	3.260
5300	9.635	53.433	64.587	-	25.382	3.353
5400	9.648	53.582	64.782	-	25.976	3.446
5500	9.662	53.731	64.977	-	26.570	3.539
5600	9.675	53.880	65.172	-	27.164	3.632
5700	9.689	54.029	65.367	-	27.758	3.725
5800	9.702	54.178	65.562	-	28.352	3.818
5900	9.715	54.327	65.757	-	28.946	3.911
6000	9.729	54.476	65.952	-	29.540	4.004

Dec. 31, 1967

LITHIUM MONOXIDE UNINEGATIVE ION (LiO⁻) (IDEAL GAS) GFW = 22.93895

Ground State Configuration [1²s]
 $S^\circ_{298.15} = [47.6 \pm 0.3] \text{ gibbs/mol}$
 $\Delta H^\circ_0 = [-16 \pm 15] \text{ kcal/mol}$
 $\Delta H^\circ_{298.15} = [-16 \pm 15] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	$\frac{g_i}{O}$	$\frac{g_i}{[1]}$
$\omega_e X_e = [4.5] \text{ cm}^{-1}$		
$\omega_e = [750] \text{ cm}^{-1}$		
$\sigma = 1$		
$q_e = [0.0121] \text{ cm}^{-1}$		
$r_e = [1.6] \text{ \AA}$		

Heat of Formation

Data on the electron affinity (E.A.) of LiO (g) are unavailable, therefore the value of $\Delta H^\circ_{298}(\text{LiO}^-, \text{g})$ is estimated. We first assume that the enthalpy change (ΔH°_0) of the reaction (1) $\text{LiO}^-(\text{g}) = \text{Li}(\text{g}) + \text{O}^-(\text{g})$ is close to the average of the ΔH°_0 values for the reactions (2) $\text{LiO}(\text{g}) = \text{Li}(\text{g}) + \text{O}(\text{g})$ and (3) $\text{LiF}(\text{g}) = \text{Li}(\text{g}) + \text{F}(\text{g})$. The atom F(g) is isoelectronic with O⁻(g). In other words, the ΔH°_0 for reaction (1) is approximately $1/2(76.91 + 135.84) = 106.4 \text{ kcal/mol}$. Then we compare the ΔH°_0 values for the reactions (4) $\text{HO}(\text{g}) = \text{H}(\text{g}) + \text{O}(\text{g})$, (5) $\text{HO}^-(\text{g}) = \text{H}(\text{g}) + \text{O}^-(\text{g})$, and (6) $\text{HF}(\text{g}) = \text{H}(\text{g}) + \text{F}(\text{g})$, and find that ΔH°_0 for reaction (5) is experimentally determined as 109.7 kcal/mol which is about 8 kcal/mol more negative than the average of ΔH°_0 values for reactions (4) and (6). Based on this fact we estimate $\Delta H^\circ_0 = 96.4 \text{ kcal/mol}$ for reaction (1), yielding $\Delta H^\circ_{298}(\text{LiO}^-, \text{g}) = -15.5 \text{ kcal/mol}$.

Applying the difference in electron affinity between H(g) and Li(g) to OH(g) gives an approximate value, E. A. = 1.7 eV (39.2 kcal/mol) for LiO(g). The value of E. A. for H(g), Li(g) and OH(g) are taken from U. S. Bur. Std. Rept. 8628, Jan. 1, 1965. Based on $\Delta H^\circ_0 = 39.2 \text{ kcal/mol}$ for the reaction $\text{LiO}^-(\text{g}) = \text{LiO}(\text{g}) + e^-(\text{g})$, we derive $\Delta H^\circ_{298} = -19.1 \text{ kcal/mol}$ for $\text{LiO}^-(\text{g})$, which is in reasonable agreement with the above estimated value.

The value of ΔH°_{298} for $\text{LiO}^-(\text{g})$ is tentatively adopted as $-16 \pm 15 \text{ kcal/mol}$. Using this ΔH°_{298} value, we derive E. A. = $1.6 \pm 0.7 \text{ eV}$ for $\text{LiO}(\text{g})$. The electron affinity of OH(g) is $1.8 \pm 0.1 \text{ eV}$.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of LiF(g) which is isoelectronic with LiO⁻(g). The values of ω_e , $\omega_e X_e$ and r_e are estimated by comparison with the observed data for LiF(g). The values of B_e and q_e are calculated from r_e , ω_e and $\omega_e X_e$ by use of the method suggested by G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950. The enthalpy at 0°K is -2.137 kcal/mol .

Lithium, Diatomic (Li_2)
(Ideal Gas) Mol. Wt. = 13.880

T, °K.	C_p^0	$S^0 - (F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K _p
0	7.800	38.310	50.788	50.788	50.788	INFINITE
100	7.309	38.310	50.782	50.782	50.782	INFINITE
200	6.214	43.684	47.828	47.828	47.828	47.885
300	5.182	47.050	47.050	47.050	47.050	29.700
400	4.627	47.104	47.051	47.051	47.051	29.471
500	4.242	47.059	47.052	47.052	47.052	29.471
600	3.922	47.059	47.052	47.052	47.052	29.471
700	3.632	47.059	47.052	47.052	47.052	29.471
800	3.378	47.059	47.052	47.052	47.052	29.471
900	3.152	47.059	47.052	47.052	47.052	29.471
1000	2.954	47.059	47.052	47.052	47.052	29.471
1100	2.784	47.059	47.052	47.052	47.052	29.471
1200	2.644	47.059	47.052	47.052	47.052	29.471
1300	2.534	47.059	47.052	47.052	47.052	29.471
1400	2.444	47.059	47.052	47.052	47.052	29.471
1500	2.374	47.059	47.052	47.052	47.052	29.471
1600	2.324	47.059	47.052	47.052	47.052	29.471
1700	2.284	47.059	47.052	47.052	47.052	29.471
1800	2.254	47.059	47.052	47.052	47.052	29.471
1900	2.234	47.059	47.052	47.052	47.052	29.471
2000	2.224	47.059	47.052	47.052	47.052	29.471
2100	2.224	47.059	47.052	47.052	47.052	29.471
2200	2.224	47.059	47.052	47.052	47.052	29.471
2300	2.224	47.059	47.052	47.052	47.052	29.471
2400	2.224	47.059	47.052	47.052	47.052	29.471
2500	2.224	47.059	47.052	47.052	47.052	29.471
2600	2.224	47.059	47.052	47.052	47.052	29.471
2700	2.224	47.059	47.052	47.052	47.052	29.471
2800	2.224	47.059	47.052	47.052	47.052	29.471
2900	2.224	47.059	47.052	47.052	47.052	29.471
3000	2.224	47.059	47.052	47.052	47.052	29.471
3100	2.224	47.059	47.052	47.052	47.052	29.471
3200	2.224	47.059	47.052	47.052	47.052	29.471
3300	2.224	47.059	47.052	47.052	47.052	29.471
3400	2.224	47.059	47.052	47.052	47.052	29.471
3500	2.224	47.059	47.052	47.052	47.052	29.471
3600	2.224	47.059	47.052	47.052	47.052	29.471
3700	2.224	47.059	47.052	47.052	47.052	29.471
3800	2.224	47.059	47.052	47.052	47.052	29.471
3900	2.224	47.059	47.052	47.052	47.052	29.471
4000	2.224	47.059	47.052	47.052	47.052	29.471
4100	2.267	71.898	62.576	62.576	62.576	3.094
4200	2.299	71.898	62.576	62.576	62.576	3.131
4300	2.342	71.898	62.576	62.576	62.576	3.167
4400	2.384	71.898	62.576	62.576	62.576	3.201
4500	2.426	71.898	62.576	62.576	62.576	3.234
4600	2.469	71.898	62.576	62.576	62.576	3.265
4700	2.511	71.898	62.576	62.576	62.576	3.295
4800	2.554	71.898	62.576	62.576	62.576	3.325
4900	2.597	71.898	62.576	62.576	62.576	3.355
5000	2.640	71.898	62.576	62.576	62.576	3.381
5100	2.683	71.898	62.576	62.576	62.576	3.408
5200	2.726	71.898	62.576	62.576	62.576	3.434
5300	2.769	71.898	62.576	62.576	62.576	3.459
5400	2.812	71.898	62.576	62.576	62.576	3.482
5500	2.855	71.898	62.576	62.576	62.576	3.508
5600	2.898	71.898	62.576	62.576	62.576	3.531
5700	2.941	71.898	62.576	62.576	62.576	3.555
5800	2.984	71.898	62.576	62.576	62.576	3.577
5900	3.027	71.898	62.576	62.576	62.576	3.597
6000	3.070	71.898	62.576	62.576	62.576	3.622

June 9, 1950

Li_2

MOL. WT. = 13.880

(IDEAL GAS)

LITHIUM, DIATOMIC (Li_2)

ΔH_f^0 298.15 = 50.4 $\pm$ 0.9 kcal. mole⁻¹
 $S_{298.15}^0$ = 47.050 cal. deg. mole⁻¹

ΔH_f^0 = 50.298 kcal. mole⁻¹
Ground State Configuration Σ^+

$\omega_e x_e$ = 2.625 cm.⁻¹
 ω_e = 353.59 cm.⁻¹
 α_e = 0.00718 cm.⁻¹
 r_e = 2.673 Å

ω_e = 353.59 cm.⁻¹
 B_e = 0.6812 cm.⁻¹

$\sigma = 2$

Heat of Formation.

Same as the heat of sublimation to the diatomic gas; see notes on Li (crystal).

Heat Capacity and Entropy.

The spectroscopic constants of Li_2 listed by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Co., Inc., New York (1950) have been corrected for the presence of 7.5% Li^6 in naturally occurring lithium, J. R. Stehn and E. P. Clancy, "Chart of the Nuclides", General Electric Co., Schenectady (1956).

$$\Delta H_f^\circ = -141.6 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -143.1 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = [14] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = 9.056 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1843^\circ\text{K.}$$

Heat of Formation.

The selected heat of formation was calculated as follows:

Reaction	ΔH_f° 298.15 kcal. mole ⁻¹	Ref.
(I) $\text{Li}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{LiOH}(\infty \text{H}_2\text{O})$	-31.74 ± 0.08	(a)
(II) $\text{Li}(c) + 1/2 \text{O}_2(g) = \text{LiOH}(\infty \text{H}_2\text{O})$	-121.572 ± 0.019	(b)
(III) $\text{H}_2(g) + 1/2 \text{O}_2(g) = \text{H}_2\text{O}(l)$	-68.3174	(c)
(IV) $2\text{Li}(c) + 1/2 \text{O}_2(g) = \text{Li}_2\text{O}(c)$	-143.1 ± 0.5	(d)
(a) V. P. Kolesov, S. M. Skuratov, and I. D. Zaklin, Russian J. Inorganic Chemistry, 3 , 558 (1959).		
(b) S. R. Gunn and L. G. Green, J. Am. Chem. Soc., 80 , 4782 (1958).		
(c) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties" National Bureau of Standards Circular 500, 1952 (reprinted 1961).		
(d) Reaction (IV) is the sum of $-(I) + 2(II) - (III)$.		

Kolesov, et al. (loc. cit.) measured the enthalpy of the reaction of Li_2O with water at 20° in 5 experiments. The mean ΔH_f° was -31.41 ± 0.08 kcal. This was brought to 298°K by Kolesov using enthalpy data of (a) H. L. Johnston and T. W. Bauer, J. Am. Chem. Soc., **73**, 1119 (1951), for Li_2O , (b) N. S. Osborne, J. P. Stimson, and D. C. Oimings, J. Res. Natl. Bur. Stds. A, **23**, 197 (1939) for H_2O , (c) F. T. Quaker and K. N. Schminke, J. Am. Chem. Soc., **55**, 1013 (1933) for O_2 of $\text{LiOH}(\text{aq})$ and (d) Rossini, et al., (loc. cit.) for aqueous LiOH . In addition to the above, N. N. Beketov, Bull. Acad. Sci. Russ. **32**, 186 (1898) and H. R. Porrand, Compt Rend. **144**, 1403 (1907) have reported experimental heats for Li_2O . Rossini et al. and Johnston and Bauer have reported heats of formation for Li_2O recalculated from older data. L. G. Fasolino, in a Natl. Research Corp. Quarterly Report, July 1 to Sept. 30, 1962, reported a ΔH_f° 298 of -141.1 ± 4.2 kcal. He measured the heat of combustion of $\text{Li}(c)$ in $\text{O}_2(g)$ in a Parr bomb.

Heat Capacity and Entropy.

The low temperature C_p data of H. L. Johnston and T. W. Bauer, (loc. cit.) from 17° to -298°K. was joined graphically to the high temperature C_p data of C. H. Shomate and A. J. Cohen, J. Am. Chem. Soc. **77**, 285 (1955) [425° - 1045°K.] and E. N. Rodgina, and K. A. Gornolukii, Russian J. Phys. Chem. **35**, 898 (1961) [370° - 1125°K.]. The $S_{298.15}^\circ$ was reported by Johnston and Bauer using S_{16}° (extrap.) = $0.003 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

The melting point of Li_2O is uncertain. The selected melting point, 1843°K. , was measured by A. E. van Arkel, E. A. Flood, and M. P. H. Bright, Can. J. Chem. **31**, 1009 (1953). L. Brewer and J. L. Margrave, J. Phys. Chem. **59**, 421 (1955) reported the melting point 1700°K. They also stated that H. van Kester and P. Jaeger, Proc. Roy. Acad. Sci., Amsterdam **16**, 857 (1914) had reported 1700° (1973°K.) as the melting point. The heat of melting, $[14] \text{ kcal. mole}^{-1}$, was estimated by A. Glassner, "The Thermodynamic Properties of the Oxides, Fluorides, and Chlorides to 2500°K. ", Argonne National Laboratory, University of Chicago, ANL-5750, 1957.

Heat of Sublimation.

$\text{Li}_2\text{O}(c)$ vaporizes to $\text{Li}_2\text{O}(g)$, $\text{LiO}(g)$, $\text{Li}_2\text{O}_2(g)$, $\text{Li}(g)$, and $\text{O}_2(g)$ [J. Berkowitz, W. A. Chupka, G. D. Blue and J. L. Margrave, J. Phys. Chem., **63**, 644 (1959); D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, J. Chem. Phys. **39**, 2463 (1963); D. L. Hildenbrand, W. F. Hall, and N. D. Potter, J. Chem. Phys. **39**, 296 (1963); D. L. Hildenbrand, L. P. Theard, W. F. Hall, and N. D. Potter, Fifth Quarterly Technical Report, U-2289, Aeronautics Division of Philco Corporation, 15 September 1963; L. P. Firsova and A. N. Nesmeyanov, Russian J. Phys. Chem., **34**, 1232 (1960). The major species (0° - 1700°K.) are reported to be $\text{Li}_2\text{O}(g)$, $\text{Li}(g)$, and $\text{O}_2(g)$ with lesser amounts of $\text{LiO}(g)$ and $\text{Li}_2\text{O}_2(g)$. Hildenbrand, et al., U-2298, have reported about equal amounts of Li_2O and Li^+ (1300 to 1550°K.) and about $1/30$ th of this amount of LiO^+ . White, et al., calculated ΔH_g° from their mass spectra data. They made two different calculations (a) for $\text{Li}_2\text{O}(c) \rightarrow \text{Li}_2\text{O}(g)$, and (b) for $\text{Li}_2\text{O}(g) \rightarrow 2\text{Li}(g) + 1/2 \text{O}_2(g)$, and found: (a) 102.5 kcal. and (b) 99.0 kcal. They used a weighted average of (a) and (b) and obtained 101.6 kcal. at 0°K. The selected ΔH_g° 298 of $102.3 \pm 3 \text{ kcal.}$ was obtained in the same manner using their data and the present JANAF functions, i.e. (a) 104.2 kcal. and (b) 100.3 kcal. Knudsen-effusion data of White et al., corrected for dissociation pressure with JANAF values gives Li_2O pressures slightly different than those reported. The recalculated pressures give a 3rd law ΔH_g° 298 of 101.7 kcal. for both cells. The corresponding 2nd law values are 85 and 95.5 kcal. for cell 7 and 8. The 3rd law treatment of both sets of data show relatively large trends of ΔH_g° with T which are probably too large to be only due to errors in the functions. (Continued on Lithium Oxide $\text{Li}_2\text{O}(g)$ table)

Lithium Monoxide (Li₂O)

(Crystal) Mol. Wt. = 29.880

T, °K.	C_p	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF°	Log K _p
0	0.000	0.000	INFINITE	-1.732	-141.585	-139.714	INFINITE
100	2.497	8.868	17.447	-1.668	-142.115	-139.714	305.461
200	6.892	4.680	10.125	-1.089	-142.752	-137.172	149.887
298	12.927	9.056	6.056	-0.000	-143.100	-134.348	98.475
300	12.997	9.136	6.056	-0.024	-143.105	-134.294	97.829
400	15.297	13.221	9.597	1.449	-143.277	-131.328	71.751
500	16.630	16.786	10.687	3.050	-144.678	-128.175	56.023
600	17.644	19.905	11.969	4.762	-144.969	-124.824	45.465
700	18.500	22.691	13.105	6.470	-144.950	-121.456	37.922
800	19.240	25.118	14.125	8.165	-144.875	-118.073	31.873
900	19.860	27.154	15.043	9.848	-144.740	-114.789	27.873
1000	20.405	28.654	15.729	11.416	-144.444	-111.480	24.363
1100	21.225	31.648	18.432	14.538	-144.143	-108.198	21.496
1200	22.090	34.519	19.612	16.889	-143.782	-104.746	19.102
1300	22.675	36.969	21.048	18.410	-143.380	-101.102	16.710
1400	23.000	38.525	22.508	20.000	-142.942	-97.536	14.381
1500	23.260	40.018	23.931	21.739	-142.459	-95.382	13.896
1600	23.502	41.435	25.319	23.619	-141.947	-92.658	12.601
1700	23.652	42.793	26.652	25.646	-141.504	-90.514	11.422
1800	23.730	44.076	27.932	27.810	-141.042	-88.536	10.351
1900	23.750	45.316	29.162	29.910	-140.563	-86.689	9.371
2000	24.240	46.504	30.344	32.044	-140.063	-84.989	8.469
2100	24.447	47.646	31.478	34.210	-139.546	-83.516	7.635
2200	24.652	48.743	32.562	36.416	-139.013	-82.167	6.865
2300	24.853	49.808	33.601	38.661	-138.462	-80.942	6.155
2400	25.053	50.835	34.595	40.946	-137.894	-79.842	5.503
2500	25.249	51.835	35.545	43.270	-137.310	-78.859	4.909
2600	25.443	52.793	36.453	45.634	-136.713	-77.992	4.371
2700	25.634	53.713	37.321	48.038	-136.104	-77.243	3.887
2800	25.820	54.598	38.156	50.482	-135.482	-76.610	3.453
2900	26.007	55.438	38.942	52.966	-134.848	-76.000	3.067
3000	26.190	56.222	39.682	55.490	-134.205	-75.413	2.729

Dilithium Monoxide (Li_2O)

(Liquid) Mol. Wt. = 29.880

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	ΔH°_f	ΔF°_f	Log K _p
0						
100	12.927	13.160	13.160	0.000	-132.601	91.330
200	12.987	13.249	13.160	0.074	-132.555	90.734
300	13.027	13.319	13.160	0.174	-132.508	89.953
400	13.057	13.379	13.160	0.294	-132.462	88.984
500	13.077	13.430	13.160	0.434	-132.416	87.834
600	13.087	13.470	13.160	0.594	-132.370	86.504
700	13.087	13.499	13.160	0.774	-132.324	85.004
800	13.077	13.519	13.160	0.974	-132.278	83.334
900	13.057	13.529	13.160	1.194	-132.232	81.504
1000	13.027	13.529	13.160	1.434	-132.186	79.514
1100	12.987	13.519	13.160	1.694	-132.140	77.364
1200	12.927	13.499	13.160	1.974	-132.094	75.054
1300	12.847	13.469	13.160	2.274	-132.048	72.584
1400	12.747	13.429	13.160	2.594	-131.992	69.954
1500	12.627	13.379	13.160	2.934	-131.926	67.164
1600	12.487	13.319	13.160	3.294	-131.850	64.214
1700	12.327	13.249	13.160	3.674	-131.764	61.114
1800	12.147	13.169	13.160	4.074	-131.668	57.864
1900	11.947	13.079	13.160	4.494	-131.562	54.464
2000	11.727	12.979	13.160	4.934	-131.446	50.914
2100	11.487	12.869	13.160	5.394	-131.320	47.214
2200	11.227	12.749	13.160	5.874	-131.184	43.364
2300	10.947	12.619	13.160	6.374	-131.038	39.364
2400	10.647	12.479	13.160	6.894	-130.882	35.214
2500	10.327	12.329	13.160	7.434	-130.716	30.914
2600	9.987	12.169	13.160	7.994	-130.540	26.464
2700	9.627	12.009	13.160	8.574	-130.354	21.864
2800	9.247	11.849	13.160	9.174	-130.158	17.114
2900	8.847	11.679	13.160	9.794	-129.952	12.214
3000	8.427	11.509	13.160	10.434	-129.736	7.164
3100	7.987	11.329	13.160	11.094	-129.510	2.014
3200	7.527	11.149	13.160	11.774	-129.274	-3.234
3300	7.047	10.969	13.160	12.474	-129.028	-8.574
3400	6.547	10.779	13.160	13.194	-128.772	-13.914
3500	6.027	10.579	13.160	13.934	-128.506	-19.254
3600	5.487	10.369	13.160	14.694	-128.230	-24.594
3700	4.927	10.149	13.160	15.474	-127.944	-29.934
3800	4.347	9.919	13.160	16.274	-127.648	-35.274
3900	3.747	9.679	13.160	17.094	-127.342	-40.614
4000	3.127	9.429	13.160	17.934	-127.026	-45.954

Dec. 31, 1960; Mar. 31, 1964

Li_2O

(LIQUID) MOL. WT. = 29.880

DILITHIUM MONOXIDE (Li_2O)

$S^\circ_{298.15} = 13.160 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^\circ_f = -132.129 \text{ kcal. mole}^{-1}$
 $\Delta H^\circ_m = [14] \text{ kcal. mole}^{-1}$
 $\Delta H^\circ_v = \text{Unknown}$

Heat of Formation.

$\Delta H^\circ_f (l)$ was obtained from $\Delta H^\circ_f (c)$ by adding ΔH_m and the difference between $H_{1843-H_{298}}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated at 8 cal. deg.⁻¹ g. atom⁻¹ from comparisons with similar compounds and from Kopp's rule. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See melting data given on the Li_2O crystal table.

Vaporization Data.

The vapor over $\text{Li}_2\text{O}(c)$ at 1700°K. is composed of $\text{Li}_2\text{O}(g)$, $\text{Li}(g)$, $\text{O}_2(g)$, $\text{LiO}(g)$, and $\text{Li}_2\text{O}_2(g)$. Thus a boiling point becomes almost meaningless. The value, 2836°K. listed above is the temperature at which the free energy of $\text{Li}_2\text{O}(g)$ and the free energy of $\text{Li}_2\text{O}(l)$ are equal. L. Brewer, Chem. Rev. 52, (1953) estimated a boiling point of 2600°K.

Li_2O

Dilithium Monoxide (Li₂O)
(Ideal Gas)

Mol. Wt. = 29.880

DILITHIUM MONOXIDE (Li₂O) (IDEAL GAS)

MOL. WT. = 29.880



T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈)/T	H ^o - H ₂₉₈	ΔH _f ^o	Log K _p
0	∞	∞	∞	∞	∞
100	9.825	42.987	2.586	39.636	INFINITE
200	10.946	50.184	5.790	41.284	90.221
298	11.893	54.732	8.000	43.105	47.101
300	11.910	54.846	8.022	43.105	32.813
400	12.879	61.250	11.135	44.797	32.633
500	13.287	64.256	14.537	47.700	20.836
600	13.682	63.710	17.907	48.762	17.761
700	13.957	65.841	21.285	49.754	15.533
800	14.232	67.718	24.608	50.689	13.847
900	14.507	69.384	27.874	51.527	12.524
1000	14.771	70.905	31.132	52.274	11.457
1100	14.983	72.282	34.384	53.236	10.576
1200	15.157	73.545	37.631	54.482	9.837
1300	15.308	74.701	40.866	56.079	9.207
1400	15.438	75.767	44.091	57.981	8.683
1500	15.551	76.760	47.306	60.193	8.187
1600	15.658	77.753	50.515	62.624	7.768
1700	15.721	78.645	53.717	65.273	7.404
1800	15.760	79.487	56.914	68.048	7.054
1900	15.788	80.284	60.106	70.941	6.721
2000	15.811	81.042	63.294	73.950	6.406
2100	15.830	81.756	66.477	77.075	6.109
2200	15.845	82.431	69.645	80.316	5.828
2300	15.857	83.067	72.799	83.672	5.561
2400	15.866	83.674	75.939	87.144	5.307
2500	15.872	84.251	79.068	90.732	5.064
2600	15.875	84.797	82.186	94.437	4.832
2700	15.876	85.312	85.294	98.260	4.610
2800	15.876	85.797	88.389	102.199	4.397
2900	15.875	86.251	91.468	106.352	4.193
3000	15.872	86.674	94.521	110.718	3.997
3100	15.867	87.066	97.558	115.294	3.817
3200	15.860	87.436	100.568	120.080	3.651
3300	15.851	87.783	103.551	125.074	3.497
3400	15.840	88.107	106.516	130.284	3.354
3500	15.828	88.407	109.454	135.706	3.222
3600	15.814	88.683	112.366	141.338	3.099
3700	15.798	88.935	115.251	147.180	2.984
3800	15.780	89.163	118.109	153.231	2.876
3900	15.760	89.367	120.941	159.491	2.774
4000	15.738	89.547	123.746	165.959	2.677
4100	15.714	89.701	126.524	172.634	2.584
4200	15.688	89.830	129.274	179.514	2.495
4300	15.660	89.935	132.004	186.697	2.410
4400	15.630	89.997	134.714	194.184	2.328
4500	15.598	90.017	137.404	201.974	2.250
4600	15.564	90.004	140.074	210.066	2.176
4700	15.528	90.000	142.724	218.461	2.106
4800	15.490	90.000	145.354	227.159	2.040
4900	15.450	90.000	147.964	236.161	1.977
5000	15.408	90.000	150.554	245.466	1.917
5100	15.364	90.000	153.124	255.074	1.860
5200	15.318	90.000	155.674	264.984	1.806
5300	15.270	90.000	158.204	275.194	1.754
5400	15.220	90.000	160.714	285.704	1.704
5500	15.168	90.000	163.204	296.514	1.656
5600	15.114	90.000	165.674	307.624	1.610
5700	15.058	90.000	168.124	319.034	1.566
5800	14.999	90.000	170.554	330.744	1.524
5900	14.938	90.000	172.964	342.754	1.483
6000	14.875	90.000	175.354	355.064	1.443

Dec. 31, 1960 Mar. 31, 1964

Point Group P_{∞h}
 $\Delta H_f^o = -39.6 \pm 2.5$ kcal. mole⁻¹
 ΔH_f^o 298.15 = -39.9 ± 2.5 kcal. mole⁻¹
 $S^o_{298.15} = 54.732$ cal. deg.⁻¹ mole⁻¹
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies
 $\omega, \text{ cm.}^{-1}$

[760] (1)
 [140] (2)
 987 (1)

Bond Distance: Li-O = [1.59] Å
 Bond Angle: Li-O-Li = 180°
 Rotational Constant: B₀ = 0.48045 cm.⁻¹
 $\sigma = 2$

Heat of Formation.

The heat of formation was calculated from the heat of formation of the crystal and the heat of sublimation.

Heat Capacity and Entropy.

D. White, K. S. Seshairi, and D. F. Dever, and D. E. Mann, and M. J. Linevsky, *J. Chem. Phys.* 39, 2463 (1963) made an estimate of the bond distance Li-O = 1.59 Å based on an analysis of their vibrational spectra. They found that Li₂O was a linear molecule. A. Buchler and J. L. Stauffer, *J. Chem. Phys.* 39, 2299 (1963) have shown from electric deflection experiments that Li₂O is very probably linear. They also report from the results of an effusion experiment evidence that the electron diffraction data and Li-O bond distance, 1.82 Å reported by F. A. Akishin and N. G. Rambidi, *Dokl. Akad. Nauk. SSSR* 118, 973 (1958) [English Translation, *Proc. Acad. Sci. USSR, Phys. Chem. Sect.* 118, 83 (1958)] are for Mo-O in Li₂MoO₄ rather than for Li-O in Li₂O. Buchler and Stauffer (loc. cit.) estimate an Li-O distance of 1.55 Å. White, et al., (loc. cit.) have estimated the vibrational frequencies $\nu_1 = [760]$ cm.⁻¹ and $\nu_2 = [140]$ cm.⁻¹ and assigned $\nu_3 = 987$ cm.⁻¹ from their infrared matrix spectra. The principal moments of inertia calculated from the molecular constants are: I_A = 0, and I_B = I_C = 5.8256 × 10⁻³⁹ g. cm.².

Heat of Sublimation (continued from Li₂O(c) table).

A sample of LiAlO₂ was melted 7 times in argon in an arc-image furnace, H. Prophet, "Melting Point of Lithium Aluminate", ARPA-1-150, Dow Chemical Co., Mar. 9, 1961. The sample decomposed on fusion and successive melting points approached that of Al₂O₃. The residue was found to be 95% Al₂O₃ and 5% LiAl₂O₄. The sample and residue were characterized by X-ray diffraction. A reasonable assumption from this is that $\Delta F^o_{298}(3000^\circ\text{K}) = 0$ for 2LiAlO₂(c) = Al₂O₃(c) + Li₂O(g). From this ΔF^o , a ΔH^o_{298} for Li₂O of 50 kcal. was calculated. A vapor pressure study of the molecular species over the decomposing LiAlO₂ might help resolve the discrepancies in lithium oxide ΔH^o_f values.



Lithium Dioxide (Li_2O_2)
(Crystal) Mol. Wt. = 45.880



MOL. WT. = 45.880

(CRYSTAL)

LITHIUM DIOXIDE (Li_2O_2)

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	keal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0						
200	16.880	13.500	+0.00	-151.200	-136.468	100.029
298						
300	16.950	13.605	+0.31	-151.206	-136.477	99.346
400	19.760	18.911	1.4205	-151.305	-131.614	71.798
500	21.703	23.536	3.059	-152.756	-126.288	55.108
600	23.290	27.038	5.211	-152.725	-120.930	46.269
700	24.770	31.036	8.612	-152.502	-115.718	39.127
800	26.070	34.726	12.086	-152.144	-110.487	30.192
900	27.350	37.871	16.512	-151.668	-105.307	25.571
1000	28.610	40.818	21.196	-151.077	-100.185	21.894
1100	29.850	43.603	25.895	-150.369	-95.130	18.000
1200	31.070	46.253	30.591	-149.567	-90.144	16.617
1300	32.261	48.787	35.287	-148.604	-85.232	14.328
1400	33.438	51.221	39.983	-147.558	-80.365	12.550
1500	34.600	53.568	44.679	-146.393	-75.538	11.020
1600	35.748	55.847	49.376	-145.115	-70.960	9.692
1700	36.883	58.039	54.074	-143.819	-63.712	8.190
1800	38.003	60.179	58.772	-142.508	-54.932	6.669
1900	39.108	62.263	63.470	-141.196	-46.260	5.321
2000	40.200	64.297	68.168	-139.822	-37.699	4.119

ΔH_f° = Unknown

S_{298.15}° = [13.5 ± 1.0] cal. deg.⁻¹ mole⁻¹

ΔH_f° 298.15 = -151.2 ± 2.0 kcal. mole⁻¹

T_d = 468°K.

Heat of Formation.

ΔH_f° 298.15 was reported by R. de Forcrand, Compt. rend. 130, 1465 (1900), based on the measured heats of the reactions of $\text{Li}_2\text{O}_2(\text{c})$ with $\text{HCl}(\text{aq.})$ and $\text{LiOH}(\text{aq.})$ with $\text{H}_2\text{O}_2(\text{aq.})$.

Heat Capacity and Entropy.

Both C_p and S_{298.15} were estimated by comparison with those of the $\text{Na}_2\text{O}_2(\text{c})$, respectively.

Temperature of Decomposition.

T_d was reported to be about 300°C. by N. M. Wiederhorn, N. F. Surprenant, and A. J. Leffler, "Research on New Methods of Separation of Air into O₂ and N₂ Components," C-63025, First-Quarterly Progress Report, September 1961, Arthur D. Little, Inc. The value adopted was reported by Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use", June, 1949, obtained from M. Centnerzwer and M. Elmenthal, Bull. intern. acad. polonaise, Classe. sci. math. nat., A 499 (1933).

June 30, 1963; Sept. 30, 1963



Dilithium Dioxide (Li_2O_2)
(Ideal Gas) Mol. Wt. = 45.880

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	INFINITE
100	10.400	50.000	3,789	57,504	57,504	INFINITE
200	10.405	49.814	7,412	57,493	57,493	126.935
300	11.386	50.000	11,035	57,480	57,480	126.935
400	11.383	65.357	14,658	57,467	57,467	43.048
500	17.409	65.357	18,281	57,454	57,454	43.048
600	17.409	65.357	21,904	57,441	57,441	43.048
700	17.409	65.357	25,527	57,428	57,428	43.048
800	17.409	65.357	29,150	57,415	57,415	43.048
900	17.409	65.357	32,773	57,402	57,402	43.048
1000	17.409	65.357	36,396	57,389	57,389	43.048
1100	17.409	65.357	39,996	57,376	57,376	43.048
1200	17.409	65.357	43,596	57,363	57,363	43.048
1300	17.409	65.357	47,196	57,350	57,350	43.048
1400	17.409	65.357	50,796	57,337	57,337	43.048
1500	17.409	65.357	54,396	57,324	57,324	43.048
1600	17.409	65.357	57,996	57,311	57,311	43.048
1700	17.409	65.357	61,596	57,298	57,298	43.048
1800	17.409	65.357	65,196	57,285	57,285	43.048
1900	17.409	65.357	68,796	57,272	57,272	43.048
2000	17.409	65.357	72,396	57,259	57,259	43.048
2100	17.409	65.357	75,996	57,246	57,246	43.048
2200	17.409	65.357	79,596	57,233	57,233	43.048
2300	17.409	65.357	83,196	57,220	57,220	43.048
2400	17.409	65.357	86,796	57,207	57,207	43.048
2500	17.409	65.357	90,396	57,194	57,194	43.048
2600	17.409	65.357	93,996	57,181	57,181	43.048
2700	17.409	65.357	97,596	57,168	57,168	43.048
2800	17.409	65.357	101,196	57,155	57,155	43.048
2900	17.409	65.357	104,796	57,142	57,142	43.048
3000	17.409	65.357	108,396	57,129	57,129	43.048
3100	17.409	65.357	111,996	57,116	57,116	43.048
3200	17.409	65.357	115,596	57,103	57,103	43.048
3300	17.409	65.357	119,196	57,090	57,090	43.048
3400	17.409	65.357	122,796	57,077	57,077	43.048
3500	17.409	65.357	126,396	57,064	57,064	43.048
3600	17.409	65.357	129,996	57,051	57,051	43.048
3700	17.409	65.357	133,596	57,038	57,038	43.048
3800	17.409	65.357	137,196	57,025	57,025	43.048
3900	17.409	65.357	140,796	57,012	57,012	43.048
4000	17.409	65.357	144,396	57,000	57,000	43.048
4100	17.409	65.357	147,996	56,987	56,987	43.048
4200	17.409	65.357	151,596	56,974	56,974	43.048
4300	17.409	65.357	155,196	56,961	56,961	43.048
4400	17.409	65.357	158,796	56,948	56,948	43.048
4500	17.409	65.357	162,396	56,935	56,935	43.048
4600	17.409	65.357	165,996	56,922	56,922	43.048
4700	17.409	65.357	169,596	56,909	56,909	43.048
4800	17.409	65.357	173,196	56,896	56,896	43.048
4900	17.409	65.357	176,796	56,883	56,883	43.048
5000	17.409	65.357	180,396	56,870	56,870	43.048
5100	17.409	65.357	183,996	56,857	56,857	43.048
5200	17.409	65.357	187,596	56,844	56,844	43.048
5300	17.409	65.357	191,196	56,831	56,831	43.048
5400	17.409	65.357	194,796	56,818	56,818	43.048
5500	17.409	65.357	198,396	56,805	56,805	43.048
5600	17.409	65.357	201,996	56,792	56,792	43.048
5700	17.409	65.357	205,596	56,779	56,779	43.048
5800	17.409	65.357	209,196	56,766	56,766	43.048
5900	17.409	65.357	212,796	56,753	56,753	43.048
6000	17.409	65.357	216,396	56,740	56,740	43.048

Mar. 31, 1964

DILITHIUM DIOXIDE (Li_2O_2) (IDEAL GAS)

MOL. WT. = 45.880

Point Group [D_{2h}]
 $S_{298.15}^\circ = [65.357] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = [-57.5 \pm 6] \text{ kcal. mole}^{-1}$
 $\Delta G_f^\circ = [-58.0 \pm 6] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
[400] (1)	[270] (1)
[250] (1)	[330] (1)
[300] (1)	[530] (1)

Bond Distance: Li-O = [1.90] Å

Bond Angle: O-Li-O = [116]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.66304 \times 10^{-115}] \text{ g.}^3 \text{ cm.}^6$

$\sigma = 4$

Heat of Formation.

The heat of formation, -58 kcal., was calculated from an equilibrium constant for the reaction $1/2 \text{ O}_2(\text{g}) + \text{Li}_2\text{O}(\text{g}) \rightarrow \text{Li}_2\text{O}_2(\text{g})$ and the current JANAP functions. The equilibrium constant, 0.39, was estimated by D. White, K. S. Seshadri, D. F. Dever, and D. E. Mann, and M. J. Linevsky, J. Chem. Phys. **39**, 2463 (1963), from their mass spectrometric data.

Heat Capacity and Entropy.

White, et al., (loc. cit.), from their spectral data have assigned two observed frequencies and estimated the remaining frequencies using the ionic model calculations of J. Berkowitz, J. Chem. Phys. **23**, 1386 (1958); **32**, 1519 (1960) as a guide. They proposed a planar rhombic structure of D_{2h} symmetry, similar to the alkali halide dimers, for the previously undetected Li_2O_2 molecule, and estimated the angle, 116°, and bond distance, 1.90 Å, from their matrix spectra. The principal moments calculated from these molecular constants are: $I_A = 13.793 \times 10^{-39} \text{ g. cm.}^2$, $I_B = 2.356 \times 10^{-39}$, and $I_C = 16.129 \times 10^{-39} \text{ g. cm.}^2$.

Li_2O_2

Li_2O_2

T, °K	Cp ^b	$\mu\text{Btu}/\text{mol}$ S ^c	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH°	ΔG°	Log Kp
0	.300	.000	INFINITE	-3.479	-391.627	-391.627	INFINITE
100	6.513	2.934	35.600	-3.267	-392.756	-392.756	844.476
200	17.217	10.746	21.191	-2.064	-393.748	-393.748	194.476
298	24.336	15.151	15.151	.000	-394.250	-394.250	973.002
300	24.142	15.140	15.191	.045	-394.245	-372.424	271.311
400	28.400	26.019	20.196	2.689	-394.417	-365.117	159.491
500	30.547	33.498	22.215	5.642	-395.941	-357.635	150.322
600	32.100	39.209	24.542	9.776	-395.933	-349.972	127.877
700	33.377	44.254	27.019	12.051	-395.810	-342.321	106.877
800	34.520	48.758	29.479	15.447	-395.595	-334.667	91.435
900	35.508	52.912	31.857	19.950	-395.307	-327.009	74.430
1000	36.401	56.700	34.154	24.546	-394.956	-319.534	60.435
1100	37.146	60.204	36.345	29.224	-394.545	-312.015	48.992
1200	37.800	63.473	38.449	33.960	-394.084	-304.536	39.463
1300	38.450	66.532	40.530	38.693	-393.574	-297.020	29.946
1400	39.183	69.412	42.591	43.427	-393.018	-289.502	20.428
1500	39.800	72.137	44.639	48.163	-392.415	-282.031	11.136
1600	40.400	74.735	46.694	52.896	-391.768	-274.512	3.565
1700	40.990	77.192	48.746	57.619	-391.144	-266.974	34.065
1800	41.560	79.551	50.813	62.346	-390.546	-259.426	30.699
1900	42.110	81.813	52.871	67.070	-389.976	-251.868	27.676
2000	42.640	83.986	54.915	71.793	-389.435	-244.295	24.972
2100	43.160	86.079	56.945	76.516	-388.921	-236.715	22.532
2200	43.680	88.098	58.972	81.239	-388.432	-229.126	20.320
2300	44.190	90.048	60.998	85.962	-387.967	-221.532	18.306
2400	44.690	91.935	62.998	90.685	-387.526	-213.935	16.465
2500	45.000	93.763	64.995	95.408	-387.109	-206.332	14.777

$\Delta H^\circ_0 = -391.83 \pm 1.0 \text{ kcal/mol}$
 $\Delta H^\circ_{298.15} = -394.24 \pm 1.0 \text{ kcal/mol}$
 $\Delta H^\circ = 6.7 \pm 0.5 \text{ kcal/mol}$

$S^\circ_{298.15} = 19.19 \pm 0.3 \text{ gibbs/mol}$

$T_m = 1474 \pm 1^\circ \text{K}$

Heat of Formation

The heats of solution of $\text{LiCl}(\text{c})$, $\text{Li}_2\text{SO}_4(\text{c})$, $\text{SiO}_2(\text{quartz})$ and $\text{Li}_2\text{SiO}_3(\text{c})$ in 20 per cent hydrofluoric acid at 74.7°C were measured by F. C. Kraeck, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 89 (1953). The authors derived two values of $\Delta H^\circ_{\text{soln}}$ of $\text{Li}_2\text{O}(\text{c})$ from those of $\text{LiCl}(\text{c})$ and $\text{Li}_2\text{SO}_4(\text{c})$, presumably employing auxiliary data from U. S. Natl. Bur. Std. Circ. 500, 1952. We recalculate $\Delta H^\circ_{\text{soln}}$ of $\text{Li}_2\text{O}(\text{c})$ as -59.74 (chloride scheme, originally -59.36) and -59.83 kcal/mol (sulfate scheme, originally -60.86), using recent ΔH°_{298} values for $\text{LiCl}(\text{c})$, $\text{Li}_2\text{SO}_4(\text{c})$, $\text{HCl}(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, and $\text{Li}_2\text{O}(\text{c})$. The corresponding enthalpy changes, ΔH°_{298} , for the reaction $\text{Li}_2\text{O}(\text{c}) + \text{SiO}_2(\text{quartz}) = \text{Li}_2\text{SiO}_3(\text{c})$ are derived as -33.08 and -34.17 kcal/mol. Adopting the weighted average $\Delta H^\circ_{298} = -33.44$ kcal/mol with $\Delta H^\circ_{298}(\text{Li}_2\text{O}, \text{c}) = -143.1$ kcal/mol and $\Delta H^\circ_{298}(\text{SiO}_2, \text{quartz}) = -217.7$ kcal/mol, we obtain $\Delta H^\circ_{298} = -394.24$ kcal/mol for $\text{Li}_2\text{SiO}_3(\text{c})$. This $\Delta H^\circ_{298}(\text{Li}_2\text{SiO}_3, \text{c})$ value is independent of future changes in ΔH°_{298} of $\text{Li}_2\text{O}(\text{c})$ but the values of $\Delta H^\circ_{\text{soln}}$ and ΔH° are not independent.

The heats of solution of $\text{LiOH}(\text{c})$ and $\text{Li}_2\text{SiO}_3(\text{c})$ in 20 percent $\text{HF}(\text{aq})$ at 50°C were measured by W. E. Hatton, D. L. Hildenbrand, G. C. Sinke, and D. R. Stull, unpublished work, Thermal Laboratory, The Dow Chemical Co., Midland, Michigan, 1959. The Li_2SiO_3 sample was prepared from lithium carbonate and silica by fusion under vacuum at 1500°C . Analysis gave 66.74 percent SiO_2 and 15.12 percent Li . The corresponding calculated values are 66.79 and 15.43.

Also present were 0.5 percent K and 0.06 percent Na. Corrections were made for impurities in the heat of formation measurements. The results are given as follows:

	ΔH°_{298} , kcal/mol
$2\text{LiOH}(\text{c}, 25^\circ\text{C}) + 2\text{HF}(\text{sol}, 50^\circ\text{C}) + 2\text{LiF}(\text{sol}, 50^\circ\text{C}) + 2\text{H}_2\text{O}(\text{sol}, 50^\circ\text{C})$	-38.728
$\text{SiO}_2(\text{c}, 25^\circ\text{C}) + 6\text{HF}(\text{sol}, 50^\circ\text{C}) + \text{H}_2\text{SiF}_6(\text{sol}, 50^\circ\text{C}) + 2\text{H}_2\text{O}(\text{sol}, 50^\circ\text{C})$	-32.810
$3\text{H}_2\text{O}(\text{sol}, 50^\circ\text{C}) + 2\text{LiF}(\text{sol}, 50^\circ\text{C}) + \text{H}_2\text{SiF}_6(\text{sol}, 50^\circ\text{C}) - \text{Li}_2\text{SiO}_3(\text{c}, 25^\circ\text{C}) + 8\text{HF}(\text{sol}, 50^\circ\text{C})$	+58.650
$\text{H}_2\text{O}(\text{sol}, 50^\circ\text{C}) - \text{H}_2\text{O}(\text{l}, 25^\circ\text{C})$	-0.450
$2\text{LiOH}(\text{c}, 25^\circ\text{C}) + \text{SiO}_2(\text{c}, 25^\circ\text{C}) + \text{Li}_2\text{SiO}_3(\text{c}, 25^\circ\text{C}) + \text{H}_2\text{O}(\text{l}, 25^\circ\text{C})$	-13.14 $\pm$ 0.70

The ΔH°_{298} for the second reaction was determined by D. R. Torgeson and T. G. Sahana, J. Am. Chem. Soc. 70, 2156 (1948). Based on the calculated enthalpy change for the overall reaction, $\Delta H^\circ_{298} = -13.14$ kcal/mol and $\Delta H^\circ_{298} = -115.84$, -217.7 and -68.32 kcal/mol for $\text{LiOH}(\text{c})$, $\text{SiO}_2(\text{low quartz})$, and $\text{H}_2\text{O}(\text{l})$, respectively, we derived $\Delta H^\circ_{298}(\text{Li}_2\text{SiO}_3, \text{c}) = -394.21 \pm 1.0$ kcal/mol, which is in agreement with the adopted value.

C. Kroger and E. Fingas, Z. Anorg. Allgem. Chem. 213, 12 (1933), measured the equilibrium pressure of CO_2 over a mixture of $\text{Li}_2\text{CO}_3(\text{c})$, $\text{SiO}_2(\text{quartz})$, and $\text{Li}_2\text{SiO}_3(\text{c})$ from 585 to 781°K . The enthalpy change (ΔH°_{298}) of the reaction $\text{Li}_2\text{CO}_3(\text{c}) + \text{SiO}_2(\text{c}) = \text{Li}_2\text{SiO}_3(\text{c}) + \text{CO}_2(\text{g})$ is evaluated by the second and third law methods to be 30.94 and 29.47 kcal/mol, respectively. Using $\Delta H^\circ_{298} = -290.84$, -217.7 and -94.05 kcal/mol for $\text{Li}_2\text{CO}_3(\text{c})$, $\text{SiO}_2(\text{c})$ and $\text{CO}_2(\text{g})$, respectively, and third law ΔH°_{298} , we obtain $\Delta H^\circ_{298}(\text{Li}_2\text{SiO}_3, \text{c}) = -394.82 \pm 5$ kcal/mol, which is not used.

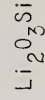
Heat Capacity and Entropy

The low temperature heat capacities, 75 - 340°K , were measured by Hatton et al., loc. cit., with an adiabatic vacuum calorimeter, using a nickel-plated copper sample container. During the filling and sealing of the calorimeter, the compound was handled in an anhydrous, CO_2 -free atmosphere so as to avoid contamination. The purity of the sample is not well established. The high temperature heat capacities are estimated by summation of the Cp's of the constituent oxides Li_2O and SiO_2 , and a subsequent correction based upon a comparison of the heat capacities of $\text{Na}_2\text{SiO}_3(\text{c})$ and its constituent oxides. These estimated Cp values are plotted, and the resulting curve is joined smoothly with the low temperature Cp curve at 298°K . The entropy, S°_{298} , is derived using the measured low temperature heat capacities, based on $S^\circ_{298} = 0.023$ eu.

Melting Data

See $\text{Li}_2\text{SiO}_3(\text{l})$ table for details.

Lithium Metasilicate (Li_2SiO_3)
(Liquid) $\text{GFW} = 89.9622$



T, °K	C_p^0	S^0	$-(C_p^0 - H^0_{298})/T$	kcal/mol $H^0 - H^0_{298}$	ΔH_f^0	ΔG_f^0	Log K_p
0							
100							
200							
298	24.036	22.958	22.958	- .000	- 385.441	- 367.802	269.665
300	24.142	23.107	22.959	.095	- 384.447	- 367.755	267.910
400	24.400	30.686	23.663	2.689	- 380.618	- 360.925	197.146
500	30.547	37.265	25.982	5.642	- 370.142	- 353.719	154.611
600	35.100	42.076	28.349	8.774	- 360.138	- 346.433	126.188
700	38.320	52.555	33.246	15.447	- 349.031	- 339.400	100.890
800	38.520	52.555	33.246	15.447	- 349.031	- 339.400	100.890
900	35.508	56.679	35.624	18.950	- 389.508	- 324.911	70.874
1000	40.000	60.467	37.921	22.546	- 389.157	- 317.506	69.391
1100	40.300	64.280	40.147	26.546	- 389.426	- 310.377	61.666
1200	40.300	67.962	42.385	30.546	- 387.032	- 294.309	49.614
1300	40.300	71.926	44.393	34.546	- 385.363	- 289.355	43.170
1400	40.300	76.686	46.322	38.546	- 385.710	- 282.449	41.153
1500	40.300	79.297	50.176	46.546	- 385.073	- 275.593	37.643
1600	40.300	81.979	51.675	54.546	- 485.515	- 254.229	30.868
1700	40.300	84.141	55.328	59.546	- 484.502	- 242.516	27.896
1800	40.300	86.193	58.920	62.546	- 463.499	- 230.562	25.227
1900	40.300	90.185	58.456	65.546	- 462.503	- 219.256	22.618
2000	40.300	92.784	61.372	74.546	- 460.565	- 194.182	18.642
2100	40.300	95.486	62.758	78.546	- 459.584	- 184.705	16.820
2200	40.300	97.119	64.100	82.546	- 459.634	- 173.274	15.148
2300	40.300	98.698	65.401	86.546	- 457.694	- 161.879	13.607
2400	40.300	100.552	65.882	94.546	- 455.856	- 139.191	10.864
2500	40.300	103.056	69.074	95.546	- 454.960	- 127.898	9.639
2600	40.300	104.412	70.230	102.546	- 454.075	- 116.634	8.697
2700	40.300	105.723	71.354	106.546	- 453.209	- 105.396	7.430
2800	40.300	106.223	72.515	114.546	- 452.521	- 93.175	6.498
2900	40.300	109.418	74.552	118.546	- 450.703	- 71.956	4.619
3000	40.300	110.578	75.565	122.546	- 449.900	- 60.733	3.792
3100	40.300	111.704	76.553	126.546	- 541.078	- 47.382	2.875
3200	40.300	112.867	77.440	134.546	- 539.549	- 34.925	1.189
3300	40.300	114.906	79.382	138.546	- 538.593	- 6.323	.354
3400	40.300	115.919	80.282	142.546	- 537.739	- 7.309	.399

LITHIUM METASILICATE (Li_2SiO_3)
(LIQUID)

$S^0_{298.15} = 22.958$ gibbs/mol

$T_m = 1474 \pm 1^\circ\text{K}$

$\Delta H_f^{298.15} = -385.441$ kcal/mol

$\Delta H_m^0 = 6.7 \pm 0.5$ kcal/mol

$\text{GFW} = 89.9622$

Heat of Formation

$\Delta H_f^0(t)$ is obtained from $\Delta H_f^{298}(c)$ by adding ΔH_m^0 and the difference between $H^0_{1474} - H^0_{298}$ for crystal and liquid.

Tchernobaieff, Rev. Met. 21, 729 (1905), measured the heat of reaction between SiO_2 and Li_2CO_3 in a bomb calorimeter, using carbon as the auxiliary combustible material. Based on the derived $\Delta H_{298} = 24.99$ kcal/mol for the reaction $\text{Li}_2\text{CO}_3(c) + \text{SiO}_2(c) \rightarrow \text{Li}_2\text{SiO}_3(\text{gl}) + \text{CO}_2(g)$, the heat of formation for $\text{Li}_2\text{SiO}_3(\text{gl})$ is evaluated as -389.30 kcal/mol, which is in fair agreement with the adopted value.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for $\text{Na}_2\text{SiO}_3(l)$, $\text{Na}_2\text{O}(l)$ and $\text{Li}_2\text{O}(l)$. A glass transition is assumed at 1000°K ; i.e., the heat capacities below 1000°K are taken to be the same as those for $\text{Li}_2\text{SiO}_3(c)$.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting point has been reported as 1474 ± 1 and 1461°K by F. C. Kracek, J. Phys. Chem. 31, 2841 (1930), and H. S. Van Klooster, Z. Anorg. Chem. 69, 135 (1911), respectively. The value reported by Kracek is adopted.

R. Schwarz and H. Sturm, Ber. 12, 1730 (1914), used a cooling-curve method to compare the heats of fusion of $\text{Li}_2\text{SiO}_3(c)$ and $\text{NaCl}(c)$. From the reported ratio, $\epsilon(\text{Li}_2\text{SiO}_3)/\epsilon(\text{NaCl}) = 0.261/0.402$, where ϵ = heat of fusion in kcal/g, and heat of fusion of $\text{NaCl}(c)$, the value $\Delta H_m^0 = 6.7$ kcal/mol is derived.



Lithium Metatitanate (Li_2TiO_3)
(Crystal) Mol. Wt. = 109.780



MOL. WT. = 109.780

LITHIUM METATITANATE (Li_2TiO_3)

(CRYSTAL)

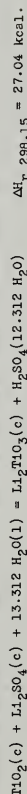
T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	-0.000	0.000	INFINITE	-3.942	-396.770	-396.770	INFINITE
100	7.443	3.377	40.417	-3.704	-397.073	-397.073	855.658
200	16.757	12.640	24.215	-2.315	-398.942	-398.942	420.352
298	26.256	21.930	21.930	-0.000	-399.300	-377.591	276.768
300	26.470	22.093	21.931	-0.049	-399.304	-377.456	274.964
400	30.440	30.263	23.018	2.898	-399.383	-370.156	202.234
500	32.420	37.285	25.188	6.049	-400.814	-362.703	156.530
600	33.820	43.328	27.720	9.365	-400.729	-355.085	129.333
700	34.690	48.522	30.335	12.591	-400.559	-349.487	109.487
800	35.090	52.920	32.850	15.740	-400.359	-345.090	90.713
900	36.250	57.562	35.428	19.921	-400.053	-332.356	80.713
1000	36.780	61.409	37.836	23.573	-399.762	-324.893	71.002
1100	37.240	64.937	40.142	27.275	-399.448	-317.422	63.063
1200	37.560	68.174	42.346	31.018	-399.099	-309.944	56.446
1300	37.780	71.174	44.254	34.804	-398.724	-299.524	50.946
1400	38.120	74.032	46.065	38.524	-398.384	-284.976	46.046
1500	42.200	78.560	48.410	45.224	-396.227	-267.559	41.895
1600	43.000	81.309	50.481	49.484	-395.455	-260.337	38.290
1700	43.800	83.940	52.278	53.924	-394.713	-270.513	34.775
1800	44.500	86.399	53.876	58.744	-394.000	-277.864	31.503
1900	45.200	88.809	55.376	62.764	-393.326	-287.476	28.503
2000	46.200	91.248	57.586	67.324	-464.420	-236.470	25.639
2100	47.000	93.521	59.243	71.984	-462.916	-225.108	23.426
2200	47.800	95.126	60.452	76.724	-461.344	-213.850	21.250
2300	48.400	96.484	61.484	81.484	-459.800	-202.700	19.100
2400	49.400	98.954	63.916	86.444	-457.987	-191.464	17.434
2500	50.200	101.987	65.417	91.424	-456.207	-180.396	15.769
2600	51.000	103.971	66.862	96.484	-454.357	-169.403	14.239
2700	51.600	105.717	68.272	101.624	-452.462	-158.476	12.727
2800	52.000	107.280	69.560	106.840	-450.524	-147.624	11.227
2900	53.400	109.669	70.999	112.144	-448.442	-136.845	10.312
3000	54.200	111.493	72.118	117.524	-446.298	-126.136	9.189

June 30, 1961; Mar. 31, 1964

$\Delta H_f^\circ 0 = -396.8 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -399.3 \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = 21.930 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_f = 1485^\circ\text{K.}$
 $T_m = 1820^\circ\text{K.}$
 $\Delta H_m^\circ = 2.75 \text{ kcal. mole}^{-1}$
 $\Delta H_m = 26.33 \text{ kcal. mole}^{-1}$

Heat of Formation.

The $\Delta H_f^\circ 298.15$ was calculated from measurements of solution calorimetry by S. S. Todd and K. K. Kelley, "Heat and Free Energy Data for Tricalcium Dittitanate, Spinel, Lithium Metatitanate and Zinc Titanium Spinel", U. S. Bureau Mines Report Invest. 5193 (1956), according to the following equation:



The $\Delta H_f^\circ 298.15 \text{ TiO}_2(c)$ value for rutile was obtained from the JANAF Tables and the other $\Delta H_f^\circ 298.15$ values were obtained from "Selected Values of Chemical Thermodynamic Properties" NBS Circular 500 (1952).

Heat Capacity and Entropy.

The low temperature heat capacities were taken from E. G. King, J. Am. Chem. Soc. 77, 2150 (1955). These low temperature heat capacities were fit to the high temperature heat contents from A. U. Christensen, K. C. Conway, and K. K. Kelley, "High Temperature Heat Contents and Entropies of Aluminates and Ferrites of Lithium, Sodium, and of Lithium Titanate", U. S. Bur. Mines Rept. Invest. 5565 (1960).

The $S_{298.15}^\circ = 21.9$ was obtained from E. G. King, loc. cit. based on the measured $S_{298.15}^\circ \text{S}_2^\circ$ and the extrapolated $S_{51}^\circ \text{S}_0^\circ$.

Transition Data.

A. U. Christensen, K. C. Conway, and K. K. Kelley, loc. cit. reported that lithium metatitanate undergoes a transition from the α to the β form at $1,485^\circ\text{K.}$ with an absorption of $2.750 \text{ kcal. mole}^{-1}$.

Melting Data.

The T_m and ΔH_m were obtained from A. U. Christensen, K. C. Conway, and K. K. Kelley, loc. cit.



Lithium Metatitanate (Li_2TiO_3)
(Liquid) Mol. Wt. = 109.780



LITHIUM METATITANATE (Li_2TiO_3) (LIQUID) MOL. WT. = 109.780

T, °K.	C_p	S°	$-\int_0^T \frac{C_p - H^\circ_{298}}{T} dT$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0							
100	26.256	35.355	35.355	0.000	-374.374	-356.667	261.432
200	26.470	35.518	35.356	0.049	-374.378	-356.558	259.740
300	30.440	43.088	36.443	2.898	-374.457	-350.600	191.550
400	32.420	50.710	38.613	6.049	-375.488	-344.459	150.569
500	33.820	56.753	41.145	9.365	-375.803	-338.214	123.189
600	34.860	62.047	43.760	12.801	-375.828	-331.965	103.639
700	35.620	66.754	46.346	16.327	-375.593	-325.744	88.985
800	36.250	70.987	48.853	19.921	-375.127	-319.552	77.594
900	36.780	74.834	51.261	23.573	-374.436	-313.392	68.486
1000	37.240	78.362	53.567	27.275	-374.522	-307.263	61.045
1100	37.600	81.619	55.771	31.018	-375.143	-301.128	54.840
1200	38.000	85.340	57.900	35.672	-373.924	-295.004	49.592
1300	38.400	88.808	59.989	40.472	-372.580	-288.983	45.110
1400	38.800	92.209	62.028	45.272	-371.253	-283.059	41.240
1500	39.200	95.307	64.012	50.072	-369.941	-277.220	37.865
1600	39.600	98.217	65.939	54.872	-368.739	-268.810	34.556
1700	40.000	100.961	67.809	59.672	-367.098	-258.658	31.428
1800	40.400	103.556	69.623	64.472	-365.475	-248.998	28.640
1900	40.800	106.018	71.382	69.272	-363.546	-239.136	26.130
2000	41.200	108.360	73.087	74.072	-361.902	-229.255	23.858
2100	41.600	110.593	74.742	78.872	-360.270	-219.452	21.800
2200	42.000	112.727	76.347	83.672	-358.644	-209.725	19.927
2300	42.400	114.769	77.906	88.472	-357.033	-200.067	18.218
2400	42.800	116.729	79.420	93.272	-355.433	-190.477	16.651
2500	43.200	118.611	80.891	98.072	-353.843	-180.953	15.210
2600	43.600	120.423	82.322	102.872	-352.268	-171.487	13.880
2700	44.000	122.169	83.714	107.672	-350.704	-162.078	12.650
2800	44.400	123.853	85.069	112.472	-349.158	-152.724	11.509
2900	44.800	125.480	86.389	117.272	-347.624	-143.424	10.448
3000	45.200	127.054	87.676	122.072	-346.107	-134.171	9.459
3100	45.600	128.578	88.930	126.872	-344.604	-124.979	8.535
3200	46.000	130.055	90.154	131.672	-343.119	-115.825	7.670
3300	46.400	131.488	91.349	136.472	-341.652	-106.716	6.859
3400	46.800	132.879	92.516	141.272	-340.199	-97.655	6.098
3500	47.200	134.232	93.656	146.072	-338.762	-88.645	5.393
3600	47.600	135.547	94.771	150.872	-337.343	-79.671	4.748
3700	48.000	136.827	95.861	155.672	-335.940	-70.731	4.150
3800	48.400	138.074	96.927	160.472	-334.552	-61.824	3.600
3900	48.800	139.289	97.971	165.272	-333.179	-52.950	3.090
4000	49.200	140.471	99.000	170.072	-331.821	-44.101	2.610

$S^\circ_{298.15} = 35.355$ cal. mole⁻¹ deg.⁻¹
 $\Delta H^\circ_f 298.15 = -374.374$ kcal. mole⁻¹
 $\Delta F^\circ_f 298.15 = -356.667$ kcal. mole⁻¹
 $T_m = 1820^\circ\text{K.}$

Heat of Formation.

The $\Delta H^\circ_f 298.15$ was obtained from the heat of formation of the crystal by adding ΔH_m and the difference between $H_{1820} - H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacities were reported by A. U. Christensen, K. C. Conway, and K. K. Kelley, "High-Temperature Heat Contents and Entropies of Aluminates and Ferrites of Lithium, Sodium, and of Lithium Titanate", U. S. Bureau Mines Report Invest. 5565 (1960). The measured heat capacity is extrapolated to an assumed glass transition temperature of 1214°K., below which the heat capacity is taken to be equal to that of the crystal.

The $S^\circ_{298.15}$ was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The T_m and ΔH_m were obtained from A. U. Christensen, K. C. Conway and K. K. Kelley, loc. cit.



T, °K	C_p	$\frac{\text{gkcal/mol}}{S}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔC_p	Log Kp
0							
100							
200							
298	33.300	30.000	10.000	.000	- 612.070	- 577.659	423.636
300	33.200	30.205	10.001	.061	- 612.081	- 577.447	420.669
400	41.038	31.419	3.867	3.867	- 612.329	- 565.467	309.164
500	44.350	50.843	31.344	8.269	- 613.678	- 554.085	242.190
600	49.160	59.527	37.831	13.019	- 613.359	- 542.192	197.493
700	51.360	67.275	41.494	18.047	- 612.845	- 530.370	165.589
800	53.200	74.256	45.150	23.274	- 612.195	- 519.436	141.685
900	54.850	80.619	48.752	28.681	- 611.431	- 508.982	123.112
1000	56.250	86.472	52.235	34.237	- 610.571	- 498.421	108.274
1100	57.508	91.494	55.597	39.926	- 609.625	- 488.352	96.152
1200	58.500	96.246	58.835	45.733	- 608.604	- 478.874	86.087
1300	59.316	101.531	61.953	51.855	- 607.507	- 469.294	77.531
1400	60.240	106.273	64.972	57.822	- 606.169	- 459.107	70.265
1500	60.215	110.447	67.865	63.472	- 605.043	- 448.394	63.962
1600	61.500	114.401	70.651	69.999	- 603.840	- 427.965	58.487
1700	62.500	118.149	73.336	76.162	- 602.492	- 408.163	53.242
1800	62.400	121.706	75.925	82.406	- 600.985	- 397.567	48.271
1900	62.438	125.087	78.425	88.458	- 600.264	- 381.091	43.835
2000	62.500	128.304	80.839	94.931	- 600.534	- 364.759	39.853
2100	62.953	131.370	83.173	101.213	- 600.815	- 348.610	36.259
2200	62.700	134.295	85.430	107.501	- 600.105	- 332.194	33.000
2300	62.740	137.072	87.616	113.793	- 600.406	- 316.354	30.032
2400	62.373	139.771	89.738	120.089	- 600.721	- 299.984	27.317
2500	61.300	142.342	91.787	126.384	- 603.050	- 283.993	24.827

 $\Delta H^\circ_{298} = \text{Unknown}$ $\Delta H^\circ_{298, 15} = -612.07 \pm 1.0 \text{ kcal/mol}$ $\Delta H^\circ = 0.225 \text{ kcal/mol}$ $\Delta H^\circ = \{12.86\} \text{ kcal/mol}$ $T_m = 1307 \pm 1^\circ\text{K}$

Heat of Formation

The heats of solution of $\text{LiCl}(\text{c})$, $\text{Li}_2\text{SO}_4(\text{c})$, $\text{SiO}_2(\text{quartz})$ and $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ in 20 per cent hydrofluoric acid at 74.7°C were measured by F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953). The authors derived two values of $\Delta H^\circ_{\text{soln}}$ of $\text{Li}_2\text{O}(\text{c})$ from those of $\text{LiCl}(\text{c})$ and $\text{Li}_2\text{SO}_4(\text{c})$, presumably employing auxiliary data from U. S. Natl. Bur. Std., Circ. 500, 1952. We recalculate $\Delta H^\circ_{\text{soln}}$ of $\text{Li}_2\text{O}(\text{c})$ as -58.74 (chloride scheme, originally -59.36) and -59.83 kcal/mol (sulfate scheme, originally -60.86), using recent ΔH°_{298} values for $\text{LiCl}(\text{c})$, $\text{Li}_2\text{SO}_4(\text{c})$, $\text{HCl}(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, and $\text{Li}_2\text{O}(\text{c})$. The corresponding enthalpy changes, ΔH°_{298} , for the reaction $\text{Li}_2\text{O}(\text{c}) + 2\text{SiO}_2(\text{quartz}) = \text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ are derived as -33.21 and -34.30 kcal/mol. Adopting the weighted average $\Delta H^\circ_{298} = -33.57$ kcal/mol with $\Delta H^\circ_{298}(\text{Li}_2\text{O}, \text{c}) = -143.1$ kcal/mol and $\Delta H^\circ_{298}(\text{SiO}_2, \text{quartz}) = -217.7$ kcal/mol, we obtain $\Delta H^\circ_{298} = -612.07$ kcal/mol for $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$. This $\Delta H^\circ_{298}(\text{Li}_2\text{Si}_2\text{O}_5, \text{c})$ value is independent of future changes in ΔH°_{298} of $\text{Li}_2\text{O}(\text{c})$ but the values of $\Delta H^\circ_{\text{soln}}$ and ΔH° are not independent.

The heats of solution of $\text{LiOH}(\text{c})$ and $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ in 20 per cent $\text{H}^\circ(\text{aq})$ at 80°C were measured by W. E. Hatton, G. C. Sinke, D. L. Hildenbrand, and D. R. Stull, unpublished work, Thermal Laboratory, The Dow Chemical Co., Midland, Michigan, 1959. By use of a reaction scheme similar to that described on the $\text{Li}_2\text{SiO}_3(\text{c})$ table, the enthalpy change at 298°K for the reaction $2\text{LiOH}(\text{c}) + 2\text{SiO}_2(\text{c}) = \text{Li}_2\text{Si}_2\text{O}_5(\text{c}) + \text{H}_2\text{O}(\text{l})$ was calculated to be -13.44 kcal/mol. Incorporating this value with $\Delta H^\circ_{298} = -115.84$, -217.7 and -68.315 kcal/mol for $\text{LiOH}(\text{c})$, $\text{SiO}_2(\text{c})$, and $\text{H}_2\text{O}(\text{l})$, respectively, we obtain $\Delta H^\circ_{298}(\text{Li}_2\text{Si}_2\text{O}_5, \text{c}) = -612.20 \pm 2.0$ kcal/mol, which is in excellent agreement with the adopted value.

Heat Capacity and Entropy

Both heat capacities and S°_{298} are estimated by comparison with those for $\text{Na}_2\text{Si}_2\text{O}_5(\text{c})$, $\text{Na}_2\text{O}(\text{c})$ and $\text{Li}_2\text{O}(\text{c})$.

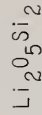
Transition Data

The transition temperature, $T_t = 1209^\circ\text{K}$, is taken from F. C. Kracek, J. Am. Chem. Soc. 61, 2863 (1939). This author estimated a heat of transition of 1 to 2 cal/g based on the arrest in the cooling and heating curves. The value of ΔH°_t is calculated assuming the heat of transition at 1209°K is 1.5 cal/g.

Melting Data

Incongruent melting of $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ at 1033° has been reported by F. C. Kracek, J. Phys. Chem. 34, 2841 (1930); J. Am. Chem. Soc. 61, 2863 (1939). The liquidus temperature of 1034° at the composition 19.92 per cent Li_2O and 80.08 per cent SiO_2 , reported by Kracek (1939), is adopted as T_m . The heat of melting is evaluated such that $\Delta H^\circ_m + \Delta H^\circ_{298} = 11.43$ kcal/mol, where the value 11.43 kcal/mol is the difference between ΔH°_{298} for $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ and $\text{Li}_2\text{Si}_2\text{O}_5(\text{l})$. The latter were determined by solution calorimetry by Kracek (see Heat of Formation sections in $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ and $\text{Li}_2\text{Si}_2\text{O}_5(\text{l})$ tables).

Lithium Disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$)
(Liquid) GFW = 150.047



GFW = 150.047

(LIQUID)

LITHIUM DISILICATE ($\text{Li}_2\text{Si}_2\text{O}_5$)

$\Delta H_f^{298.15} = -600.640 \pm 1.0 \text{ kcal/mol}$

$\Delta H_m^* = [12.86] \text{ kcal/mol}$

$S_{298.15}^* = [38.297] \text{ gibbs/mol}$

$T_m = 1307^\circ\text{K}$

Heat of Formation

The heats of solution of LiCl(c) , $\text{Li}_2\text{SO}_4(\text{c})$, $\text{SiO}_2(\text{quartz})$ and $\text{Li}_2\text{Si}_2\text{O}_5(\text{gl})$ in 20 percent hydrofluoric acid at 74.7°C were measured by F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953). Following the same procedure as described in $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ table, we derived the enthalpy changes, ΔH_f^{298} , for the reaction $\text{Li}_2\text{O(c)} + 2\text{SiO}_2(\text{quartz}) = \text{Li}_2\text{Si}_2\text{O}_5(\text{gl})$ as -21.78 and -22.87 kcal/mol . Adopting the weighted average $\Delta H_f^{298} = -22.14 \text{ kcal/mol}$ with $\Delta H_f^{298}(\text{Li}_2\text{O, c}) = -143.1 \text{ kcal/mol}$ and $\Delta H_f^{298}(\text{SiO}_2, \text{quartz}) = -217.7 \text{ kcal/mol}$, we obtain $\Delta H_f^{298} = -600.640 \text{ kcal/mol}$ for $\text{Li}_2\text{Si}_2\text{O}_5(\text{gl})$. This $\Delta H_f^{298}(\text{Li}_2\text{Si}_2\text{O}_5, \text{gl})$ value is independent of future changes in ΔH_f^* of $\text{Li}_2\text{O(c)}$ but the values of ΔH_{soln} and ΔH_f^* are not independent.

Heat Capacity and Entropy

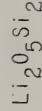
The heat capacity is estimated by comparison with those for $\text{Na}_2\text{Si}_2\text{O}_5(\text{c})$, $\text{Na}_2\text{SiO}_3(\text{c})$ and $\text{Li}_2\text{SiO}_3(\text{c})$. A glass transition temperature at 800°K is assumed, i.e. the heat capacities below 800°K are taken from those for $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ and above 800°K are assumed to be constant.

The S_{298}^* value is obtained from $S_{298}^*(\text{c})$ by adding ΔS_m^* and the difference between $S_{1307}^* - S_{298}^*$ for crystal and liquid.

Melting Data

See $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ table for details.

T, °K	C_p^*	$S^* - (C_p^* - H^{298})/T$	$H^* - H^{298}$	kcal/mol ΔH_f^*	ΔG_f^*	Log Kp
0						
100	33.000	38.297	0.001	-600.640	-568.703	016.870
200	33.200	38.502	0.061	-600.651	-569.506	016.156
300	33.400	38.716	0.187	-600.699	-570.736	015.433
400	33.600	38.935	0.347	-600.786	-572.364	014.708
500	33.800	39.159	0.524	-600.909	-574.404	013.983
600	34.000	39.388	0.716	-601.069	-576.854	013.258
700	34.200	39.622	0.924	-601.269	-579.714	012.533
800	34.400	39.861	1.147	-601.509	-582.874	011.808
900	34.600	40.105	1.387	-601.789	-586.334	011.083
1000	34.800	40.354	1.643	-602.109	-590.094	010.358
1100	35.000	40.608	1.917	-602.469	-594.154	009.633
1200	35.200	40.867	2.209	-602.869	-598.514	008.908
1300	35.400	41.131	2.519	-603.309	-603.174	008.183
1400	35.600	41.400	2.847	-603.789	-608.134	007.458
1500	35.800	41.674	3.193	-604.309	-613.394	006.733
1600	36.000	41.953	3.557	-604.869	-618.954	006.008
1700	36.200	42.237	3.939	-605.469	-624.814	005.283
1800	36.400	42.526	4.339	-606.109	-630.974	004.558
1900	36.600	42.820	4.757	-606.789	-637.434	003.833
2000	36.800	43.119	5.193	-607.509	-644.194	003.108
2100	37.000	43.423	5.647	-608.269	-651.254	002.383
2200	37.200	43.732	6.119	-609.069	-658.614	001.658
2300	37.400	44.046	6.609	-609.909	-666.274	000.933
2400	37.600	44.365	7.117	-610.789	-674.234	000.208
2500	37.800	44.689	7.643	-611.709	-682.494	-000.517
2600	38.000	45.018	8.187	-612.669	-691.054	-001.242
2700	38.200	45.352	8.749	-613.669	-699.914	-001.967
2800	38.400	45.691	9.329	-614.709	-709.074	-002.692
2900	38.600	46.035	9.927	-615.789	-718.534	-003.417
3000	38.800	46.384	10.543	-616.909	-728.294	-004.142



T, °K	C_p	$\frac{\text{gibbs/mol}}{\text{S}^\circ}$	$-(\text{G}^\circ - \text{H}^\circ_{298})/\text{T}$	$\text{H}^\circ - \text{H}^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta \text{H}^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	18.480	9.000	9.000	0.000	- 47.200	- 36.840	27.005
300	18.530	9.114	9.000	0.034	- 47.205	- 36.777	26.792
400	20.990	14.785	9.757	2.011	- 47.440	- 33.261	18.173
500	23.340	19.722	11.266	4.228	- 48.824	- 29.471	12.882
600	25.660	24.184	13.052	6.679	- 49.872	- 25.389	9.248
700	27.840	28.308	14.941	9.357	- 49.658	- 21.324	6.658
800	29.640	32.149	16.855	12.235	- 49.228	- 17.305	4.727
900	30.960	35.720	18.795	15.268	- 48.647	- 13.347	3.241
1000	31.900	39.033	20.619	18.414	- 47.959	- 9.461	2.068
1100	32.540	42.105	22.434	21.638	- 47.193	- 5.647	1.122
1200	33.070	44.956	24.194	24.914	- 46.381	- 1.908	0.347
1300	33.250	47.606	25.894	28.226	- 45.532	1.764	- 0.297
1400	33.450	50.078	27.534	31.561	- 44.663	5.371	- 0.838
1500	33.600	52.391	29.115	34.914	- 43.773	8.913	- 1.299
1600	33.720	54.564	30.638	38.281	- 42.868	12.398	- 1.693
1700	33.800	56.611	32.107	41.657	- 41.904	19.806	- 2.546
1800	33.840	58.544	33.522	45.039	- 40.928	29.586	- 3.592
1900	33.890	60.374	34.888	48.425	- 40.000	38.284	- 4.519
2000	33.920	62.113	36.206	51.815	- 39.129	48.898	- 5.343
2100	33.960	63.769	37.479	55.209	- 38.300	59.438	- 6.082
2200	34.000	65.350	38.710	58.607	- 37.511	67.913	- 6.747

$\Delta \text{H}^\circ_0 = \text{Unknown}$
 $\Delta \text{H}^\circ_{298.15} = -47.2 \pm 1.0 \text{ kcal/mol}$

Heat of Formation.
 The adopted $\Delta \text{H}^\circ_{298.15} = -47.2 \pm 1.0 \text{ kcal/mol}$ was determined calorimetrically by Neumann et al.¹ by heating $\text{Li}(\text{c})$ at 600°C under 5 atm N_2 pressure for 1 minute. The $\Delta \text{H}^\circ_{291} = -131.1 \text{ kcal/mol}$ of reaction $\text{Li}_3\text{N}(\text{c}) + 3 \text{H}_2\text{O}(\text{l}) = 3 \text{LiOH}(\text{aq}) + \text{NH}_3(\text{g})$ was measured by Guntz.² Based on this $\Delta \text{H}^\circ_{291}$ the heat of formation was calculated to be $-47.02 \pm 2 \text{ kcal/mol}$ which is in very good agreement with that of Neumann et al.¹. Unfortunately the author does not report the amount of water in $\text{LiOH}(\text{aq})$ and we assumed 300 H_2O as the best estimate. Heat of formation for $\text{NH}_3(\text{g}) = [-19.17] \text{ kcal/mol}$ and $\text{H}_2\text{O}(\text{l}) = [-68.315] \text{ kcal/mol}$ were taken from Wagman et al.³. The ΔH° of $\text{LiOH} + 300 \text{H}_2$ (-121.30 kcal/mol) was derived from the heats of formation and solution of $\text{LiOH}(\text{c})$ (see JANAF table) and the heat of dilution selected by Parker.⁴

Reference: 1. B. Neumann, C. Kroger and H. Haebler, Z. anorg. allgem. Chem. **204**, 81-96 (1932).
 2. A. Guntz, Compt. rend **123**, 995-8 (1896).
 3. D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, Washington, 1965.
 4. V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, Washington, D. C., 1965.

Heat Capacity and Entropy.

S. Satoh, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **35**, 182 (1939), has measured enthalpies (273-578°K) and derived an equation for the specific heat of Li_3N . The adopted heat capacities were obtained from this equation. Above 773°K the heat capacities were graphically extrapolated. The entropy was estimated from the contribution 3.5 eu per Li given by W. M. Latimer, "Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, 1952, and a -1.5 eu contribution for N.

Magnesium (Mg)

(Reference State) At. Wt. = 24.32

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	(H° - H ₂₉₈)/T	cal. mole ⁻¹	H° - H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.00	0.00	INFINITE	-	1.106	0.00	0.00	0.00	0.00
100	3.768	9.273	12.605	-	1.042	0.00	0.00	0.00	0.00
200	5.440	5.533	7.693	-	1.480	0.00	0.00	0.00	0.00
298	5.073	7.814	7.814	-	0.000	0.00	0.00	0.00	0.00
300	5.960	7.851	7.814	0.11	0.000	0.00	0.00	0.00	0.00
400	6.290	9.613	8.052	1.625	0.000	0.00	0.00	0.00	0.00
500	6.560	11.047	8.512	1.267	0.000	0.00	0.00	0.00	0.00
600	6.802	12.264	9.036	1.936	0.00	0.00	0.00	0.00	0.00
700	7.080	13.133	9.577	2.629	0.00	0.00	0.00	0.00	0.00
800	7.420	14.300	10.108	3.354	0.00	0.00	0.00	0.00	0.00
900	7.820	15.136	10.524	4.112	0.00	0.00	0.00	0.00	0.00
1000	7.880	18.339	11.304	7.034	0.00	0.00	0.00	0.00	0.00
1100	8.140	19.102	11.979	7.836	0.00	0.00	0.00	0.00	0.00
1200	8.400	19.821	12.602	9.363	0.00	0.00	0.00	0.00	0.00
1300	8.660	20.504	13.184	9.516	0.00	0.00	0.00	0.00	0.00
1400	8.920	21.156	13.726	9.580	0.00	0.00	0.00	0.00	0.00
1500	4.968	43.430	14.023	41.257	0.00	0.00	0.00	0.00	0.00
1600	4.968	43.850	17.754	41.754	0.00	0.00	0.00	0.00	0.00
1700	4.968	44.152	19.298	42.251	0.00	0.00	0.00	0.00	0.00
1800	4.968	44.436	20.587	42.748	0.00	0.00	0.00	0.00	0.00
1900	4.968	44.704	21.724	43.244	0.00	0.00	0.00	0.00	0.00
2000	4.969	44.959	22.658	43.741	0.00	0.00	0.00	0.00	0.00
2100	4.969	45.201	24.136	44.238	0.00	0.00	0.00	0.00	0.00
2200	4.970	45.433	25.098	44.735	0.00	0.00	0.00	0.00	0.00
2300	4.972	45.654	25.987	45.232	0.00	0.00	0.00	0.00	0.00
2400	4.974	45.865	26.811	45.729	0.00	0.00	0.00	0.00	0.00
2500	4.978	46.069	27.578	46.227	0.00	0.00	0.00	0.00	0.00
2600	4.983	46.264	28.292	46.725	0.00	0.00	0.00	0.00	0.00
2700	4.989	46.452	28.962	47.224	0.00	0.00	0.00	0.00	0.00
2800	4.998	46.633	29.582	47.723	0.00	0.00	0.00	0.00	0.00
2900	5.009	46.809	30.160	48.223	0.00	0.00	0.00	0.00	0.00
3000	5.023	46.979	30.737	48.725	0.00	0.00	0.00	0.00	0.00
3100	5.040	47.144	31.264	49.228	0.00	0.00	0.00	0.00	0.00
3200	5.060	47.304	31.763	49.733	0.00	0.00	0.00	0.00	0.00
3300	5.085	47.460	32.246	50.240	0.00	0.00	0.00	0.00	0.00
3400	5.114	47.613	32.686	50.750	0.00	0.00	0.00	0.00	0.00
3500	5.146	47.761	33.115	51.263	0.00	0.00	0.00	0.00	0.00
3600	5.186	47.907	33.524	51.780	0.00	0.00	0.00	0.00	0.00
3700	5.229	48.050	33.914	52.301	0.00	0.00	0.00	0.00	0.00
3800	5.278	48.190	34.288	52.826	0.00	0.00	0.00	0.00	0.00
3900	5.332	48.327	34.648	53.356	0.00	0.00	0.00	0.00	0.00
4000	5.392	48.463	34.990	53.892	0.00	0.00	0.00	0.00	0.00
4100	5.457	48.597	35.320	54.435	0.00	0.00	0.00	0.00	0.00
4200	5.528	48.729	35.648	54.984	0.00	0.00	0.00	0.00	0.00
4300	5.604	48.860	35.964	55.541	0.00	0.00	0.00	0.00	0.00
4400	5.686	48.993	36.239	56.105	0.00	0.00	0.00	0.00	0.00
4500	5.773	49.119	36.524	56.678	0.00	0.00	0.00	0.00	0.00
4600	5.866	49.247	36.779	57.260	0.00	0.00	0.00	0.00	0.00
4700	5.964	49.374	37.065	57.851	0.00	0.00	0.00	0.00	0.00
4800	6.067	49.501	37.323	58.453	0.00	0.00	0.00	0.00	0.00
4900	6.176	49.627	37.573	59.068	0.00	0.00	0.00	0.00	0.00
5000	6.289	49.753	37.815	59.688	0.00	0.00	0.00	0.00	0.00
5100	6.407	49.878	38.050	60.323	0.00	0.00	0.00	0.00	0.00
5200	6.530	50.004	38.272	60.973	0.00	0.00	0.00	0.00	0.00
5300	6.658	50.130	38.501	61.639	0.00	0.00	0.00	0.00	0.00
5400	6.791	50.255	38.726	62.321	0.00	0.00	0.00	0.00	0.00
5500	6.927	50.381	38.946	62.987	0.00	0.00	0.00	0.00	0.00
5600	7.069	50.507	39.175	63.687	0.00	0.00	0.00	0.00	0.00
5700	7.215	50.634	39.375	64.401	0.00	0.00	0.00	0.00	0.00
5800	7.367	50.760	39.531	65.130	0.00	0.00	0.00	0.00	0.00
5900	7.523	50.888	39.722	65.875	0.00	0.00	0.00	0.00	0.00
6000	7.684	51.015	39.912	66.635	0.00	0.00	0.00	0.00	0.00

See crystal, liquid, and ideal monatomic gas for details.

MAGNESIUM (ME)

(REFERENCE STATE)

Crystal
Liquid
Ideal gas, monatomic

Below 922°K
922°K to 1378°K
above 1378°K

Mg

AT. WT. = 24.32

Mg

T, °K	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	.000	INFINITE	- 1.196	.000	.000	INFINITE
100	3.768	2.273	12.695	.000	.000	.000
200	5.440	5.533	7.933	.000	.000	.000
298	5.953	7.814	.000	.000	.000	.000
300	5.960	7.851	.011	.000	.000	.005
400	6.290	9.613	8.052	.000	.000	.000
500	6.560	11.047	8.512	.000	.000	.000
600	6.802	12.264	9.038	.000	.000	.000
700	7.020	13.303	9.564	.000	.000	.000
800	7.220	14.207	10.077	.000	.000	.000
900	7.410	14.997	10.574	.000	.000	.000
1000	7.590	15.676	11.055	.000	.000	.000
1100	7.760	16.245	11.521	.000	.000	.000
1200	7.920	16.705	11.973	.000	.000	.000
1300	8.070	17.157	12.411	.000	.000	.000
1400	8.210	17.601	12.835	.000	.000	.000
1500	8.350	18.037	13.246	.000	.000	.000
1600	8.480	18.465	13.643	.000	.000	.000
1700	8.610	18.885	14.027	.000	.000	.000
1800	8.740	19.297	14.398	.000	.000	.000
1900	8.870	19.701	14.755	.000	.000	.000
2000	8.990	20.097	15.098	.000	.000	.000

Dec. 31, 1950; Sept. 30, 1952

MAGNESIUM (Mg)

(CRYSTAL)

AT. WT. = 24.32

$$\Delta H_f^\circ 298.15 = 0$$

$$S_{298.15}^\circ = 7.814 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m = 2.14 \text{ kcal. mole}^{-1}$$

$$T_m = 922 \pm 0.5^\circ \text{K}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The following heat capacity measurements were considered in drawing a smooth curve of C_p with T : P. L. Smith (1.25-4.2°K) Phil. Mag. 45, 744 (1955); J. R. Clement and H. R. Jeffers (3-13°K) Phys. Rev. 105, 1435 (1957); K. Clausius and J. V. Vaughn (11.3-228.4°K) J. Am. Chem. Soc. 52, 4686, (1930); R. S. Craig, C. A. Krier, L. W. Coffey, E. A. Bates, and W. E. Wallace (12-320°K) J. Am. Chem. Soc. 76, 238 (1954); W. Mannchen and K. Bornkessel (190-300°K) Z. Metallkunde 51, 482-5 (1960); H. Seelkamp (291-773°K) Z. anorg. Chem. 195, 345 (1931); and D. R. Stull and R. A. McDonald (700-900°K) J. Am. Chem. Soc. 77, 5293 (1955). The following heat capacity measurements were noted but not used as the data were either not tabulated, or erratic, or inconsistent or would not have altered the C_p - T curve: D. L. Martin (0.4-1.5°K) Proc. Phys. Soc. (London) 76, 1482-8 (1961); I. Rethermann, S. A. Friedberg, and J. E. Goldman (1.6-4.2°K) Phys. Rev. 87, 562 (1952); E. P. Eastman and W. H. Rodenbush (74.9-288.5°K) J. Am. Chem. Soc. 40, 489 (1918); W. O. Saba, K. P. Sterrett, R. S. Craig, and W. E. Wallace (238-543°K) J. Am. Chem. Soc. 79, 3537 (1957); F. M. Jaeger and T. J. Poppema (273-873°K) Rec. Trav. chim. 55, 492 (1936); J. H. Averbey and E. Griffiths (323-899°K) Proc. Phys. Soc. 36, 378 (1926); E. D. Eastman, A. M. Williams and T. F. Young (373-873°K) J. Am. Chem. Soc. 46, 1178 (1926); and P. Schübel (323-773°K) Z. anorg. Chem. 87, 81 (1914). $S_{298.15}^\circ$ was obtained by numerical integration using the low temperature C_p data cited above.

Melting.

Melting point is from J. L. Houghton and R. J. M. Payne (922 ± 0.5°K) J. Inst. Met. 54, 279 (1934). Also noted but not used were: R. Chadwick (923°K) J. Inst. Met. 39, 285-300 (1928); W. R. D. Jones (920.5°K) J. Inst. Met. 46, 395-419 (1931).

The heat of melting is from D. R. Stull and R. A. McDonald (loc. cit.)

Heat of Sublimation.

Is obtained by third law calculations from the vapor pressure data on the solid by P. F. Coleman and A. E. Egerton, Phil. Trans. Roy. Soc. (London) A234, 177-204 (1935) and the value is confirmed by similar use of the vapor pressure data on the liquid by E. Scheil and P. Wolf, Z. Metallkunde 50, 229-33 (1959); A. Wejnarth, Tek. Tid. 72, 33-9, 44-8 (1942); A. Schneider and E. K. Stoll, Z. Elektrochem. 47, 513-26 (1941); E. Baur and R. Brunner, Helv. Chim. Acta, 17, 958-69 (1934); and H. Hartmann and R. Schneider, Z. anorg. Chem. 180, 275-83 (1929). Additional data noted but not used on the vapor pressure are values not tabulated or they were erratic of the solid are by J. F. Smith and R. L. Smythe, Acta Metallurgica, 7, 261-7 (1959); A. Ruckner, Metallwirtschaft, 15, 64-5 (1936); W. Leitgeb, Metallwirtschaft, 14, 269 (1935); and of the liquid by P. A. Vetter and O. Kubaschewski, Z. Elektrochem. 57, 243 (1953); W. Leitgeb, Z. anorg. Chem. 202, 312 (1931); C. Zwikker, Physica, 9, 246 (1928); O. Ruff and H. Hartmann, Z. anorg. Chem., 135, 29-45 (1924); and J. Johnston, Ind. Eng. Chem., 9, 876 (1917).

Magnesium (Mg)

(Liquid) At. Wt. = 24.32

T, °K.	C_p^o	$S^o - (F^o - H_{298}^o)/T$	$H^o - H_{298}^o$	ΔH_f^o	ΔF_f^o	Log K_p
0						
100						
200						
298	5.953	10.159	10.159	0.000	2.158	1.459 - 1.069
300	5.960	10.196	10.159	0.011	2.158	1.455 - 1.060
400	6.290	11.958	10.497	0.025	2.158	1.219 - 0.800
500	6.560	13.392	10.857	1.267	2.158	0.986 - 0.431
600	6.802	14.609	11.383	1.936	2.158	0.750 - 0.273
700	7.080	15.679	11.922	2.630	2.158	0.517 - 0.161
800	7.310	16.523	12.468	3.348	2.158	0.282 - 0.074
900	7.490	17.179	12.965	4.090	2.158	0.048 - 0.112
1000	7.680	17.688	13.424	4.874	2.158	0.000 - 0.000
1100	8.140	18.102	13.843	5.675	0.000	0.000
1200	8.400	18.421	14.203	6.502	0.000	0.000
1300	8.520	18.575	14.506	7.352	0.000	0.000
1400	8.590	18.655	14.760	8.222	0.000	0.000
1500	8.620	18.687	14.979	9.119	2.666	0.388
1600	8.640	18.696	15.070	10.070	2.952	0.659
1700	8.650	18.696	15.077	11.077	2.952	0.895
1800	8.650	18.696	15.077	12.141	2.952	1.092
1900	8.650	18.696	15.077	13.269	2.952	1.252
2000	8.650	18.696	15.077	14.464	2.952	1.382
2100	8.650	18.696	15.077	15.729	2.952	1.482
2200	8.650	18.696	15.077	17.064	2.952	1.553
2300	8.650	18.696	15.077	18.469	2.952	1.600
2400	8.650	18.696	15.077	19.944	2.952	1.622
2500	8.650	18.696	15.077	21.489	2.952	1.621
2600	8.650	18.696	15.077	23.104	2.952	1.601
2700	8.650	18.696	15.077	24.789	2.952	1.561
2800	8.650	18.696	15.077	26.544	2.952	1.501
2900	8.650	18.696	15.077	28.369	2.952	1.421
3000	8.650	18.696	15.077	30.264	2.952	1.321

MAGNESIUM (Mg)

(LIQUID)

AT. WT. = 24.32

ΔH_f^o 298.15 = [2.158] kcal. mole⁻¹

$T_m = 922 \pm 0.5^\circ K$

$T_b = 1379^\circ K$

Heat of Formation.

ΔH_f^o 298.15 (= ΔH_m 298.15) obtained from ΔH_m 922 by adding $H_{922} - H_{298.15}$ for solid and subtracting $H_{922} - H_{298.15}$ for liquid.

Heat Capacity and Entropy.

The heat capacity measurements of D. R. Stull and R. A. McDonald (950-1100°K) J. Am. Chem. Soc. 77, 5293 (1955) were used. Outside of the observed range C_p was extrapolated linearly with temperature. Below T_m the linear extrapolation was continued until the C_p curve for the solid is encountered at 710°K. At lower temperatures the C_p of the crystal is used. $S_{298.15}^o$ was calculated from that of the solid.

Melting.

See crystal for details.

Vaporization.

The normal boiling point was calculated by the third law and ΔH_v 298.15. This compares with 1377°K computed from the general vapor pressure equation for liquid Mg given on p 221 of *Chemical Thermodynamics* of the American Chemical Society, 1952, and experimentally determined values: 1376 ± 5°K by A. Schneider and U. Eick, Z. Elektrochem. 45, 888 (1953); 1380°K by E. Baur and R. Brunner, Helv. Chim. Acta 17, 958 (1934); 1370°K by W. Leitgeb, Z. anorg. Chem. 202, 305 (1931); and 1395°K by Greenwood, Chem. News 104, 31 (1911).

The ΔH_v 1378 is based on the liquid and ideal gas tables.

Mg

AT. WT. = 24.32

(IDEAL GAS)

MAGNESIUM, MONATOMIC (Mg)

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	.000	INFINITE	- 1.481	34.996	34.996	INFINITE
100	4.968	30.076	39.921	.984	35.339	- 71.153
200	4.968	34.520	35.958	.488	35.273	- 72.676
298	4.968	35.504	.000	.000	35.281	- 73.059
300	4.968	35.535	.009	.000	35.279	- 73.059
400	4.968	36.964	5.506	.506	35.162	- 73.233
500	4.968	38.072	1.003	1.003	35.017	- 73.399
600	4.968	39.978	1.500	1.500	34.845	- 73.554
700	4.968	40.744	1.996	1.996	34.648	- 73.695
800	4.968	40.407	2.493	2.493	34.420	- 73.821
900	4.968	40.993	2.990	2.990	34.156	- 73.934
1000	4.968	41.516	3.487	3.487	33.734	- 74.035
1100	4.968	41.990	3.984	3.984	33.249	- 74.122
1200	4.968	42.422	4.481	4.481	32.702	- 74.196
1300	4.968	42.820	4.977	4.977	32.192	- 74.257
1400	4.968	43.188	5.474	5.474	31.617	- 74.306
1500	4.968	43.530	5.971	5.971	31.000	- 74.344
1600	4.968	43.851	6.468	6.468	30.349	- 74.372
1700	4.968	44.152	6.965	6.965	29.664	- 74.391
1800	4.968	44.436	7.461	7.461	28.946	- 74.400
1900	4.968	44.705	7.958	7.958	28.195	- 74.400
2000	4.969	44.960	8.455	8.455	27.412	- 74.399
2100	4.969	45.202	8.952	8.952	26.597	- 74.388
2200	4.970	45.433	9.449	9.449	25.751	- 74.367
2300	4.972	45.654	9.946	9.946	24.874	- 74.336
2400	4.974	45.866	10.443	10.443	23.966	- 74.295
2500	4.978	46.066	10.941	10.941	23.027	- 74.244
2600	4.983	46.264	11.439	11.439	22.067	- 74.183
2700	4.989	46.453	11.938	11.938	21.086	- 74.112
2800	4.998	46.634	12.437	12.437	20.084	- 74.031
2900	5.009	46.810	12.937	12.937	19.061	- 73.939
3000	5.023	46.980	13.439	13.439	18.017	- 73.837
3100	5.040	47.145	13.942	13.942	16.954	- 73.724
3200	5.060	47.305	14.447	14.447	15.872	- 73.600
3300	5.085	47.461	14.954	14.954	14.771	- 73.465
3400	5.114	47.613	15.465	15.465	13.652	- 73.319
3500	5.148	47.762	15.977	15.977	12.516	- 73.172
3600	5.186	47.908	16.494	16.494	11.363	- 73.024
3700	5.229	48.050	17.014	17.014	10.194	- 72.874
3800	5.278	48.190	17.540	17.540	9.019	- 72.721
3900	5.332	48.328	18.070	18.070	7.838	- 72.565
4000	5.392	48.464	18.606	18.606	6.651	- 72.406
4100	5.457	48.598	19.149	19.149	5.458	- 72.244
4200	5.528	48.730	19.698	19.698	4.259	- 72.079
4300	5.604	48.861	20.254	20.254	3.054	- 71.912
4400	5.686	48.991	20.819	20.819	1.843	- 71.742
4500	5.773	49.120	21.392	21.392	.627	- 71.569
4600	5.865	49.248	21.971	21.971	.000	- 71.393
4700	5.964	49.375	22.556	22.556	.000	- 71.214
4800	6.067	49.501	23.147	23.147	.000	- 71.032
4900	6.176	49.628	23.743	23.743	.000	- 70.847
5000	6.289	49.754	24.344	24.344	.000	- 70.659
5100	6.407	49.879	24.950	24.950	.000	- 70.468
5200	6.530	50.005	25.561	25.561	.000	- 70.274
5300	6.658	50.130	26.177	26.177	.000	- 70.077
5400	6.790	50.256	26.800	26.800	.000	- 69.877
5500	6.927	50.382	27.428	27.428	.000	- 69.674
5600	7.069	50.508	28.061	28.061	.000	- 69.468
5700	7.215	50.634	28.700	28.700	.000	- 69.259
5800	7.367	50.761	29.344	29.344	.000	- 69.047
5900	7.523	50.888	30.000	30.000	.000	- 68.832
6000	7.684	51.016	31.349	31.349	.000	- 68.614

Dec. 31, 1960; Sept. 30, 1962

$\Delta H_f^\circ 0 = 35.0 \pm 0.01 \text{ kcal. mole}^{-1}$
 Ground State 1S_0
 $\Delta H_f^\circ 298.15 = 35.28 \pm 0.01 \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = 35.504 \text{ cal. mole}^{-1} \text{ deg}^{-1}$

Electronic Levels and Multiplicities

$\epsilon_i, \text{ cm}^{-1}$	g_i	$\epsilon_i, \text{ cm}^{-1}$	g_i
0.00	1	46403.14	5
21850.37	1	57020	9
21870.43	3	57204	28
21911.14	5	57854	12
35051.36	3	58469	58
41197.37	3	59315	51
43503.0	1	59878	51
		60397	102
		60887	154

Heat of Formation.

$\Delta H_f^\circ 298.15$ ($-\Delta H_s 298.15$) is calculated as described on the table for crystal.

Heat Capacity and Entropy.

Thermodynamic functions were calculated using electronic levels and multiplicities from C. E. Moore [Natl. Bur. Standards Circ. 467, Vol. 1 (1949)]. Higher levels were averaged.

Magnesium Unipositive Ion (Mg⁺)

(Ideal Gas) GFW = 24.31145

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0							
100	4.264	34.879	36.879	.000	211.559	201.406	-147.635
200	4.268	36.910	38.879	.009	211.566	201.393	-146.678
295	4.268	38.339	37.078	.504	211.946	197.876	-108.115
300	4.268	38.448	37.442	1.003	212.208	194.319	-94.937
400	4.264	40.323	37.854	1.500	212.423	190.691	-69.459
500	4.268	41.119	38.247	1.994	212.722	187.012	-58.386
600	4.268	41.782	38.622	2.480	213.000	183.280	-49.306
700	4.264	42.358	38.985	2.960	213.258	179.500	-43.598
800	4.264	42.862	39.340	3.437	213.496	175.666	-39.453
900	4.264	43.300	39.684	3.911	213.714	171.776	-35.453
1000	4.264	43.685	39.923	4.380	213.914	167.830	-31.499
1100	4.264	44.023	40.157	4.844	214.096	163.830	-27.499
1200	4.264	44.317	40.387	5.304	214.262	159.776	-23.446
1300	4.264	44.570	40.612	5.760	214.414	155.666	-19.346
1400	4.264	44.785	40.832	6.212	214.554	151.500	-15.199
1500	4.264	44.965	41.048	6.660	214.682	147.286	-11.000
1600	4.264	45.114	41.260	7.104	214.798	143.022	-6.754
1700	4.264	45.237	41.468	7.544	214.902	138.710	-2.466
1800	4.264	45.337	41.672	7.980	215.000	134.350	1.822
1900	4.264	45.416	41.872	8.412	215.096	129.946	6.066
2000	4.264	45.476	42.068	8.840	215.182	125.490	9.766
2100	4.264	45.517	42.252	9.264	215.260	120.982	12.910
2200	4.264	45.540	42.432	9.684	215.330	116.422	15.500
2300	4.264	45.548	42.608	10.100	215.392	111.810	17.530
2400	4.264	45.544	42.780	10.512	215.448	107.146	19.000
2500	4.264	45.528	42.948	10.920	215.498	102.430	20.000
2600	4.264	45.500	43.112	11.324	215.542	97.662	20.500
2700	4.264	45.460	43.272	11.714	215.580	92.842	20.500
2800	4.264	45.408	43.428	12.100	215.612	87.972	20.000
2900	4.264	45.344	43.580	12.480	215.638	83.052	19.000
3000	4.264	45.268	43.728	12.856	215.658	78.082	17.500
3100	4.264	45.180	43.872	13.228	215.672	73.062	15.500
3200	4.264	45.080	44.012	13.596	215.682	67.992	13.000
3300	4.264	44.968	44.148	13.960	215.688	62.872	10.000
3400	4.264	44.844	44.280	14.320	215.690	57.702	6.000
3500	4.264	44.708	44.408	14.676	215.688	52.482	1.000
3600	4.264	44.560	44.532	15.028	215.682	47.212	-4.000
3700	4.264	44.400	44.652	15.376	215.672	41.892	-9.000
3800	4.264	44.228	44.770	15.720	215.658	36.522	-14.000
3900	4.264	44.044	44.884	16.060	215.640	31.102	-19.000
4000	4.264	43.848	44.994	16.400	215.618	25.632	-24.000
4100	4.264	43.640	45.100	16.740	215.592	20.112	-29.000
4200	4.264	43.420	45.204	17.080	215.562	14.542	-34.000
4300	4.264	43.188	45.304	17.416	215.528	8.922	-39.000
4400	4.264	42.944	45.400	17.748	215.490	3.252	-44.000
4500	4.264	42.688	45.492	18.076	215.448	-2.468	-49.000
4600	4.264	42.420	45.580	18.400	215.402	-8.188	-54.000
4700	4.264	42.140	45.664	18.720	215.352	-13.908	-59.000
4800	4.264	41.848	45.744	19.036	215.300	-19.628	-64.000
4900	4.264	41.544	45.820	19.348	215.246	-25.348	-69.000
5000	4.264	41.228	45.892	19.656	215.190	-31.068	-74.000
5100	4.264	40.900	45.960	19.960	215.132	-36.788	-79.000
5200	4.264	40.560	46.024	20.260	215.072	-42.508	-84.000
5300	4.264	40.208	46.084	20.556	215.010	-48.228	-89.000
5400	4.264	39.844	46.140	20.848	214.946	-53.948	-94.000
5500	4.264	39.468	46.192	21.136	214.880	-59.668	-99.000
5600	4.264	39.080	46.240	21.420	214.812	-65.388	-104.000
5700	4.264	38.680	46.284	21.700	214.742	-71.108	-109.000
5800	4.264	38.268	46.324	21.976	214.670	-76.828	-114.000
5900	4.264	37.844	46.360	22.248	214.596	-82.548	-119.000
6000	4.264	37.408	46.392	22.516	214.520	-88.268	-124.000

Dec. 31, 1967

MAGNESIUM UNIPOSITIVE ION(Mg⁺)

Ground State Configuration 1s₀

S_{298.15} = 36.879 gibbs/mol

ΔHf°₀ = 211.3 ± 0.1 kcal/mol

ΔHf°_{298.15} = 211.6 ± 0.1 kcal/mol

(IDEAL GAS)

GFW = 24.31145

Mg⁺

Electronic Levels and Quantum Weights

e _i , cm ⁻¹	g _i	e _i , cm ⁻¹	g _i
0.0	2	106879.10	76
35730.45	6	112273.43	44
71209.04	12	114385.15	44
80641.13	6	115847.07	32
94271.23	32	117578.72	96

Heat of Formation

We derive the heat of formation at 0°K from the reaction Mg(g) - e⁻(g) + Mg⁺(g) using the JANAF auxiliary value for Mg(g) and an ionization potential of 176.278 kcal/mol from C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, Vol. I, 1949.

Heat Capacity and Entropy

We take the electronic levels and quantum weights from C. E. Moore, loc. cit. H°₀ - H°₂₉₈ = -1.481 kcal/mol at 0°K.

Mg⁺

(Ideal Gas) Mol. Wt. = 38.328

MOL. WT. = 38.328

(IDEAL GAS)

MONOMAGNESIUM MONONITRIDE (MgN)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	+0.00	INFINITE	-2.148	69.084	69.084	INFINITE
100	9.668	45.789	60.321	-1.453	68.282	146.064
200	7.311	50.696	54.412	-0.743	69.079	70.309
298	7.823	53.713	51.713	+0.000	69.000	45.547
300	7.832	53.761	51.713	+0.14	68.997	45.235
400	8.208	56.070	54.025	+0.18	68.938	32.682
500	8.449	57.929	54.626	1.552	68.678	25.159
600	8.607	59.484	55.310	2.505	68.506	20.171
700	8.716	60.820	56.004	3.371	68.316	15.611
800	8.795	61.973	56.697	4.163	68.105	11.649
900	8.854	63.028	57.329	5.130	67.837	8.486
1000	8.901	63.964	57.946	6.017	67.564	5.702
1100	8.939	64.814	58.533	6.909	67.285	3.332
1200	8.970	65.593	59.089	7.805	66.993	1.368
1300	9.000	66.322	59.627	8.706	66.689	-0.289
1400	9.023	66.980	60.120	9.605	66.370	-1.638
1500	9.046	67.603	60.558	10.508	66.038	-2.697
1600	9.066	68.188	61.054	11.414	65.692	-3.461
1700	9.085	68.738	61.460	12.321	65.331	-4.331
1800	9.102	69.256	61.879	13.230	64.955	-5.301
1900	9.119	69.750	62.307	14.142	64.565	-6.372
2000	9.136	70.219	62.651	15.054	64.160	-7.544
2100	9.151	70.665	63.061	15.969	63.741	-8.817
2200	9.166	71.091	63.416	16.885	63.307	-10.192
2300	9.180	71.498	63.736	17.802	62.858	-11.668
2400	9.195	71.890	64.029	18.721	62.394	-13.244
2500	9.209	72.265	64.409	19.641	61.915	-14.920
2600	9.223	72.627	64.718	20.562	61.421	-16.696
2700	9.236	72.975	65.017	21.485	60.912	-18.572
2800	9.248	73.310	65.299	22.410	60.388	-20.548
2900	9.263	73.636	65.589	23.335	59.849	-22.624
3000	9.276	73.950	65.863	24.262	59.294	-24.800
3100	9.288	74.255	66.129	25.190	58.725	-27.076
3200	9.301	74.550	66.387	26.120	58.141	-29.452
3300	9.316	74.836	66.638	27.053	57.542	-31.928
3400	9.330	75.114	66.884	27.983	56.928	-34.504
3500	9.339	75.385	67.123	28.916	56.300	-37.180
3600	9.351	75.648	67.356	29.850	55.659	-40.056
3700	9.364	75.904	67.584	30.786	55.004	-43.132
3800	9.376	76.154	67.806	31.723	54.335	-46.408
3900	9.389	76.398	68.023	32.660	53.650	-50.084
4000	9.401	76.636	68.236	33.601	52.950	-54.060
4100	9.413	76.868	68.443	34.542	52.235	-58.336
4200	9.425	77.095	68.647	35.484	51.505	-62.912
4300	9.437	77.317	68.846	36.427	50.760	-67.788
4400	9.449	77.534	69.041	37.371	50.000	-72.964
4500	9.462	77.747	69.232	38.317	49.224	-78.440
4600	9.474	77.955	69.419	39.263	48.441	-84.216
4700	9.486	78.159	69.603	40.211	47.649	-90.292
4800	9.498	78.356	69.783	41.160	46.847	-96.668
4900	9.510	78.548	69.959	42.110	46.035	-103.344
5000	9.522	78.747	70.134	43.062	45.212	-110.320
5100	9.534	78.935	70.305	44.015	44.379	-117.596
5200	9.546	79.121	70.473	44.969	43.532	-125.172
5300	9.558	79.304	70.638	45.924	42.673	-132.948
5400	9.569	79.481	70.800	46.880	41.800	-140.924
5500	9.581	79.657	70.959	47.838	40.915	-149.100
5600	9.593	79.830	71.116	48.797	40.018	-157.476
5700	9.605	80.000	71.270	49.757	39.110	-166.052
5800	9.617	80.166	71.422	50.716	38.188	-174.828
5900	9.629	80.331	71.572	51.675	37.253	-183.804
6000	9.641	80.493	71.719	52.644	36.305	-192.980

Mar. 31, 1964

Ground State Configuration $[2\pi]$
 $\Delta H_f^0 = [69 \pm 6]$ kcal. mole⁻¹
 $S_{298.15}^0 = [53.713]$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^0 298.15 = [69 \pm 6]$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

ϵ_i , cm. ⁻¹	g_i
0	[4]

$\mu_e = [700]$ cm.⁻¹
 $\mu_e = [4.8]$ cm.⁻¹
 $\mu_e = [0.0052]$
 $\alpha_a = [1.85] \text{ \AA}$
 $r_e = 1$

Heat of Formation.

The ΔH_f^0 298.15 for MgN was estimated from bond strengths using MgO and comparison with analogous pairs of compounds such as, PN and PO, and also the bond strengths of C-N and C-O in organic compounds.

Heat Capacity and Entropy.

The r_e value for MgN was estimated from MgO by comparison with similar pairs PO and PN, SiO and SiN, and AlO and AlN. Using Guggenheim's Relation, Proc. Phys. Soc. (London) 58, 456 (1946), μ for MgO was found to lie between the single and multiple bonding cases. Magnesium nitride was assumed to be similar to MgO and $\mu_e = 700$ cm.⁻¹ was obtained. It was assumed that the $X_e \mu^{1/2}$ value for MgN was equal to that for MgO thus giving $\mu_e X_e = 4.8$ cm.⁻¹. B_e was calculated from r_e . The α_e value was calculated from B_e , μ_e and $\mu_e X_e$.

Magnesium Oxide (MgO)

(Crystal)

Mol. Wt. = 40.3114

MgO

MAGNESIUM OXIDE (MgO)

(CRYSTAL)

MOL. WT. = 40.3114

T. °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	1.000	INFINITE	0.000	INFINITE	1.235	-142.701	-142.701	INFINITE
100	1.866	6.038	12.445	1.186	-143.163	-140.920	-140.920	307.906
200	3.370	3.369	7.177	0.762	-143.640	-138.584	-138.584	151.431
298	8.882	6.440	0.000	0.000	-143.700	-135.985	-135.985	99.675
300	8.915	6.405	0.016	0.016	-143.701	-135.937	-135.937	99.025
400	10.168	9.251	6.807	0.718	-143.709	-133.346	-133.346	72.025
500	10.848	11.598	7.537	2.030	-143.664	-130.759	-130.759	57.152
600	11.285	13.616	8.386	3.138	-143.603	-128.185	-128.185	46.689
800	11.604	15.381	9.262	4.283	-143.540	-125.620	-125.620	39.218
1000	12.057	18.355	10.966	6.452	-143.463	-123.052	-123.052	28.918
1200	12.232	19.635	11.768	7.867	-143.380	-120.512	-120.512	25.740
1400	12.382	20.808	12.537	9.098	-143.297	-117.980	-117.980	22.848
1600	12.507	21.891	13.272	10.243	-143.211	-115.453	-115.453	20.438
1800	12.606	22.906	13.978	11.304	-143.122	-112.924	-112.924	18.538
2000	12.683	23.873	14.645	12.280	-143.030	-110.396	-110.396	16.598
2200	12.743	24.707	15.287	13.180	-142.936	-107.868	-107.868	14.745
2400	12.821	25.532	15.902	13.999	-142.840	-105.340	-105.340	13.147
2600	12.900	26.357	16.499	14.740	-142.742	-102.812	-102.812	11.739
2800	13.027	27.175	17.073	15.404	-142.642	-100.284	-100.284	10.476
3000	13.136	28.427	17.623	16.000	-142.540	-97.756	-97.756	9.375
3200	13.214	29.070	18.633	21.917	-173.548	-71.788	-71.788	7.471
3400	13.275	29.586	19.122	23.243	-173.175	-66.948	-66.948	6.650
3600	13.321	30.000	19.584	24.000	-172.800	-62.108	-62.108	5.920
3800	13.450	30.850	20.051	25.917	-172.437	-57.268	-57.268	5.290
4000	13.529	31.400	20.494	27.266	-172.027	-52.540	-52.540	4.763
4200	13.607	31.933	20.924	28.623	-171.634	-47.768	-47.768	4.315
4400	13.676	32.447	21.341	29.980	-171.258	-43.012	-43.012	3.961
4600	13.736	32.947	21.747	31.340	-170.890	-38.260	-38.260	3.681
4800	13.843	33.431	22.141	32.740	-170.429	-33.541	-33.541	3.428
5000	13.921	33.902	22.526	34.128	-170.020	-28.829	-28.829	3.190
5200	14.000	34.359	22.900	35.525	-169.605	-24.127	-24.127	2.971
5400	14.079	34.805	23.265	36.928	-169.187	-19.443	-19.443	2.778
5600	14.157	35.240	23.620	38.330	-168.765	-14.760	-14.760	2.606
5800	14.236	35.663	23.966	39.740	-168.340	-10.107	-10.107	2.454
6000	14.314	36.077	24.309	41.187	-167.914	-5.463	-5.463	2.319
6200	14.393	36.482	24.642	42.623	-167.484	-0.828	-0.828	2.198
6400	14.472	36.877	24.967	44.066	-167.053	3.798	3.798	2.088
6600	14.551	37.264	25.284	45.510	-166.620	8.464	8.464	1.988
6800	14.629	37.643	25.598	46.976	-166.185	13.137	13.137	1.897
7000	14.707	38.014	25.904	48.443	-165.750	17.798	17.798	1.816

ΔH_f^o 0 = -142.7 ± 0.3 kcal. mole⁻¹
 ΔH_f^o 298.15 = -143.7 ± 0.3 kcal. mole⁻¹
 ΔH_m^o = [16.5 ± 1.5] kcal. mole⁻¹
 T_m = 3098 ± 20 °K.
 T_B = 3456°K.

Heat of Formation.

C. E. Holley and E. J. Huber, J. Am. Chem. Soc. 73, 5577 (1951) reported ΔH_f^o 298 (MgO, c) = -143.7 kcal. mole⁻¹ by combustion calorimetry. Heat of solution measurements by C. H. Shomate and E. H. Huffman, J. Am. Chem. Soc. 65, 1625 (1943) yielded ΔH_f^o 298 (MgO, c) = -143.84 kcal. mole⁻¹, well within the adopted ΔH_f^o 298 (MgO, c) = -143.7 ± 0.3 kcal. mole⁻¹.

Heat Capacity and Entropy.

Low temperature heat capacities have been reported by:

1. W. Lien and N. Phillips, J. Chem. Phys. 29, 1415 (1958), 1.5-4°K.
2. W. F. Glauque and R. C. Archibald, J. Am. Chem. Soc. 59, 561 (1937), 20-301°K.
3. G. S. Parks and K. K. Kelley, J. Phys. Chem. 50, 47 (1926), 94-291°K.
4. T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) A250, 70 (1959), 10-270°K.
5. P. Gunther, Ann. Physik 51, 828 (1916), 21-84°K.

High temperature heat contents have been reported by:

6. A. C. Victor and T. B. Douglas, J. Res. N.B.S. 57A, 325 (1953), 373-1173°K.
7. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6295, (1963), 400-1800°K.

The samples of (1) and (2) were finely divided magnesia and the other samples were periclase. Periclase is taken to be the standard state. The high temperature heat content data of (6) and (7) were joined by a Shomate plot with the low temperature C_p data of (4). The heat capacity was extrapolated linearly above 1800°K to a value of 14 cal. mole⁻¹ deg.⁻¹ at 3100°K. S_{298.15} = 6.44 cal. deg.⁻¹ mole⁻¹ is from (4).

Melting Data.

T_m (MgO, c) = 3098 ± 20°K by R. N. McNally, P. I. Peters, and P. H. Ribbe, J. Am. Ceram. Soc. 44, 491 (1961) was adopted. Their value is 41°K higher than the earlier measurements of C. W. Kanolt, J. Wash. Acad. Sci. 3, 315 (1913). K. K. Kelley, Bur. Mines Bull. 393 (1936) calculated ΔH_m^o (MgO, c) = 18.5 ± 1.5 kcal./mole from melting point measurements in the MgO - ZnO system.

Sublimation Data.

T_B is the temperature at which the free energy change of the reaction MgO(c) = MgO(g) approaches zero. The difference between ΔH_f^o 298.15 for MgO(c) and MgO(g) is ΔH_B^o 298.15.

MAGNESIUM OXIDE (MgO)

(LIQUID)

MOL. WT. = 40.3114

$\Delta H_f^\circ 298.15 = [12.033] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_m^\circ = [18.5 \pm 1.5] \text{ kcal. mole}^{-1}$
 $\Delta H_v^\circ = [113.4] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [-126.137] \text{ kcal. mole}^{-1}$
 $\Delta H_m^\circ = [18.5 \pm 1.5] \text{ kcal. mole}^{-1}$
 $\Delta H_v^\circ = [113.4] \text{ kcal. mole}^{-1}$

$S_{298.15}^\circ = [12.033] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 3098^\circ \text{K.}$
 $T_B = [3533]^\circ \text{K.}$

Heat of Formation.

$\Delta H_f^\circ 298.15(1)$ was calculated from $\Delta H_f^\circ 298.15(c)$ by adding ΔH_m° and the difference between $H_m^\circ - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at 2066°K. $C_p(1)$ below 2066°K. were assumed to be equal to those of $\text{MgO}(c)$. At and above 2066°K. the heat capacities were assumed to be constant at $7.25 \text{ cal. deg.}^{-1} \text{ g. atom}^{-1}$. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $\text{MgO}(c)$ table for details.

Vaporization Data.

W. R. Mott, Tran. Am. Electrochem. Soc. 34, 255 (1918) estimated the boiling point at 3873°K. by comparing crater distances of arc image deposits with reference compounds. $T_B = 3533^\circ \text{K.}$ is the temperature at which the free energy change of the reaction $\text{MgO}(l) = \text{MgO}(g)$ approaches zero. The difference between $\Delta H_f^\circ 3533$ for $\text{MgO}(g)$ and $\text{MgO}(l)$ is ΔH_v° .

Dec. 31, 1965

MgO

Magnesium Oxide (MgO)

(Ideal Gas) Mol. Wt. = 40.3114

MgO

MAGNESIUM OXIDE (MgO) (IDEAL GAS) MOL. WT. = 40.3114

T, °K.	C _p ^o	S ^o	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	6.900	46.139	INFINITE	2.111	1.122	1.122	INFINITE
100	6.950	46.139	59.295	1.416	1.103	1.093	1.974
200	7.104	49.683	53.562	0.716	1.105	1.105	3.655
298	7.498	52.889	52.889	0.000	1.000	1.000	3.763
300	7.506	52.936	52.890	0.014	0.966	1.122	3.768
400	7.699	55.181	53.768	0.418	0.965	1.122	3.768
500	8.109	58.346	55.766	1.590	0.995	0.1174	4.010
600	8.396	58.459	54.426	2.420	0.966	1.122	4.046
700	8.545	58.765	55.097	3.267	1.144	1.304	4.060
800	8.654	60.913	55.754	4.327	1.120	1.486	4.061
900	8.734	61.817	56.407	5.407	1.100	1.668	4.061
1000	8.802	62.861	56.987	6.574	1.073	1.850	3.999
1100	8.854	63.703	57.560	7.757	1.046	2.032	3.939
1200	8.897	64.475	58.105	8.945	1.020	2.214	3.883
1300	8.934	65.189	58.622	10.138	0.995	2.396	3.830
1400	8.966	65.842	59.115	11.336	0.970	2.578	3.780
1500	8.994	66.472	59.585	12.539	0.945	2.760	3.734
1600	9.019	67.053	60.034	13.743	0.920	2.942	3.687
1700	9.042	67.600	60.463	14.947	0.895	3.124	3.647
1800	9.063	68.118	60.874	16.151	0.870	3.306	3.607
1900	9.083	68.608	61.269	17.355	0.845	3.488	3.567
2000	9.101	69.075	61.647	18.559	0.820	3.670	3.527
2100	9.119	69.519	62.012	19.763	0.795	3.852	3.487
2200	9.135	69.944	62.363	20.967	0.770	4.034	3.447
2300	9.151	70.350	62.701	22.171	0.745	4.216	3.407
2400	9.166	70.738	63.028	23.375	0.720	4.398	3.367
2500	9.182	71.113	63.344	24.579	0.695	4.580	3.327
2600	9.196	71.475	63.650	25.783	0.670	4.762	3.287
2700	9.210	71.822	63.946	26.987	0.645	4.944	3.247
2800	9.224	72.157	64.233	28.191	0.620	5.126	3.207
2900	9.238	72.481	64.512	29.395	0.595	5.308	3.167
3000	9.251	72.795	64.785	30.599	0.570	5.490	3.127
3100	9.265	73.098	65.047	31.803	0.545	5.672	3.087
3200	9.278	73.393	65.303	33.007	0.520	5.854	3.047
3300	9.291	73.678	65.552	34.211	0.495	6.036	3.007
3400	9.304	73.956	65.796	35.415	0.470	6.218	2.967
3500	9.316	74.226	66.032	36.619	0.445	6.400	2.927
3600	9.329	74.488	66.264	37.823	0.420	6.582	2.887
3700	9.341	74.744	66.489	39.027	0.395	6.764	2.847
3800	9.353	74.993	66.710	40.231	0.370	6.946	2.807
3900	9.366	75.237	66.926	41.435	0.345	7.128	2.767
4000	9.378	75.474	67.136	42.639	0.320	7.310	2.727
4100	9.390	75.706	67.342	43.843	0.295	7.492	2.687
4200	9.402	75.932	67.544	45.047	0.270	7.674	2.647
4300	9.414	76.153	67.742	46.251	0.245	7.856	2.607
4400	9.426	76.370	67.936	47.455	0.220	8.038	2.567
4500	9.438	76.582	68.125	48.659	0.195	8.220	2.527
4600	9.450	76.789	68.311	49.863	0.170	8.402	2.487
4700	9.462	76.993	68.494	51.067	0.145	8.584	2.447
4800	9.474	77.192	68.673	52.271	0.120	8.766	2.407
4900	9.485	77.388	68.849	53.475	0.095	8.948	2.367
5000	9.497	77.579	69.022	54.679	0.070	9.130	2.327
5100	9.509	77.768	69.191	55.883	0.045	9.312	2.287
5200	9.521	77.952	69.358	57.087	0.020	9.494	2.247
5300	9.532	78.134	69.522	58.291	0.000	9.676	2.207
5400	9.544	78.312	69.683	59.495	0.000	9.858	2.167
5500	9.556	78.487	69.842	60.699	0.000	10.040	2.127
5600	9.567	78.660	69.998	61.903	0.000	10.222	2.087
5700	9.579	78.829	70.151	63.107	0.000	10.404	2.047
5800	9.591	78.996	70.302	64.311	0.000	10.586	2.007
5900	9.602	79.160	70.451	65.515	0.000	10.768	1.967
6000	9.614	79.321	70.597	66.719	0.000	10.950	1.927

Dec. 31, 1980; Dec. 31, 1965

Ground State Configuration 3Σ $\Delta H_f^o = 1.0 \pm 20$ kcal. mole⁻¹ $S_{298.15}^o = 52.889$ cal. deg.⁻¹ mole⁻¹ $\Delta H_f^o 298.15 = 1.0 \pm 20$ kcal. mole⁻¹

Electronic Levels and Quantum Weights

ϵ_1 , cm. ⁻¹	g_1
0	3

 $\omega_e = 902$ cm.⁻¹ $\omega_e x_e = 13.0$ cm.⁻¹ $\sigma = 1$ $B_e = [0.625]$ cm.⁻¹ $\alpha_e = [0.0094]$ cm.⁻¹ $r_e = [1.672]$ Å

Heat of Formation.

There is considerable discordance in the heat of formation results even though results were adjusted to a common 3Σ ground state where necessary. A mean $\Delta H_f^o 298$ (MgO, g) = 1.0 ± 20 kcal. mole⁻¹ was selected.

R. L. Altman, J. Phys. Chem. 67, 365 (1963) made a Knudsen effusion and oxygen transpiration study of the vaporization of MgO. The predominant vapor species over MgO(c) were shown to be Mg(g) and O₂(g). MgO transpiration results with oxygen at 1 atm yielded a 3rd law heat of sublimation $\Delta H_g^o 298$ (MgO, g) = 162.3 kcal. mole⁻¹ and $\Delta H_f^o 298$ (MgO, g) = 18.6 kcal. mole⁻¹.

J. Drowart, O. Exsteen and G. Verhaegen, Trans. Far. Soc. 60, 1920 (1964) used the Knudsen effusion-mass spectrometer technique to determine relative ion intensities and enthalpies for the reaction $MgO(g) + O(g) \rightarrow Mg(g) + O_2(g)$. After adjusting their values for a 3Σ ground state we calculated $\Delta H_f^o 298$ (MgO, g) = 11.9 kcal. mole⁻¹. Similar calculations for their data on $MgO(g) + WO_2(g) \rightarrow Mg(g) + WO_3(g)$ yielded $\Delta H_f^o 298$ = 10.5 kcal. mole⁻¹. The agreement is fortuitous, however, since uncertainties in the JANAF values for $WO_2(g)$ and $WO_3(g)$ are on the order of 7 kcal. each.

R. F. Porter, W. A. Chupka and M. O. Inghram, J. Chem. Phys. 23, 1347 (1955) mass spectrometrically determined an upper limit for the vapor pressure of MgO(g) over MgO(c) at 1950°K. Their results reduce to a lower limit of 148.6 kcal. mole⁻¹ for $\Delta H_f^o 298.15$ (MgO, c) or a lower limit of 4.9 kcal. mole⁻¹ for $\Delta H_f^o 298$ (MgO, g).

E. Bulewicz and T. Sugden, Trans. Far. Soc. 55, 720 (1959), using a flame photometric technique, reported $D_0^o = 98 \pm 2$ kcal. mole⁻¹ for MgO. $\Delta H_f^o 298$ (MgO, g) = -4.1 kcal. mole⁻¹ was calculated.

I. Veita and L. Ourvich, Optika and Spektroskopiya 1, 22 (1956) used a flame technique to obtain $D_0^o = 100$ kcal. mole⁻¹. A 4 kcal. mole⁻¹ adjustment for 1Σ to 3Σ yields $\Delta H_f^o 298$ (MgO, g) = -2.1 kcal. mole⁻¹.

The flame method data of L. Huldt and A. Lagerquist, Arkiv Fysik 2, 333 (1950) yielded a 3Σ adjusted $D_0^o = 115$ kcal. mole⁻¹. $\Delta H_f^o 298$ (MgO, g) = -21.1 kcal. mole⁻¹ was calculated.

L. Brewer and R. F. Porter, J. Chem. Phys. 22, 1876 (1954) have shown by vapor pressure measurements on MgO(c) that the solid vaporizes mainly into molecular species. They gave spectroscopic evidence that the 1Σ electronic state of MgO(g) is not the principal vaporizing species. Using their vapor pressures for the reaction $MgO(c) = MgO(g)$ and a 3Σ ground state we calculated 2nd and 3rd law heat of sublimation at 298°K. of 120.0 and 129.1 kcal. mole⁻¹. The 3rd law value yields $\Delta H_f^o 298$ (MgO, g) = -14.6 kcal. mole⁻¹.

Heat Capacity and Entropy.

The fundamental frequency and anharmonicity correction were reported by L. Brewer and R. Porter, J. Chem. Phys. 22, 1876 (1954) and are based on a 3Σ ground state. The rotational constants were estimated by H. L. Schick 51. AVCO Corp. RAD-SR-62-251, 15 Dec. 1962. Although the ground state and spectroscopic constants are

In doubt, the free energies are probably within 8T in 3 of true values.

MgO

Magnesium Metasilicate (MgSiO₃)

GFW = 100.3962

(Crystal)

T, °K	C _p ^a	S ^b	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔH ^c	ΔG ^d	Log K ^e
0	0.000	0.000	INFINITE	INFINITE	2.895	-	-368.018	-368.018	INFINITE
100	5.715	2.657	29.737	29.737	2.708	-	-369.090	-369.090	192.958
200	14.255	6.424	17.834	17.834	1.682	-	-369.951	-369.951	359.133
298	19.561	10.197	16.197	16.197	1.000	-	-370.203	-370.203	595.118
300	19.653	16.318	16.197	16.197	0.36	-	-370.203	-370.203	595.118
400	22.513	22.404	17.008	17.008	2.158	-	-370.269	-370.269	747.114
500	24.262	27.467	18.622	18.622	4.502	-	-370.207	-370.207	1019.619
600	25.571	32.170	20.510	20.510	6.946	-	-370.081	-370.081	1292.464
700	26.478	36.197	22.448	22.448	9.610	-	-369.918	-369.918	1575.333
800	27.072	39.475	24.415	24.415	12.328	-	-369.718	-369.718	1858.202
900	28.603	43.139	26.314	26.314	15.142	-	-369.498	-369.498	2141.071
1000	28.762	46.346	28.168	28.168	18.178	-	-371.245	-371.245	2423.940
1100	28.762	49.087	29.987	29.987	21.056	-	-371.065	-371.065	2706.809
1200	28.762	51.210	31.686	31.686	23.931	-	-370.932	-370.932	2989.678
1300	28.762	52.718	33.282	33.282	27.418	-	-370.439	-370.439	3272.547
1400	29.262	56.367	34.856	34.856	30.144	-	-400.718	-400.718	3555.416
1500	29.262	58.406	36.359	36.359	33.070	-	-400.270	-400.270	3838.285
1600	29.262	60.294	37.797	37.797	35.946	-	-399.841	-399.841	4121.154
1700	29.262	62.068	39.173	39.173	38.923	-	-411.423	-411.423	4404.023
1800	29.262	63.751	40.492	40.492	41.949	-	-410.977	-410.977	4686.892
1900	29.262	65.133	41.757	41.757	44.775	-	-410.560	-410.560	4969.761
2000	29.262	66.424	42.973	42.973	47.701	-	-410.110	-410.110	5252.630
2100	29.262	68.252	44.193	44.193	50.427	-	-409.489	-409.489	5535.500
2200	29.262	69.272	45.270	45.270	53.254	-	-409.277	-409.277	5818.369
2300	29.262	70.914	46.337	46.337	56.480	-	-408.872	-408.872	6101.238
2400	29.262	72.159	47.407	47.407	59.406	-	-408.476	-408.476	6384.107
2500	29.262	73.334	48.421	48.421	62.332	-	-408.090	-408.090	6666.976

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1967

Heat Capacity and Entropy

See liquid table.

Transition Data

T₁ = 903°K is obtained from Boyd et al. (3). The authors determined the phase diagram boundary at high pressures and extrapolated to one atmosphere. T₂ = 1258°K is taken from Atlas (10). Below 903°K the phase is known as clinonastatite. Between 903° and 1258°K it is rhombic enstatite and above 1258°K it is protoenstatite. We calculate ΔH₁^o and ΔH₂^o from dT/dP (slopes of the isotherms) = 2.6°/kbar and 84°/kbar reported by Boyd et al. (3, 13) and from the densities of clinonastatite (3.210 gm/cc) and rhombic enstatite (3.208 gm/cc) reported by Stephenson et al. (11) and the density of protoenstatite (3.110 gm/cc) reported by Smith (12).

Melting Data

See liquid table.

S_{298.15} = 16.197 ± 0.2 gibbs/molT₁ = 903 °KT₂ = 1258 °KT_m = 1850 ± 2 °K

Heat of Formation

Torgeson et al. (1) report a ΔH₂₉₈^o = -8.59 ± 0.15 kcal/mol for reaction (a). They used a hydrofluoric acid solution calorimeter and measured the heats of solution of each component. They appear to have made the water-absorption correction to the heat of solution of SiO₂(c) in the wrong direction. We reverse the correction so that the new ΔH₂₉₈^o almost overlaps the range observed by King (11). We derive ΔH₂₉₈^o (MgSiO₃, c) = -370.20 ± 1.0 kcal/mol using the ΔH₂₉₈^o of MgO(c) and SiO₂(c, low quartz) from the JANAF tables.

Reesman et al. (2) calculated a ΔG₂₉₈^o = 23.72 kcal/mol for reaction (b) using aqueous solubility data. We use the ΔG₂₉₈^o of H₂O(l) and OH⁻(aq) from sources 3, ΔG₂₉₈^o of H₂SiO₄(aq) from source 4 and ΔG₂₉₈^o of Mg⁺⁺(aq) from source 6 and we obtain a ΔG₂₉₈^o (MgSiO₃, c) = -352.534 kcal/mol. We derive a ΔH₂₉₈^o (MgSiO₃, c) = -373.723 kcal/mol using the above ΔG₂₉₈^o of MgSiO₃(c) and the entropies of MgO(c), SiO₂(c) and O₂(g) from the JANAF tables.

We choose the heat of formation derived from the result of Torgeson et al. (1) which is considered to be better since it relates directly to the oxides. Also the ΔG₂₉₈^o (MgSiO₃, c) thus calculated is in very good agreement with that derived from the activities of SiO₂ and MgO (in the SiO₂ - MgO system) measured by Rein et al. (5). The ΔH₂₉₈^o (MgSiO₃, c) derived from the work of Reesman et al. is less accurate and involves uncertainties in the auxiliary data used to calculate the value.

Source	Method	Reaction
Torgeson et al.	HF solution calorimeter	(a) MgO(c) + SiO ₂ (c) = MgSiO ₃ (c)
Reesman et al.	Aqueous solubility	(b) MgSiO ₃ (c) + 3H ₂ O(l) = Mg ⁺⁺ (aq) + H ₄ SiO ₄ (aq) + 2OH ⁻ (aq)

Source

1. D. R. Torgeson and Th. G. Sahara, J. Am. Chem. Soc. 70, 2156 (1948).
2. A. L. Reesman and W. D. Kellner, Am. Mineralogist 50, 1779-39 (1965).
3. U. S. Natl. Bur. Std. Tech. Note 270-1, 1955.
4. U. S. Natl. Bur. Std. Tech. Note 270-2, 1956.
5. U. S. Natl. Bur. Std. Circ. 500, 1952.
6. R. H. Rein and J. Chipman, Trans. AIME 233, 415-426 (1965).
7. K. K. Kelley, J. Am. Chem. Soc. 65, 338-41 (1943).
8. H. Wagner, Z. Anorg. Allgem. Chem. 208, 1-22 (1932).
9. F. R. Boyd and J. L. England, Ann. Rept. Director of the Geophysical Laboratory, No. 1455, 117-120 (1965).
10. L. Atlas, J. Geol. 60, 125-47 (1952).
11. D. A. Stephenson, C. B. Sclar and J. V. Smith, Mineral. Mag. 35, 839-46 (1965).
12. J. V. Smith, Acta Cryst. 12, 515 (1969).
13. F. R. Boyd, J. L. England and B. T. C. Davis, J. Geophys. Res. 69 (10), 2101 (1964).

Heat Capacity and Entropy

Low temperature heat capacities are from the data (53 - 295°K) of Kelley (7). Wagner (8) measured the average heat capacities in the temperature range 580 - 1570°K. Using his data we derive the high temperature heat capacities which are joined smoothly with the low temperature values by a constrained fitting technique. The Cp values at 903 - 1258°K and above 1258°K are derived as 28.762 and 79.262 gibbs/mol, respectively, by assuming that the data of Wagner (8) pertain to the stable phase in these regions. The entropy is based on S₂₉₈^o = 0.49 au.

Magnesium Metasilicate (MgSiO_3)

GFW = 100.3962

(Liquid)

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf° kcal/mol	ΔGf°	Log Kp
100							
200							
298	19.581	22.112	22.112	.000	- 357.281	- 338.287	247.971
300	19.653	22.233	22.112	.036	- 357.284	- 338.169	246.356
400	22.513	28.319	22.923	2.158	- 357.350	- 331.784	181.278
500	24.262	33.582	24.537	4.502	- 357.288	- 325.396	142.230
600	25.573	38.085	26.425	6.996	- 357.168	- 319.030	116.206
700	27.172	42.125	28.285	9.610	- 356.989	- 312.685	97.435
800	29.672	45.740	30.330	12.328	- 356.799	- 306.371	83.697
900	35.000	49.054	32.224	15.142	- 356.579	- 300.079	72.869
1000	35.000	52.741	34.099	18.642	- 357.862	- 293.664	64.180
1100	35.000	56.077	35.988	22.142	- 357.058	- 287.287	57.079
1200	35.000	59.253	37.754	25.642	- 356.854	- 280.978	50.173
1300	35.000	61.924	39.507	29.142	- 355.595	- 274.729	46.186
1400	35.000	64.518	41.202	32.642	- 385.300	- 268.055	41.845
1500	35.000	66.933	42.838	36.142	- 384.279	- 259.715	37.840
1600	35.000	69.192	44.415	39.642	- 383.276	- 251.425	34.356
1700	35.000	71.314	47.401	46.642	- 381.265	- 234.266	28.444
1800	35.000	73.314	47.401	46.642	- 392.265	- 235.681	25.934
1900	35.000	75.206	48.816	50.180	- 391.250	- 216.709	23.681
2000	35.000	77.000	50.180	53.642	- 390.255	- 208.004	21.688
2100	35.000	78.709	51.859	57.142	- 389.275	- 199.351	19.898
2200	35.000	80.137	54.773	60.642	- 388.291	- 190.741	18.124
2300	35.000	81.853	54.005	67.642	- 387.321	- 182.170	16.589
2400	35.000	83.383	55.198	71.142	- 386.361	- 173.647	15.180
2500	35.000	84.812	56.355				
2600	35.000	86.188	57.476	74.642	- 385.407	- 165.156	13.882
2700	35.000	87.504	58.554	78.142	- 384.452	- 156.703	12.644
2800	35.000	88.778	59.620	81.642	- 383.526	- 148.283	11.574
2900	35.000	90.006	60.647	85.142	- 382.598	- 139.895	10.543
3000	35.000	91.193	61.645	88.642	- 381.680	- 131.543	9.583

MgO_3Si

MAGNESIUM METASILICATE (MgSiO_3)

(LIQUID)

GFW = 100.3962

$\Delta H_f^{\circ}{}_{298.15} = [-357.281 \pm 5] \text{ kcal/mol}$

$\Delta H_f^{\circ}{}_{-1} = 0.16 \text{ kcal/mol}$

$\Delta H_f^{\circ}{}_{-2} = 0.39 \text{ kcal/mol}$

$\Delta H_m^{\circ} = [18 \pm 5] \text{ kcal/mol}$

$S^{\circ}_{298.15} = [22.112] \text{ gibbs/mol}$

$T_f = 903^{\circ}\text{K}$

$T_g = 1256^{\circ}\text{K}$

$T_m = 1850 \pm 2^{\circ}\text{K}$

Heat of Formation

The heat of formation is obtained from $\Delta H_f^{\circ}{}_{298}(\text{c})$ by adding ΔH_m° and the difference between $H_m^{\circ} - H_{298}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 900°K . Below 900°K the heat capacity is obtained from the heat capacity of the crystal. Above 900°K the heat capacity is assumed constant and estimated as 35 gibbs/mol or 7 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Transition Data

See crystal table.

Melting Data

T_m is taken from N. L. Bowen and O. Andersen, Ann. J. Sci. 37, 487 (1914). $\text{MgSiO}_3(\text{c})$ melts incongruently in the temperature range 1830 - 1850°K at atmospheric pressure. ΔH_m° is estimated from the phase diagrams of the $\text{MgSiO}_3 - \text{TiO}_2$ system reported by I. D. MacGregor, Ann. Rept. Director of the Geophysical Laboratory, No. 1455, 135-9 (1965). The phase diagrams were determined at 10 and 20 kbars pressure where $\text{MgSiO}_3(\text{c})$ melts congruently.

MgO_3Si

MAGNESIUM METATITANATE (MgTiO₃) (CRYSTAL) GFW = 120.2102

$\Delta H_f^\circ = -373.63 \pm 1.5$ kcal/mol
 $\Delta H_f^\circ_{298.15} = -375.85 \pm 1.5$ kcal/mol
 $\Delta H_m^\circ = [21.6]$ kcal/mol

$S^\circ_{298.15} = 17.82 \pm 0.1$ gibbs/mol
 $T_m = 1953 \pm 20^\circ\text{K}$

Heat of Formation

The adopted heat of formation is calculated from $\Delta H_f^\circ_{298.15} = -6.35 \pm 0.25$ kcal/mol for the reaction $\text{MgO(c)} + \text{TiO}_2(\text{rutile}) \rightarrow \text{MgTiO}_3(\text{c})$ measured by K. K. Kelley, S. S. Todd and E. G. King, U. S. Bur. Mines RI 5059, 1954, using a solution calorimetric method. For the same reaction a value of $\Delta H_f^\circ_{298.15} = -5.5 \pm 0.1$ kcal/mol was obtained with a calorimetric bomb method by B. I. Ronfilov and N. N. Teodos'ev, Russ. J. Inorg. Chem. (English Transl.) 2, 1452 (1954). These authors used the oxidation of lampblack in order to initiate the formation of the titanate from the oxides. Unfortunately the desired heat of reaction was only 1.2 to 1.5 percent of the total measured heat, and consequently this result appears to be more uncertain than that measured by the solution calorimetric method.

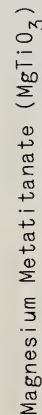
Heat Capacity and Entropy

Low temperature heat capacities are from the data ($52 - 796^\circ\text{K}$) of C. H. Shonate, J. Am. Chem. Soc. 67, 984 (1946). High temperature enthalpies have been measured ($1007 - 1720^\circ\text{K}$) by B. F. Naylor and O. A. Cook, J. Am. Chem. Soc. 83, 1003 (1961). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on $S^\circ_{298} = 0.45$ eu.

Melting Data

See liquid table.

T, °K	C_p°	gibbs/mol $S^\circ - (C_p^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	.200	.000	INFINITE	-	-373.630	INFINITE
100	6.397	2.595	33.175	-	-374.772	90.712
200	16.222	10.157	19.422	-	-375.850	99.284
298	21.760	17.320	17.320	.000	-375.850	260.027
300	22.237	17.956	17.920	.041	-375.851	258.328
400	26.154	24.763	18.727	2.414	-375.776	169.879
500	27.337	30.593	20.532	5.030	-375.544	146.027
600	28.311	35.442	22.439	7.601	-375.281	121.879
700	29.243	40.079	24.920	10.681	-374.907	101.961
800	29.967	44.033	26.979	13.643	-374.577	97.336
900	30.556	47.597	29.075	16.670	-374.268	75.970
1000	31.256	50.843	31.092	19.751	-373.110	66.845
1100	31.895	53.824	33.025	22.879	-375.832	59.376
1200	31.491	56.582	34.875	26.040	-376.513	53.149
1300	32.259	59.149	36.644	29.256	-376.782	47.876
1400	32.506	61.553	38.334	32.500	-377.249	43.287
1500	32.240	63.414	39.962	35.777	-378.455	39.063
1600	32.246	65.250	41.520	39.087	-378.720	35.374
1700	31.588	67.076	43.017	42.430	-379.895	32.125
1800	31.210	68.905	44.458	45.905	-380.241	29.242
1900	30.233	71.747	45.844	49.212	-380.459	26.668
2000	30.559	73.511	47.186	52.652	-380.205	24.338
2100	30.490	75.204	48.490	56.124	-380.437	22.227
2200	30.228	76.836	49.732	59.630	-380.646	20.310
2300	30.572	78.410	50.945	63.170	-380.827	18.564
2400	30.225	79.931	52.121	66.745	-380.982	16.967
2500	30.287	81.405	53.263	70.355	-380.112	15.501
2600	30.459	82.836	54.373	74.002	-380.211	14.150
2700	32.240	84.226	55.453	77.687	-380.242	12.903
2800	37.632	85.360	56.505	81.411	-380.322	11.747
2900	37.635	86.001	57.530	85.174	-380.331	10.673
3000	38.250	86.190	58.531	88.978	-380.308	9.674



(Liquid) Mol. Wt. = 120.2102

GFW = 120.2102

(LIQUID)

MAGNESIUM METATITANATE (MgTiO₃)

$$\Delta H_f^{\circ}{}_{298.15} = [-357.942 \pm 1.5] \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = [21.6] \text{ kcal/mol}$$

$$S^{\circ}{}_{298.15} = [26.549] \text{ gibbs/mol}$$

$$T_m = 1953 \pm 20^{\circ}\text{K}$$

Heat of Formation

$\Delta H_f^{\circ}{}_{298}$ is obtained from $\Delta H_f^{\circ}{}_{298}(c)$ by adding ΔH_m° and the difference between H_m° and H_{298}° for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1300°K. The heat capacity below 1300°K is obtained from the heat capacity of the crystal. Above 1300°K the heat capacity is assumed constant and estimated as 39 gibbs/mol or 7.8 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The incongruent melting point is obtained from Massazza (1). Previous work by Coughanour (2) indicates congruent melting point at 1903°K. The ΔH_m° is estimated from those of Na₂O·2TiO₂ and Na₂O·TiO₂ observed by Naylor (3) and CaO·TiO₂·SiO₂ observed by King (4).

Reference

1. F. Massazza and E. Sirchia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958.
2. L. W. Coughanour and V. A. DeProesse, J. Res. Natl. Bur. Std. 51, 87 (1953).
3. B. F. Naylor, J. Am. Chem. Soc. 67, 2120 (1945).
4. E. G. King, R. L. Orr and K. R. Bonnickson, J. Am. Chem. Soc. 76, 4320 (1954).

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^c	Log K _p
0							
100							
200	21.960	26.549	26.549	.000	-357.942	-339.429	248.007
300	22.037	26.695	26.549	.041	-357.943	-339.313	247.189
400	23.154	27.492	26.549	2.414	-357.864	-333.109	182.002
500	27.337	39.322	29.261	5.030	-357.636	-326.943	142.007
600	28.311	44.371	31.364	7.801	-357.333	-320.834	116.964
700	28.311	44.371	31.364	10.491	-356.999	-314.776	99.277
800	29.367	52.762	33.708	13.693	-356.669	-309.776	84.352
900	30.556	56.326	37.404	16.670	-356.360	-302.799	73.529
1000	31.056	59.572	39.821	19.821	-356.202	-295.680	64.839
1100	31.495	62.553	41.754	22.870	-357.024	-290.503	57.726
1200	31.500	62.553	41.754	25.870	-357.665	-285.322	51.795
1300	31.500	62.553	41.754	28.870	-358.250	-280.141	46.773
1400	32.000	70.768	47.945	33.156	-387.619	-271.624	42.402
1500	32.000	73.459	48.755	37.056	-386.268	-263.356	38.375
1600	32.000	75.376	50.378	40.856	-384.043	-255.238	34.944
1700	32.000	75.376	50.378	44.856	-382.644	-247.169	31.776
1800	32.000	80.570	53.683	48.756	-382.382	-239.151	29.040
1900	32.000	82.678	54.964	52.656	-381.147	-231.257	26.601
2000	32.000	84.678	55.556	55.556	-380.392	-223.248	24.393
2100	32.000	86.591	57.723	62.456	-383.197	-215.218	22.398
2200	32.000	88.129	60.453	69.256	-383.002	-207.248	20.588
2300	32.000	90.129	63.256	76.056	-380.833	-199.329	18.941
2400	32.000	91.789	66.124	82.156	-379.663	-191.462	17.435
2500	32.000	93.981	69.959	87.556	-378.503	-183.649	16.054
2600	32.000	94.011	64.135	72.056	-377.340	-175.975	14.784
2700	32.000	97.401	62.460	87.756	-377.205	-168.308	13.511
2800	32.000	97.401	62.460	91.656	-375.064	-160.384	12.525
2900	32.000	99.170	67.564	91.656	-373.940	-152.815	11.516
3000	32.000	100.492	68.440	95.556	-372.822	-145.210	10.579
3100	32.000	101.701	69.494	99.456	-371.709	-137.640	9.704
3200	32.000	103.209	71.707	107.256	-369.514	-122.413	8.120
3300	32.000	105.373	72.690	111.156	-368.431	-115.143	7.401
3400	32.000	106.504	73.630	115.056	-367.355	-107.716	6.726
3500	32.000	107.602	74.559	118.956	-447.915	-100.043	6.073
3600	32.000	108.711	75.356	122.856	-445.764	-92.413	5.402
3700	32.000	109.711	75.356	126.756	-445.764	-84.786	4.726
3800	32.000	110.724	77.222	130.656	-444.728	-77.222	4.052
3900	32.000	111.711	78.072	134.556	-443.713	-69.524	3.376
4000	32.000	111.711	78.072	138.456	-443.713	-61.824	2.700



T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S ⁰ -(F ⁰ -H ₂₉₈)/T	H ⁰ -H ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	- 3.678	- 288.853	- 288.853	INFINITE
100	8.679	4.775	- 3.354	- 300.273	- 281.922	637.995
200	21.521	23.789	- 2.008	- 301.242	- 283.268	209.540
298	23.000	21.844	0.000	- 301.574	- 274.251	201.038
300	23.050	21.887	0.043	- 301.578	- 274.092	199.675
400	26.290	29.085	2.518	- 302.238	- 264.685	144.726
500	28.540	35.199	5.262	- 302.536	- 255.506	111.682
600	30.500	40.581	8.217	- 302.637	- 246.090	89.438
700	32.100	45.404	11.346	- 302.535	- 236.648	73.685
800	33.580	49.788	14.633	- 315.396	- 228.519	62.428
900	34.950	53.823	18.060	- 314.796	- 217.693	52.863
1000	36.250	57.574	21.621	- 316.249	- 206.756	45.187
1100	37.450	61.086	25.306	- 315.487	- 195.868	38.011
1200	38.580	64.394	29.109	- 314.651	- 185.006	31.994
1300	39.620	67.520	33.016	- 313.756	- 174.237	26.292
1400	40.501	70.478	37.008	- 312.803	- 163.561	20.855
1500	40.963	73.282	41.072	- 341.806	- 150.244	15.691
1600	41.536	75.944	45.197	- 340.380	- 137.519	10.784
1700	42.040	78.478	49.376	- 338.911	- 124.684	6.055
1800	42.490	80.894	53.603	- 337.409	- 112.339	1.640
1900	42.896	83.202	57.873	- 335.875	- 99.874	11.488
2000	43.268	85.412	62.181	- 334.315	- 87.497	9.561
2100	43.611	87.531	66.525	- 332.730	- 75.194	7.826
2200	43.931	89.567	70.903	- 331.125	- 62.965	6.255
2300	44.232	91.527	75.311	- 329.499	- 50.815	4.829
2400	44.517	93.415	79.748	- 327.856	- 38.730	3.527
2500	44.788	95.238	84.214	- 326.197	- 26.722	2.336

$\Delta H_f^0 = -288.8 \pm 5$ kcal. mole⁻¹
 ΔH_f^0 298.15 = -301.6 $\pm$ 5 kcal. mole⁻¹
 $\Delta H_m^0 = 3.5$ kcal. mole⁻¹

$S_{298.15}^0 = 21.844 \pm 0.2$ cal. deg.⁻¹ mole⁻¹
 $T_m = 1400^\circ\text{K.}$

Heat of Formation.

The adopted ΔH_f^0 298.15 = -301.6 $\pm$ 5 kcal. mole⁻¹ was calculated from the ΔH_f^0 298.15 = 63.3 $\pm$ 5 kcal. mole⁻¹ for the reaction $\text{MgO}(c) + \text{SO}_3(g) = \text{MgSO}_4(c)$. The value of ΔH_f^0 298.15 was calculated by the third law method using the equilibrium data obtained from a transpiration study by Knopf and Staudte.¹ In addition Marchal² measured the total pressure of $\text{SO}_3(g)$, $\text{SO}_2(g)$ and $\text{O}_2(g)$ above $\text{MgSO}_4(c)$ and partial pressures were obtained by application of the SO_3 - SO_2 equilibrium data. Another value of ΔH_f^0 298.15 (MgSO_4, c) may be derived from the measured heat of solution of $\text{MgSO}_4(c)$ by Thomsen^{3a} and the measured heats of mixing of $\text{MgCl}_2(200 \text{ H}_2\text{O})$ with $\text{H}_2\text{SO}_4(200 \text{ H}_2\text{O})$ and $\text{MgSO}_4(200 \text{ H}_2\text{O})$ with $2\text{HCl}(100 \text{ H}_2\text{O})$ by Thomsen^{3b}.

References	Reaction	T, °K. range	Third Law drift, e.u.	ΔH_f^0 298.15 kcal. mole ⁻¹	ΔH_f^0 298.15 kcal. mole ⁻¹
1	$\text{MgO}(c) + \text{SO}_3(g) = \text{MgSO}_4(c)$	1144-1313	0.514	63.284	-301.574
2	$\text{MgO}(c) + \text{SO}_3(g) = \text{MgSO}_4(c)$	1223-1428	0.525	72.394	-310.867
3a	$\text{MgSO}_4(c) \rightarrow \text{MgSO}_4(200 \text{ H}_2\text{O})$	298.15		-20.84	
3b	$\text{MgCl}_2(200 \text{ H}_2\text{O}) + \text{H}_2\text{SO}_4(200 \text{ H}_2\text{O}) \rightarrow \text{MgSO}_4(200 \text{ H}_2\text{O}) + 2\text{HCl}(100 \text{ H}_2\text{O})$	298.15		- 3.52	-305.1*

*Combination of the reactions 3a and 3b with the following ΔH_f^0 298.15: $\text{H}_2\text{SO}_4(200 \text{ H}_2\text{O}) = -212.387$, $\text{HCl}(100 \text{ H}_2\text{O}) = -39.74$ and $\text{MgCl}_2(200 \text{ H}_2\text{O}) = -189.5$ kcal. mole⁻¹.

References

- 1 H. J. Knopf and H. Staudte, Z. physik. Chem. (Leipzig) **204**, 265-275 (1955).
- 2 G. Marchal, J. Chim. Phys. **22**, 493 (1925).
- 3a and 3b J. Thomsen, "Thermochemische Untersuchungen," vols I-IV, Barth, Leipzig (1882-1886).

Heat Capacity and Entropy.

The low temperature heat capacities 53.3-295.4°K. were measured by G. E. Moore and K. K. Kelley, J. Am. Chem. Soc. **64**, 2949 (1942). The heat capacities in the temperature range 298-1400°K. were estimated from the equation $\text{MgSO}_4(c) = \text{CaSO}_4(c) + \text{MgO}(c) - \text{CaO}(c)$. $\text{CaSO}_4(c)$ and $\text{CaO}(c)$ C_p were calculated using the equations $C_p = 16.78 + 23.60 \times 10^{-3}T$ and $C_p = 11.67 + 1.08 \times 10^{-3}T - 1.56 \times 10^{-5}T^2$ respectively, K. K. Kelley, U. S. Bur. Mines Bull. **584** (1960). The heat capacity of $\text{MgO}(c)$ was calculated from the correlation of the low temperature heat capacities and high temperature heat content using the Shomate functions to back calculate the heat capacities. The values from the two sources join smoothly at 298°K. Above the melting point (1400°K.) the heat capacity was graphically extrapolated. The entropy was calculated at 50.12°K. using the Debye and Einstein function $D(\frac{298}{1400}) + 2E(\frac{298}{1400}) + 2E(\frac{298}{1400})$ given by G. E. Moore and K. K. Kelley loc. cit. The value of $S_{50.12}^0 = 1.08$ cal. deg.⁻¹ mole⁻¹.

Melting Data.

T_m and ΔH_m^0 from K. K. Kelley, U. S. Bur. Mines Bull. **393** (1956).

Magnesium Sulfate (MgSO₄)

(Liquid) Mol. Wt. = 120.3736

MgO₄S

MOL. WT. = 120.3736

MAGNESIUM SULFATE (MgSO₄) (LIQUID)

$S_{298.15}^{\circ} = 24.464 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = -297.9 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_m^{\circ} = 3.5 \text{ kcal. mole}^{-1}$
 $T_m = 1400^{\circ}\text{K.}$

Heat of Formation.
 The $\Delta H_f^{\circ} 298.15$ was obtained from $\Delta H_f^{\circ} 298.15(c)$ by adding ΔH_m° and the difference between H_m° and $H_m^{\circ} 298.15$ for crystal and liquid.

Heat Capacity and Entropy.
 A glass transition was assumed at 1000°K. The heat capacity below 1000°K. was obtained from the heat capacity of the crystal. Above 1000°K. the heat capacity was assumed constant and estimated as $39.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ by comparison with those for $\text{MgCl}_2(l)$, $\text{KCl}(l)$ and $\text{K}_2\text{SO}_4(l)$. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.
 See $\text{MgSO}_4(c)$ table.

T. °K.	C_p°	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	ΔH_f°	ΔF_f°	Log K_p
0						
100						
200						
298	23.000	24.464	0.000	-297.864	-271.332	198.892
300						
350	23.050	24.466	-0.043	-297.868	-271.167	197.545
400	23.090	24.466	2.518	-298.528	-262.223	143.272
500	28.540	37.818	5.262	-298.826	-253.116	110.632
600	30.500	43.201	8.217	-298.907	-243.952	88.859
700	32.100	48.024	11.348	-298.845	-234.772	63.689
800	33.950	56.427	18.066	-311.100	-216.341	52.535
900	36.000	60.248	21.676	-312.484	-205.665	44.948
1000	38.000	63.870	25.476	-311.607	-195.031	38.749
1100	38.000	67.176	29.276	-310.774	-184.468	33.596
1200	38.000	70.132	32.876	-309.985	-173.901	28.455
1300	38.000	72.732	36.276	-309.235	-163.328	23.314
1400	38.000	75.056	40.676	-308.519	-152.751	18.173
1500	38.000	77.132	44.476	-307.831	-142.164	13.032
1600	38.000	78.908	48.539	-307.174	-131.563	8.891
1700	38.000	80.412	52.015	-306.546	-120.952	4.750
1800	38.000	81.639	55.230	-305.942	-110.341	0.609
1900	38.000	82.598	58.276	-305.359	-100.730	-3.532
2000	38.000	83.316	61.056	-304.796	-91.119	-7.673
2100	38.000	83.842	63.476	-304.259	-81.508	-11.814
2200	38.000	84.210	65.630	-303.746	-71.897	-15.955
2300	38.000	84.436	67.526	-303.256	-62.286	-20.096
2400	38.000	84.516	69.176	-302.789	-52.675	-24.237
2500	38.000	84.467	70.597	-302.346	-43.064	-28.378

MgO₄S

T, °K	C _p ^o	S ^o - (C _p ^o - H ^o - TS ₂₉₈)/T	H ^o - H ^o - TS ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	0.000	INFINITE	- 4.115	- 359.880	- 359.880	INFINITE
100	9.135	5.055	- 42.917	- 361.238	- 353.009	INFINITE
200	19.590	14.987	- 86.711	- 362.428	- 351.819	INFINITE
298	26.370	24.184	- 100.000	- 362.300	- 335.632	246.025
300	26.200	24.346	.048	- 362.300	- 335.467	244.388
400	29.500	32.367	2.845	- 362.128	- 326.543	176.415
500	31.450	39.171	5.898	- 361.760	- 317.683	136.659
600	32.750	45.023	9.109	- 361.359	- 308.903	112.518
700	33.460	50.156	12.440	- 360.898	- 300.195	93.725
800	34.930	54.747	15.880	- 360.412	- 291.559	79.650
900	35.950	58.920	19.424	- 359.899	- 282.982	68.717
1000	37.000	62.762	23.071	- 361.479	- 274.281	59.944
1100	38.100	66.300	26.824	- 360.868	- 265.594	52.769
1200	39.200	69.702	30.691	- 360.201	- 256.941	46.799
1300	40.300	72.884	34.664	- 359.479	- 248.386	41.757
1400	41.350	75.908	38.748	- 358.666	- 239.390	37.371
1500	42.450	78.799	42.939	- 357.822	- 228.741	33.328
1600	43.500	81.572	47.236	- 356.995	- 218.180	29.602
1700	44.600	84.242	51.641	- 356.082	- 207.700	26.702
1800	45.750	86.821	56.153	- 355.087	- 197.310	23.957
1900	46.750	89.319	60.774	- 354.005	- 187.005	21.510
2000	47.800	91.744	65.502	- 352.339	- 176.785	19.316

$\Delta H_f^\circ = -359.9 \pm 8 \text{ kcal/mol}$
 $\Delta H_f^\circ = -359.15 \pm 8 \text{ kcal/mol}$
 $\Delta H_m^\circ = \text{Unknown}$

$S_{298.15}^\circ = 24.18 \pm 0.2 \text{ gibbs/mol}$
 $T_m = \text{Unknown}$

Heat of Formation.

T. N. Rezhukhina and V. A. Levitskii¹ measured the emf, $E = 0.2433 - 0.0001264T$, for the cell reaction $\text{MgO}(c) + \text{W}(c) + 3\text{FeO}_{0.95}\text{O}(c) \rightarrow \text{MgWO}_4(c) + 2.85 \text{ Fe}(c)$, in the temperature range $1220^\circ - 1370^\circ \text{K}$. Incorporating the results with auxiliary thermal data, the authors obtained $\Delta H_f^\circ = -224,370 + 65.67T$ (cal/mol) for $\text{MgO}(c) + \text{W}(c) + 3/2\text{O}_2(g) \rightarrow \text{MgWO}_4(c)$. Third law analysis of the ΔH_f° equation gives $\Delta H_f^\circ = -218.6 \text{ kcal/mol}$, from which the adopted $\Delta H_f^\circ(298 \text{ K})$, -362.3 kcal/mol , is calculated. The second law analysis gives $\Delta H_f^\circ(298 \text{ K}) = -372.7 \text{ kcal/mol}$. The drift in the third law analysis is 8.0 eu.

T. N. Rezhukhina, Ya. I. Gerasimov and Yu. P. Simanov² determined the Gibbs energy changes $\Delta G_r^\circ = 51,300 - 27.67T$ (cal/mol) for the reaction $\text{MgWO}_4(c) + 3\text{H}_2(g) \rightarrow \text{MgO}(c) + \text{W}(c) + 3\text{H}_2\text{O}(g)$ in the temperature range $1073^\circ \text{K} - 1273^\circ \text{K}$ by a circulation method. This leads to heats of formation of -366.1 kcal/mol by the third law method and -377.2 kcal/mol by the second law method. Both determinations were performed by Rezhukhina and his co-workers, but they considered the data obtained by the emf method to be more reliable than that derived from heterogeneous equilibria.

Heat Capacity and Entropy.

Low temperature heat capacities, $52.92^\circ - 296.09^\circ \text{K}$, were measured calorimetrically by E. G. King and W. W. Weller.³ The heat capacities above 300°K are estimated by comparison with those of $\text{CaWO}_4(c)$,⁴ $\text{CaO}(c)$,⁵ and $\text{MgO}(c)$.⁶ These two sets of data are joined smoothly at 298°K by a graphical method.

The entropy, $S_{298}^\circ = 21.184 \text{ eu}$, is taken from King and Weller,³ based on an extrapolation of $S_{298}^\circ = 1.27 \text{ eu}$. No spin-magnetic entropy is predicted below 51°K based on the diamagnetism observed by Ya. I. Gerasimov.⁷

References.

1. T. N. Rezhukhina and V. A. Levitskii, Russ. J. Phys. Chem. (English Transl.) **37**, 1277 (1963).
2. T. N. Rezhukhina, Ya. I. Gerasimov and Yu. P. Simanov, Vestnik Moskov. Univ. **4**, No. 6, 103 (1949).
3. E. G. King and W. W. Weller, U. S. Bur. Mines Rept. Invest. 5791 (1961).
4. R. A. Yakovleva and T. N. Rezhukhina, Russ. J. Phys. Chem. (English Transl.) **34**, 390 (1960).
5. K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960).
6. JANAP MgO table (Dec. 31, 1965).
7. Ya. I. Gerasimov, Papers Presented to Section on Inorganic Chemistry, 16th Intern. Congress Pure and Applied Chem. Paris (1967), pp. 227-35, Butterworths Scientific Publications, London, 1968.



Magnesium Dtitanate (MgTi₂O₅)
(Crystal) GFW = 200.109

T, °K	Cp ^a	gibbs/mol S ^b - (C ^a - H ²⁹⁸)/T	—H ²⁹⁸ — H ²⁹⁸ —H ²⁹⁸ /T	—H ²⁹⁸ — H ²⁹⁸ —H ²⁹⁸ /T	ΔG ^c	Log K ^p
0	11.200	5.000	1.000	1.000	594.825	INFINITE
100	11.200	5.310	1.000	1.000	594.825	1260.576
200	26.618	18.078	3.062	3.062	599.500	630.376
298	35.100	32.410	3.000	3.000	599.750	615.028
300	35.214	32.427	3.005	3.005	599.750	612.317
400	39.516	43.424	3.859	3.859	599.614	597.723
500	42.824	52.563	4.705	4.705	599.275	593.593
600	46.396	60.434	5.549	5.549	598.844	593.945
700	49.504	67.348	6.396	6.396	598.367	162.795
800	52.111	73.525	7.243	7.243	597.880	139.452
900	54.297	79.120	8.090	8.090	597.397	121.211
1000	56.204	84.245	8.937	8.937	596.906	109.770
1100	57.259	88.984	9.784	9.784	596.550	94.873
1200	57.276	93.401	10.631	10.631	596.224	84.953
1300	57.266	97.545	11.478	11.478	595.924	76.553
1400	57.236	101.454	12.325	12.325	595.649	69.288
1500	57.190	105.159	13.172	13.172	595.396	62.751
1600	57.132	108.687	14.019	14.019	595.150	57.042
1700	57.064	112.057	14.866	14.866	594.916	52.014
1800	56.988	115.288	15.713	15.713	594.694	47.555
1900	56.906	118.389	16.560	16.560	594.482	43.645
2000	56.819	121.357	17.407	17.407	594.280	39.265
2100	56.728	124.279	18.254	18.254	594.086	34.691
2200	56.633	127.078	19.101	19.101	593.900	30.023
2300	56.534	129.793	19.948	19.948	593.723	25.264
2400	56.433	132.431	20.795	20.795	593.556	20.481
2500	56.330	135.000	21.642	21.642	593.400	15.625
2600	56.224	137.499	22.489	22.489	593.253	10.786
2700	56.117	139.940	23.336	23.336	593.116	6.061
2800	56.008	142.324	24.183	24.183	592.988	1.441
2900	55.898	144.656	25.030	25.030	592.869	-3.184
3000	55.787	146.939	25.877	25.877	592.759	-7.919

MAGNESIUM DITITANATE (MgTi₂O₅) (CRYSTAL)

GFW = 200.109

$\Delta H_f^\circ = -596.43 \pm 2.5 \text{ kcal/mol}$

$\Delta H_f^\circ = -599.75 \pm 2.5 \text{ kcal/mol}$

$\Delta H_m^\circ = [35] \text{ kcal/mol}$

$S_{298.15}^\circ = 32.41 \pm 1.5 \text{ gibbs/mol}$

$T_m = 1963 \pm 20^\circ\text{K}$

Heat of Formation

ΔH_f° is calculated from $\Delta H_f^\circ = -4.45 \pm 0.45 \text{ kcal/mol}$ for the reaction $\text{MgO}(c) + 2\text{TiO}_2(\text{rutile}) = \text{MgTi}_2\text{O}_5(c)$ measured by K. K. Kelley, S. S. Todd and E. G. King, U. S. Bur. Mines RI 5059, 1954, using a solution calorimetric method. The uncertainty of $\pm 2.5 \text{ kcal/mol}$ assigned to the heat of formation is due primarily to $\text{TiO}_2(\text{rutile})$.

Heat Capacity and Entropy

Low temperature heat capacities are from the data ($52 - 296^\circ\text{K}$) of S. S. Todd, J. Am. Chem. Soc. **74**, 4669 (1952). High temperature enthalpies have been measured ($397 - 1812^\circ\text{K}$) by R. L. Orr and J. P. Coughlin, J. Am. Chem. Soc. **74**, 3186 (1952). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on $S_{51}^\circ - S_0^\circ = 1.11 \text{ eu}$.

Kelley et al., loc. cit., suggested that there may be a zero-point entropy due to randomness of the cations. The authors estimated S_0° from the following alternative assumptions: (a) all the Mg and Ti ions are randomly distributed among the lattice sites giving 3.79 eu and (b) all the Mg and one-half of the Ti ions are randomly distributed giving 2.75 eu . These assumptions were proposed in order to make MgTi_2O_5 stable relative to MgTiO_3 at high temperatures. Phase data of F. Massazza and E. Sirchia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958, indicate that MgTi_2O_5 melts congruently at $1963\text{-}20^\circ\text{K}$ and that there is a eutectic with MgTiO_3 at $1873\text{-}20^\circ\text{K}$. These data require that $\Delta G^\circ < 0$ for $\text{MgTiO}_3(c) + \text{TiO}_2(\text{rutile}) \rightarrow \text{MgTi}_2\text{O}_5(c)$ in this temperature range. To make $\Delta G^\circ < 0$ would require that $S_{298.15}^\circ$ be $> 32.035 \text{ eu}$. We adopt a compromise zero-point entropy of 2 eu between the upper (3.79 eu) and the lower (0.35 eu) limits.

Melting Data

See liquid table.



Magnesium D titanate (MgTi₂O₅)
(Liquid) GFW = 200.109

MgO₅Ti₂

MAGNESIUM DITITANATE (MgTi₂O₅)

(LIQUID)

GFW = 200.109

$$\Delta H_{298.15}^{\circ} = [-569.385 \pm 2] \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = [35] \text{ kcal/mol}$$

$$S_{298.15}^{\circ} = [47.27] \text{ gibbs/mol}$$

$$T_m = 1963 \pm 20^{\circ} \text{K}$$

Heat of Formation

The heat of formation is obtained from $\Delta H_{298}^{\circ}(\text{c})$ by adding ΔH_m° and the difference between H_m° and H_{298}° for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1300°K. Below 1300°K the heat capacity is obtained from the heat capacity of the crystal. Above 1300°K the heat capacity is assumed constant and estimated as 62/4 gibbs/mol or 7.8 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The congruent melting point is obtained from Massazza (1). Previous work by Coughanour (2) indicates congruent melting at 1925°K. The ΔH_m° is estimated from those of Na₂O·2TiO₂ and Na₂O·TiO₂ observed by Naylor (3) and CaO·TiO₂·SiO₂ observed by King (4).

References

1. F. Massazza and E. Sircchia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958.
2. L. W. Coughanour and V. A. DeProsse, J. Res. Natl. Bur. Stds. **51**, 87 (1953).
3. B. V. Naylor, J. Am. Chem. Soc. **67**, 2120 (1945).
4. E. G. King, R. L. Orr and K. R. Bonnickson, J. Am. Chem. Soc. **76**, 4320 (1954).

June 30, 1961; June 30, 1967

MgO₅Ti₂

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^c	Log K _p
0							
100							
200							
298	35.100	47.270	47.270	.000	- 569.385	- 560.255	396.017
300							
400	38.216	56.286	48.711	3.829	- 569.385	- 560.078	393.883
500	42.228	67.823	51.563	7.929	- 569.385	- 559.910	391.751
600	46.396	75.294	54.879	12.249	- 569.385	- 559.742	389.617
700	50.604	82.208	58.300	16.736	- 569.385	- 559.574	387.483
800	54.852	88.591	61.718	21.341	- 569.385	- 559.406	385.349
900	59.140	94.343	65.141	26.114	- 569.385	- 559.238	383.215
1000	63.468	99.565	68.499	31.088	- 569.385	- 559.070	381.081
1100	67.836	104.267	71.789	36.229	- 569.385	- 558.902	378.947
1200	72.244	108.444	74.949	41.588	- 569.385	- 558.734	376.813
1300	76.692	112.096	78.000	47.188	- 569.385	- 558.566	374.679
1400	81.180	115.233	80.952	52.948	- 569.385	- 558.398	372.545
1500	85.708	117.856	83.704	58.788	- 569.385	- 558.230	370.411
1600	90.276	120.000	86.256	64.628	- 569.385	- 558.062	368.277
1700	94.884	121.668	88.608	70.468	- 569.385	- 557.894	366.143
1800	99.532	122.856	90.760	76.208	- 569.385	- 557.726	364.009
1900	104.220	123.576	92.608	81.848	- 569.385	- 557.558	361.875
2000	108.948	123.840	94.152	87.288	- 569.385	- 557.390	359.741
2100	113.716	123.648	95.400	92.428	- 569.385	- 557.222	357.607
2200	118.524	123.000	96.352	97.268	- 569.385	- 557.054	355.473
2300	123.372	121.912	97.000	101.808	- 569.385	- 556.886	353.339
2400	128.160	120.384	97.352	106.048	- 569.385	- 556.718	351.205
2500	132.888	118.416	97.304	110.088	- 569.385	- 556.550	349.071
2600	137.556	115.904	96.856	113.828	- 569.385	- 556.382	346.937
2700	142.164	112.848	95.904	117.128	- 569.385	- 556.214	344.803
2800	146.712	109.248	93.456	119.968	- 569.385	- 556.046	342.669
2900	151.200	105.104	89.408	122.208	- 569.385	- 555.878	340.535
3000	155.632	100.416	83.760	123.848	- 569.385	- 555.710	338.401
3100	160.000	95.184	76.512	124.888	- 569.385	- 555.542	336.267
3200	164.312	89.408	68.656	125.228	- 569.385	- 555.374	334.133
3300	168.560	83.056	59.200	124.868	- 569.385	- 555.206	332.000
3400	172.744	76.112	48.256	123.692	- 569.385	- 555.038	329.866
3500	176.864	68.576	35.712	121.664	- 569.385	- 554.870	327.732
3600	180.920	60.336	21.664	118.784	- 569.385	- 554.702	325.598
3700	184.912	51.392	6.816	114.048	- 569.385	- 554.534	323.464
3800	188.840	41.744	- 9.072	107.456	- 569.385	- 554.366	321.330
3900	192.704	31.376	- 19.616	98.912	- 569.385	- 554.198	319.196
4000	196.504	20.288	- 29.776	88.416	- 569.385	- 554.030	317.062

Magnesium Sulfide (MgS)

(Solid) Mol. Wt. = 56.39

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF°	Log K _p
0						
100						
200						
298	10.000	11.000	.000	- 83.000	- 81.672	59.864
300	10.000	11.062	.019	- 83.003	- 81.663	59.869
400	10.250	13.261	1.027	- 83.703	- 81.172	44.346
500	10.500	16.275	2.064	- 84.281	- 80.478	35.175
600	10.750	18.212	3.127	- 84.604	- 79.680	29.022
700	11.000	20.000	4.200	- 84.600	- 78.797	24.616
800	11.250	21.373	5.327	- 84.536	- 77.128	21.616
900	11.500	22.712	6.464	- 84.598	- 76.698	18.624
1000	11.750	23.937	7.627	- 100.796	- 74.083	16.190
1100	12.000	25.068	8.818	- 100.853	- 71.811	14.187
1200	12.250	26.114	10.027	- 100.972	- 68.700	11.703
1300	12.500	27.114	11.266	- 100.972	- 66.085	9.817
1400	12.750	28.049	12.527	- 131.464	- 62.892	8.451
1500	13.000	28.937	13.814	- 131.122	- 58.008	
1600	13.250	29.784	15.127	- 130.754	- 53.145	7.259
1700	13.500	30.590	16.464	- 129.882	- 48.186	6.280
1800	13.750	31.378	17.827	- 129.966	- 43.692	5.451
1900	14.000	32.128	19.214	- 129.506	- 38.699	4.708
2000	14.250	32.848	20.627	- 129.041	- 33.932	
2100	14.500	33.550	22.064	- 128.553	- 29.191	3.038
2200	14.750	34.237	23.527	- 128.049	- 24.679	2.490
2300	15.000	34.901	25.014	- 127.502	- 19.775	1.975
2400	15.250	35.535	26.527	- 126.930	- 15.101	1.375
2500	15.500	36.163	28.064	- 126.353	- 10.454	.914
2600	15.750	36.775	29.627	- 125.782	- 5.831	.490
2700	16.000	37.361	31.214	- 125.184	- 1.129	.269
2800	16.250	37.924	32.827	- 124.569	3.563	.095
2900	16.500	38.535	34.464	- 123.937	7.898	
3000	16.750	39.099	36.127	- 123.061	12.428	

Magnesium Sulfide (MgS)
(Solid)

Mol. Wt. = 56.39

 $\Delta H_f^\circ 298.15 = -83 \text{ kcal. mole}^{-1}$ $S_{298.15} = [11] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^\circ 298.15$ from National Bureau of Standards Circular 500. Other data estimated.

(Ideal Gas) Mol. Wt. = 56.39 INTERIM TABLE

T, °K.	C _p ^o	S ^o	$-(F^o - H_{298}^o)/T$	$H^o - H_{298}^o$	ΔH_f^o	ΔF_f^o	Log K _p
0	0.000	INFINITE	INFINITE	2.206	33.243	33.243	INFINITE
100	7.019	49.187	64.247	1.510	33.621	29.227	63.873
200	7.650	54.226	58.123	1.779	33.909	24.864	57.172
298	8.278	57.367	55.357	2.000	34.200	20.506	51.171
300	8.231	57.418	55.387	2.015	34.194	20.621	51.021
400	8.453	59.438	57.713	2.630	34.320	16.500	45.015
500	8.611	61.742	58.335	3.170	34.599	12.628	39.519
600	8.705	63.321	59.038	3.650	34.947	8.897	34.241
700	8.764	64.668	59.748	4.084	35.330	5.296	29.153
800	8.804	65.841	60.438	4.422	35.759	1.935	24.135
900	8.832	66.880	61.097	4.684	36.224	-1.509	19.166
1000	8.853	67.811	61.723	4.868	36.725	-3.266	14.220
1100	8.868	68.658	62.317	4.978	37.262	-4.997	9.253
1200	8.880	69.426	62.877	5.024	37.834	-6.661	4.213
1300	8.889	70.139	63.408	5.036	38.440	-8.293	-0.823
1400	8.896	70.794	63.913	5.040	39.080	-9.898	-1.872
1500	8.902	71.412	64.393	5.050	39.752	-11.476	-2.823
1600	8.907	71.987	64.849	5.059	40.455	-13.028	-3.687
1700	8.911	72.527	65.285	5.067	41.188	-14.553	-4.467
1800	8.914	73.036	65.702	5.072	41.948	-16.054	-5.167
1900	8.917	73.518	66.101	5.076	42.734	-17.531	-5.791
2000	8.920	73.976	66.483	5.079	43.544	-18.984	-6.341
2100	8.922	74.411	66.850	5.081	44.376	-20.414	-6.817
2200	8.924	74.826	67.204	5.083	45.228	-21.822	-7.219
2300	8.925	75.223	67.544	5.084	46.099	-23.209	-7.547
2400	8.927	75.603	67.872	5.085	46.988	-24.574	-7.795
2500	8.928	75.967	68.188	5.086	47.894	-25.927	-8.061
2600	8.929	76.317	68.494	5.087	48.816	-27.267	-8.343
2700	8.930	76.654	68.790	5.088	49.754	-28.593	-8.641
2800	8.931	76.979	69.077	5.089	50.706	-29.906	-8.954
2900	8.932	77.293	69.355	5.090	51.674	-31.206	-9.281
3000	8.932	77.595	69.624	5.091	52.656	-32.493	-9.621
3100	8.933	77.888	69.886	5.092	53.652	-33.767	-9.973
3200	8.934	78.172	70.140	5.093	54.662	-35.028	-10.336
3300	8.934	78.447	70.388	5.094	55.686	-36.275	-10.709
3400	8.935	78.714	70.629	5.095	56.724	-37.508	-11.091
3500	8.935	78.973	70.864	5.096	57.776	-38.727	-11.481
3600	8.936	79.226	71.093	5.097	58.840	-39.932	-11.878
3700	8.936	79.469	71.314	5.098	59.916	-41.123	-12.281
3800	8.936	79.707	71.528	5.099	61.004	-42.299	-12.689
3900	8.937	79.940	71.746	5.100	62.104	-43.461	-13.101
4000	8.937	80.166	71.958	5.101	63.216	-44.608	-13.516
4100	8.937	80.387	72.165	5.102	64.340	-45.741	-13.934
4200	8.937	80.602	72.355	5.103	65.476	-46.860	-14.354
4300	8.938	80.812	72.550	5.104	66.624	-47.965	-14.776
4400	8.938	81.016	72.740	5.105	67.784	-49.056	-15.199
4500	8.938	81.219	72.926	5.106	68.956	-50.132	-15.623
4600	8.938	81.415	73.108	5.107	70.139	-51.194	-16.047
4700	8.939	81.607	73.287	5.108	71.334	-52.241	-16.471
4800	8.939	81.795	73.462	5.109	72.540	-53.274	-16.895
4900	8.939	81.980	73.634	5.110	73.756	-54.293	-17.318
5000	8.939	82.160	73.803	5.111	74.982	-55.298	-17.741
5100	8.939	82.337	73.969	5.112	76.218	-56.288	-18.164
5200	8.939	82.511	74.131	5.113	77.464	-57.263	-18.587
5300	8.939	82.681	74.291	5.114	78.720	-58.223	-19.009
5400	8.939	82.848	74.448	5.115	79.986	-59.168	-19.431
5500	8.940	83.012	74.602	5.116	81.262	-60.098	-19.853
5600	8.940	83.173	74.756	5.117	82.548	-61.013	-20.275
5700	8.940	83.332	74.903	5.118	83.844	-61.913	-20.696
5800	8.940	83.487	75.050	5.119	85.150	-62.798	-21.117
5900	8.940	83.640	75.194	5.120	86.466	-63.668	-21.537
6000	8.940	83.790	75.336	5.121	87.792	-64.523	-21.956

December 31, 1960.

Magnesium Sulfide (MgS) (Ideal Gas)

Mol. Wt. = 56.39

 ΔH_f^o 298.15 = 33.2 kcal. mole⁻¹ $S_{298.15}^o$ = 57.387 cal. deg. ⁻¹ mole⁻¹

C_p, D₀, and other data from R. Altman, Rocketdyne Engineering, Canoga Park, Calif., "Thermodynamic Properties of Propellant Combustion Products", July, 1959. ΔH_f^o 298.15 calculated from D₀.

Magnesium Orthosilicate (Mg_2SiO_4)
(Crystal)

GFW = 140.7076

T, °K	Cp ^a	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	-	0.130	-517.119	-517.119	INFINITE	
100	7.724	3.958	42.286	3.641	-516.440	-516.151	1114.033	
200	20.589	12.945	25.110	2.433	-516.979	-501.310	547.806	
298	28.367	22.739	22.739	.000	-520.300	-491.858	360.541	
300	28.477	22.915	22.740	.053	-520.304	-491.882	358.100	
400	32.677	31.749	23.917	3.141	-520.373	-482.424	293.420	
500	35.539	39.411	26.270	6.570	-520.234	-472.571	206.561	
600	37.388	46.062	29.026	10.221	-519.999	-463.063	168.670	
700	38.793	51.945	31.666	14.033	-519.714	-453.573	141.618	
800	40.081	57.052	34.063	17.945	-519.422	-444.088	120.578	
900	41.281	61.482	37.463	22.013	-519.142	-434.780	105.576	
1000	41.732	66.305	40.159	26.145	-523.126	-425.056	92.896	
1100	42.488	70.318	42.721	30.357	-522.831	-415.268	82.506	
1200	43.180	74.047	45.178	34.641	-522.542	-405.503	73.852	
1300	43.830	77.594	47.464	39.004	-522.252	-395.753	65.733	
1400	44.440	80.977	49.738	43.404	-521.952	-385.080	58.044	
1500	45.007	83.882	51.965	47.876	-521.674	-370.997	54.054	
1600	45.559	86.405	54.052	52.405	-520.578	-356.990	48.763	
1700	46.091	89.593	56.061	56.987	-520.442	-342.942	44.088	
1800	46.606	92.426	57.986	61.568	-520.275	-328.359	39.466	
1900	47.106	95.000	59.846	66.149	-520.082	-313.736	34.894	
2000	47.601	97.194	61.672	71.044	-520.683	-299.399	32.717	
2100	48.082	99.528	63.420	75.828	-520.353	-285.018	29.662	
2200	48.555	101.776	65.112	80.660	-520.789	-270.699	26.861	
2300	49.022	103.941	66.757	85.334	-521.389	-256.253	24.366	
2400	49.478	106.040	68.367	89.947	-522.047	-241.784	22.071	
2500	49.932	108.070	69.896	95.434	-520.681	-228.125	19.943	
2600	50.380	110.037	71.402	100.450	-520.175	-214.046	17.992	
2700	50.824	111.946	72.869	105.510	-520.639	-200.034	16.192	
2800	51.261	113.809	74.281	110.613	-521.068	-186.173	14.578	
2900	51.701	115.639	75.651	115.751	-521.466	-172.528	13.045	
3000	52.133	117.369	77.051	120.955	-522.834	-158.331	11.534	



MAGNESIUM ORTHOSILICATE (Mg_2SiO_4)

(CRYSTAL)

GFW = 140.7076

$\Delta H_f^\circ = -517.12 \pm 1.0$ kcal/mol
 $\Delta H_f^\circ_{298.15} = -520.30 \pm 1.0$ kcal/mol
 $\Delta H_m^\circ = [17 \pm 5]$ kcal/mol

$S^\circ_{298.15} = 22.739 \pm 0.2$ gibbs/mol
 $T_m = 2171 \pm 11$ °K

Heat of Formation

Torgeson et al. (1) have reported a $\Delta H_f^\circ_{298} = -15.1 \pm 0.2$ kcal/mol for reaction (a). They used an HF solution calorimeter and measured the heats of solution of each component. We derive ΔH_f° (Mg_2SiO_4 , c) = -520.30 ± 1.0 kcal/mol using the ΔH_f° of MgO (c) and SiO_2 (c, low quartz) from JANAF tables.

Kapustinikii et al. (2) used the same method but measured only $\Delta H_f^\circ_{298} = 95.00 \pm 0.47$ kcal/mol for reaction (b). We calculate ΔH_f° (Mg_2SiO_4 , c) = -522.27 kcal/mol using the ΔH_f° of H_2SiF_6 (aq) from source 3 and the ΔH_f° of H_2O (l) and H^+ (aq) from source 4.

Reesman et al. (3) calculated a $\Delta G_f^\circ_{298} = 42.45$ kcal/mol for reaction (c) using aqueous solubility data. We use the $\Delta G_f^\circ_{298}$ of H_2O (c) and OH^- (aq) from source 4, $\Delta G_f^\circ_{298}$ of H_4SiO_4 (aq) from source 3 and $\Delta G_f^\circ_{298}$ of Mg^{++} (aq) from source 6 and we obtain a $\Delta G_f^\circ_{298}$ (Mg_2SiO_4 , c) = -498.764 kcal/mol. We derive a $\Delta H_f^\circ_{298}$ (Mg_2SiO_4 , c) = -524.848 kcal/mol using the above $\Delta G_f^\circ_{298}$ of Mg_2SiO_4 (c) and the entropies of Mg (c), Si (c) and O_2 (g) from the JANAF tables.

The adopted value is from the work of Torgeson et al. (1) which is considered to be the most reliable since it relates directly to the oxides. The other reported values are less accurate and involve uncertainties in the auxiliary data used to derive the heat of formation.

Source	Method	Reaction	ΔH_f° kcal/mol	ΔG_f° kcal/mol	ΔH_f° kcal/mol
Torgeson et al.	Hydrofluoric acid solution calorimeter	(a) $2MgO(c) + SiO_2(c) = Mg_2SiO_4(c)$	-15.10±0.2	-520.3	
Kapustinikii et al.	Hydrofluoric acid solution calorimeter	(b) $Mg_2SiO_4(c) + OHF(4.44H_2O) = 2MgF_2(c) + H_2SiF_6(714HF \cdot 3220H_2O + 4H_2O(l))$	95.0±0.47	-522.27	
Reesman et al.	Aqueous solubility	(c) $Mg_2SiO_4(c) + H_2O(l) = 2Mg^{++}(aq) + H_4SiO_4(aq) + 4OH^-(aq)$	42.46	-524.848	

Source

1. D. R. Torgeson and Th. G. Sahara, J. Am. Chem. Soc. **70**, 2156 (1948).
2. A. F. Kapustinikii and K. K. Samplavskaya, Russ. J. Inorg. Chem. (Engl. transl.) **5**, 1141 (1961).
3. U. S. Natl. Bur. Std. Tech. Note 270-2, 1966.
4. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
5. A. L. Reesman and W. D. Keller, Am. Mineralogist **50**, 1729-39 (1965).
6. U. S. Natl. Bur. Std. Circ. 500, 1952.
7. K. K. Kelley, J. Am. Chem. Soc. **65**, 339-41 (1943).
8. R. L. Orr, J. Am. Chem. Soc. **75**, 528-9 (1953).
9. B. T. C. Davis and J. L. England, J. Geophys. Res. **69**, 1113-1116 (1964).
10. I. D. MacGregor, Ann. Rept. Director of the Geophysical Laboratory, No. 1455, 135-9 (1965).

Heat Capacity and Entropy

Low temperature heat capacities are from the data (53-295°K) of Kelley (7). High temperature enthalpies have been measured (398-1808°K) by Orr (8). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on $S^\circ_0 = 0.60$ eu.

Melting Data

T_m is obtained from Davis et al. (9). ΔH_m° is estimated from MacGregor's (10) phase diagrams of the Mg_2SiO_4 - TiO_2 system. The phase diagrams were determined at 10 and 20 kbars pressure.



Magnesium Orthosilicate (Mg_2SiO_4)

(Liquid) GFW = 140.7076



GFW = 140.7076

(LIQUID)

MAGNESIUM ORTHOSILICATE (Mg_2SiO_4)

$\Delta H_f^{298.15} = [-505.229 \pm 5] \text{ kcal/mol}$

$\Delta H_m^* = [17 \pm 5] \text{ kcal/mol}$

$S_{298.15}^* = [29.407] \text{ gibbs/mol}$

$T_m = 2171 \pm 11^\circ K$

Heat of Formation

The heat of formation is obtained from $\Delta H_f^{298}(c)$ by adding ΔH_m^* and the difference between H_m^* and H_{298}^* for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at $1400^\circ K$. Below $1400^\circ K$ the heat capacity is obtained from the heat capacity of the crystal. Above $1400^\circ K$ the heat capacity is assumed constant and estimated as 49 gibbs/mol or 7 gibbs/g-atom . The entropy is obtained in a manner analogous to that of the heat of formation.

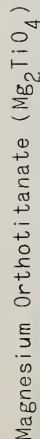
Melting Data

See crystal table.

T, °K	Cp*	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG_f°	Log Kp
100							
200	28.367	29.407	29.407	.000	- 505.229	- 478.775	350.951
250	28.477	29.583	29.408	.053	- 505.233	- 478.611	348.668
300	32.877	30.565	30.565	3.141	- 505.302	- 469.721	256.643
400	35.539	32.938	32.938	6.570	- 505.163	- 460.834	201.430
500	37.388	35.494	35.494	10.221	- 504.928	- 451.993	164.438
600	38.793	38.256	38.256	14.033	- 504.643	- 443.190	138.370
700	39.929	41.396	41.396	17.971	- 504.351	- 434.435	118.692
800	40.891	44.151	44.151	22.013	- 504.071	- 425.710	103.377
900	41.732	46.827	46.827	26.145	- 508.055	- 416.653	91.059
1000	42.488	49.389	49.389	30.357	- 507.760	- 407.531	80.868
1100	43.184	51.854	51.854	34.748	- 507.476	- 398.331	72.555
1200	43.824	54.202	54.202	39.291	- 507.196	- 389.357	65.457
1300	44.400	56.462	56.462	43.904	- 506.924	- 379.344	59.218
1400	44.900	58.643	58.643	48.304	- 506.664	- 369.344	53.318
1500	45.000	60.755	60.755	52.504	- 506.417	- 359.344	48.159
1600	45.000	62.800	62.800	56.504	- 506.175	- 349.344	43.423
1700	45.000	64.777	64.777	60.304	- 505.938	- 339.344	39.550
1800	45.000	66.690	66.690	63.904	- 505.706	- 329.344	35.858
1900	45.000	68.540	68.540	67.304	- 505.478	- 319.344	32.571
2000	45.000	70.331	70.331	70.504	- 505.254	- 309.344	29.408
2100	45.000	72.066	72.066	73.504	- 505.034	- 299.344	26.464
2200	45.000	73.745	73.745	76.304	- 504.817	- 289.344	23.694
2300	45.000	75.374	75.374	78.904	- 504.604	- 279.344	21.168
2400	45.000	76.958	76.958	81.304	- 504.396	- 269.344	18.874
2500	45.000	78.489	78.489	83.504	- 504.192	- 259.344	16.726
2600	45.000	79.979	79.979	85.504	- 503.992	- 249.344	14.726
2700	45.000	81.429	81.429	87.304	- 503.796	- 239.344	12.866
2800	45.000	82.837	82.837	88.904	- 503.604	- 229.344	11.146
2900	45.000	84.208	84.208	90.304	- 503.416	- 219.344	9.566
3000	45.000	85.544	85.544	91.504	- 503.232	- 209.344	8.126
3100	45.000	86.844	86.844	92.604	- 503.052	- 199.344	6.826
3200	45.000	88.115	88.115	93.604	- 502.876	- 189.344	5.646
3300	45.000	89.353	89.353	94.504	- 502.704	- 179.344	4.566
3400	45.000	90.562	90.562	95.304	- 502.536	- 169.344	3.586
3500	45.000	91.744	91.744	96.004	- 502.372	- 159.344	2.706

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1967





(Crystal) GFW = 160.5216

T, °K	C _p ^a	gibbs/mol S ^b	-(G ^c -H ^c)/T	H ^c -H ^c ₂₉₈	kcal/mol ΔH ^f	ΔG ^f	Log K _p
0	-	0.000	INFINITE	-	-514.108	-514.108	INFINITE
100	8.279	6.391	48.821	-4.243	-515.679	-507.388	1108.884
200	22.543	16.811	30.091	-2.656	-517.066	-499.714	544.969
298	36.730	27.510	27.510	-0.000	-517.300	-489.438	335.767
300	36.936	27.700	27.511	.057	-517.302	-489.265	356.429
400	34.943	37.198	28.777	3.368	-517.259	-479.919	282.216
500	37.383	45.277	31.291	6.993	-517.026	-470.606	205.702
600	39.122	52.253	34.216	12.822	-516.711	-461.354	168.048
700	40.756	58.233	36.986	18.922	-516.395	-452.100	131.085
800	41.754	63.487	40.236	24.154	-515.995	-442.810	105.367
900	42.568	68.070	43.143	28.154	-515.649	-433.505	82.769
1000	43.202	73.440	45.947	31.493	-515.566	-424.677	62.451
1100	44.380	77.671	48.541	34.933	-515.197	-416.989	48.907
1200	45.315	81.266	50.846	37.487	-514.684	-409.278	36.510
1300	46.215	85.319	53.708	40.095	-514.071	-401.572	26.718
1400	47.584	88.913	56.032	45.810	-513.271	-393.894	20.718
1500	48.426	92.125	58.385	50.610	-512.501	-386.569	16.815
1600	49.245	95.277	60.591	55.494	-511.692	-379.162	13.928
1700	50.049	98.266	62.722	60.459	-510.795	-371.762	11.050
1800	50.836	101.108	64.787	65.400	-509.825	-364.415	8.279
1900	51.549	103.936	66.787	70.421	-508.795	-357.026	5.507
2000	52.304	106.600	68.693	75.615	-507.709	-349.610	3.206
2100	53.219	109.169	70.559	81.081	-506.595	-342.184	1.216
2200	54.136	111.652	72.371	86.816	-505.458	-334.759	0.216
2300	55.057	114.058	74.141	92.727	-504.306	-327.334	0.216
2400	55.087	116.384	75.884	97.297	-503.141	-320.011	0.216
2500	55.700	118.644	77.511	102.835	-501.966	-312.686	0.216
2600	56.326	120.841	79.135	108.436	-500.784	-305.361	0.216
2700	57.044	122.984	80.720	114.229	-499.595	-298.036	0.216
2800	57.525	125.080	82.377	119.929	-498.406	-290.711	0.216
2900	58.099	127.088	83.777	125.404	-497.217	-283.386	0.216
3000	58.656	129.068	85.254	131.441	-496.028	-276.061	0.216

MAGNESIUM ORTHOTITANATE (Mg₂TiO₄) (CRYSTAL)

GFW = 160.5216

ΔH_f⁰ = -514.11 ± 1.5 kcal/mol
 ΔH_f⁰_{298.15} = -517.3 ± 1.5 kcal/mol
 ΔH_m⁰ = [31] kcal/mol

S_{298.15}⁰ = 27.51 ± 1.5 gibbs/mol
 T_m = 2013 ± 20°K

Heat of Formation

The heat of formation is calculated from ΔH_f⁰₂₉₈ = -4.1 ± 0.25 kcal/mol for the reaction 2 MgO(c) + TiO₂(rutile) → Mg₂TiO₄(c) measured by Kelley (1), using a solution calorimetric method. The uncertainty of ± 1.5 kcal/mol assigned to the heat of formation is due primarily to TiO₂(rutile).

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52 - 296°K) of Todd (2).

High temperature enthalpies have been measured (182 - 1817°K) by Orr (3). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values.

The entropy is based on S₂₉₈⁰ = 0.66 + 2.75 = 3.41 eu, where the first term is a lattice contribution and the second term is a zero-point entropy of 2Rln2 corresponding to random distribution of Ti and Mg on the octahedral sites of the spinel lattice. The adopted value is S₂₉₈⁰ = 27.51 ± 1.5 eu instead of 24.76 ± 0.15 eu as given by Todd.

Barth (4) showed from intensities of the X-ray diffraction lines that Mg₂TiO₄ is a spinel of the inverse (or variate) class. Thus, half of the Mg ions occupy the tetrahedral interstices in the oxygen lattice, while the remaining Mg ions and the Ti ions are (presumably) randomly located in the octahedral interstices. This conclusion was confirmed by Romeijn (5).

King and Kelley (3) suggested that the degree of structural randomness is not established and that it may vary with the sample of Mg₂TiO₄; thus, they recommended an intermediate value of Rln2 for the zero-point entropy. In a previous review, however, Kelley (1) used the theoretical value of 2Rln2 in order to make Mg₂TiO₄ stable relative to MgTiO₃ at high temperatures. We choose to adopt 2Rln2, although the evidence is not conclusive. Recent studies of solid state reactions by Bartsch and Werner (7) indicate that ΔG⁰ is negative for MgTiO₃(c) + MgO(c) → Mg₂TiO₄(c) at temperatures of 1673°K and above. Both Rln2 and 2Rln2 are consistent with this evidence.

Melting Data

See liquid table.

References

1. K. K. Kelley, S. S. Todd and E. G. King, U. S. Bur. Mines RI 5059, 1954.
2. S. S. Todd, J. Am. Chem. Soc. 74, 4669 (1952).
3. R. L. Orr and J. P. Coughlin, J. Am. Chem. Soc. 74, 3186 (1952).
4. T. F. M. Barth and E. Posnjak, Z. Krist. 82, 325 (1932).
5. F. C. Romeijn, Philips Res. Rep. 8, 304 (1953).
6. E. G. King and K. K. Kelley, U. S. Bur. Mines RI 5502, 1959.
7. H. J. Bartsch and I. Werner, Silikat Tech. 14, 203 (1963).



$$\Delta H_f^\circ = [-489.084 \pm 1.5] \text{ kcal/mol}$$

$$\Delta H_m^\circ = [31] \text{ kcal/mol}$$

$$S_{298.15}^\circ = [41.208] \text{ gibbs/mol}$$

$$T_m = 2013 \pm 20^\circ\text{K}$$

Heat of Formation

ΔH_f° is obtained from $\Delta H_f^\circ(298.15^\circ\text{K})$ by adding ΔH_m° and the difference between $H_m^\circ - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1400°K . Below 1400°K the heat capacity is obtained from the heat capacity of the crystal. Above 1400°K the heat capacity is assumed constant and estimated as 54.6 gibbs/mol or 7.8 gibbs/g-atom . The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The incongruent melting point is obtained from Massazza (1). Previous work by Coughanour (2) suggested congruent melting at 2005°K . The ΔH_m° is estimated from those of $\text{Na}_2\text{O} \cdot 2\text{TiO}_2$ and $\text{Na}_2\text{O} \cdot \text{TiO}_2$ observed by Naylor (3) and $\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ observed by King (4).

Reference

1. F. Massazza and E. Sirchia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958.
2. L. W. Coughanour and V. A. DeProse, J. Res. Natl. Bur. Stds. **51**, 87 (1953).
3. B. F. Naylor, J. Am. Chem. Soc. **67**, 2120 (1945).
4. E. G. King, R. L. Orr and K. R. Bonnickson, J. Am. Chem. Soc. **76**, 4320 (1954).

T, °K	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°	Log Kp
0							
100							
200							
298	30.730	41.208	41.208	.000	-489.084	-465.306	341.076
300	30.938	41.398	41.209	.057	-489.086	-465.158	338.867
400	34.263	50.496	42.475	3.364	-489.043	-457.182	249.793
500	37.383	58.975	48.939	5.993	-488.810	-449.239	196.362
600	39.122	65.951	57.918	10.422	-488.495	-441.354	160.766
700	40.531	72.091	59.938	14.807	-488.138	-433.526	135.353
800	41.756	77.585	51.932	18.922	-487.779	-425.752	116.310
900	42.868	82.568	56.841	23.154	-487.433	-418.018	101.509
1000	43.902	87.138	59.445	27.493	-491.350	-409.559	89.596
1100	44.880	91.350	62.339	31.033	-490.981	-401.881	79.838
1200	44.815	95.318	65.229	36.468	-491.548	-393.716	71.705
1300	44.715	99.017	67.806	41.095	-491.055	-385.583	64.822
1400	54.600	102.511	69.790	45.810	-551.285	-376.530	58.779
1500	54.600	106.278	72.099	51.270	-509.305	-364.116	53.052
1600	54.600	109.802	74.384	56.730	-507.357	-351.836	48.058
1700	54.600	113.112	76.530	62.190	-505.439	-339.672	43.668
1800	54.600	116.233	78.550	67.650	-503.555	-327.624	39.779
1900	54.600	119.195	80.706	73.110	-501.704	-315.678	36.311
2000	54.600	121.996	82.701	78.570	-500.335	-303.678	33.184
2100	54.600	124.580	84.550	84.030	-500.550	-291.689	30.357
2200	54.600	126.990	86.132	89.490	-500.738	-279.785	27.794
2300	54.600	129.617	88.338	94.950	-538.954	-267.954	25.462
2400	54.600	131.940	90.103	100.410	-537.182	-256.217	23.332
2500	54.600	134.159	91.821	105.870	-535.424	-244.552	21.379
2600	54.600	136.311	93.492	111.330	-533.674	-232.968	19.581
2700	54.600	138.371	95.112	116.790	-531.938	-221.418	17.922
2800	54.600	140.357	96.596	122.250	-530.212	-209.948	16.387
2900	54.600	142.273	98.236	127.710	-528.498	-198.533	14.962
3000	54.600	144.124	99.734	133.170	-526.798	-187.195	13.637
3100	54.600	145.916	101.195	138.630	-525.108	-175.890	12.400
3200	54.600	147.448	102.448	144.090	-523.432	-164.561	11.246
3300	54.600	149.328	104.010	149.550	-521.765	-153.475	10.144
3400	54.600	150.958	105.367	155.010	-520.120	-142.333	9.149
3500	54.600	152.541	106.592	160.470	-518.484	-131.255	8.196
3600	54.600	154.079	107.987	165.930	-516.850	-119.204	7.282
3700	54.600	155.575	109.253	171.390	-515.253	-107.118	6.268
3800	54.600	157.031	110.491	176.850	-513.685	-95.035	5.310
3900	54.600	158.449	111.703	182.310	-512.144	-82.935	4.405
4000	54.600	159.831	112.889	187.770	-510.628	-70.821	3.546

Dimagnesium Silicide (Mg_2Si)
(Crystal) Mol. Wt. = 76.73

INTERIM TABLE

T, °K.	C_p^*	S^*	$-(F^* - H_{298}^*)/T$	$H^* - H_{298}^*$	ΔH_f^*	ΔF_f^*	Log K_p
0							
100							
200							
298	16.220	19.500	19.500	.000	-19.400	-18.428	13.507
300	16.251	19.600	19.500	.030	-19.401	-18.426	13.423
400	16.700	20.800	20.800	1.030	-19.631	-18.422	13.092
500	17.470	22.512	21.135	3.158	-19.635	-18.296	12.797
600	19.040	31.934	22.907	5.416	-19.662	-18.223	12.537
700	19.400	34.916	24.414	7.351	-19.699	-18.146	12.295
800	20.050	37.563	25.695	9.334	-19.766	-18.063	12.065
900	20.480	40.948	26.326	11.468	-19.876	-17.968	11.843
1000	20.690	42.176	26.699	13.429	-20.272	-17.505	11.626
1100	21.290	44.138	30.013	15.538	-23.397	-16.923	11.362
1200	21.670	46.007	31.268	17.466	-23.541	-16.328	11.111
1300	22.050	47.756	32.470	19.672	-23.703	-15.721	10.874
1400	22.430	49.404	33.621	22.066	-23.741	-15.172	10.653
1500	22.740	50.953	34.726	24.356	-24.124	-14.533	10.443
1600	23.130	52.445	35.788	26.651	-24.474	-13.877	10.241
1700	23.470	53.857	36.809	28.981	-24.694	-13.211	10.047
1800	23.800	55.208	37.794	31.345	-24.894	-12.536	9.861
1900	24.120	56.503	38.741	33.741	-25.074	-11.856	9.683
2000	24.430	57.748	39.664	36.169	-25.227	-11.174	9.513
2100	24.730	58.948	40.554	38.627	-25.356	-10.486	9.350
2200	25.020	60.105	41.417	41.114	-25.456	-9.796	9.193
2300	25.300	61.223	42.254	43.630	-25.536	-9.106	9.041
2400	25.570	62.306	43.067	46.174	-25.596	-8.416	8.893
2500	25.830	63.355	43.857	48.744	-25.636	-7.726	8.750

DIMAGNESIUM SILICIDE (Mg_2Si) (Crystal)

Mol. Wt. = 76.73

$\Delta H_f^* 298.15 = -18.6$ kcal. mole⁻¹

$S_{298.15}^* = [19.5]$ cal. deg.⁻¹ mole⁻¹

$T_m = 1375^\circ K$

$\Delta H_m^* = [15.33]$ kcal. mole⁻¹

Heat of Formation. $\Delta H_f^* 298.15$ was found in the National Bureau of Standards Circular 500 (1952).

Heat Capacity and Entropy. C_p taken from Kubaschewski and Evans, "Metallurgical Thermochemistry," 3rd Edition, Pergamon Press Ltd., New York, (1958). $S_{298.15}$ was estimated.

Melting Data. T_m was taken from NBS Circular 500 (1952). ΔH_m^* was found in Wilson, Beahm, and Cooper, "Determination and Analysis of the Potentials of Thermal Energy Storage Materials," Callery Chemical Co., Callery, Pa., June 30, 1961.

Mg_2Si

Mg_2Si

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _p
0					
100	29.561	29.561	.000	.792	2.653
200	29.700	29.561	.042	.781	2.649
300	29.800	29.561	.082	.760	2.649
400	29.870	29.561	.117	.739	2.649
500	29.910	29.561	.147	.718	2.649
600	29.930	29.561	.172	.697	2.649
700	29.940	29.561	.192	.676	2.649
800	29.940	29.561	.207	.655	2.649
900	29.940	29.561	.217	.634	2.649
1000	29.940	29.561	.222	.613	2.649
1100	29.940	29.561	.222	.592	2.649
1200	29.940	29.561	.222	.571	2.649
1300	29.940	29.561	.222	.550	2.649
1400	29.940	29.561	.222	.529	2.649
1500	29.940	29.561	.222	.508	2.649
1600	29.940	29.561	.222	.487	2.649
1700	29.940	29.561	.222	.466	2.649
1800	29.940	29.561	.222	.445	2.649
1900	29.940	29.561	.222	.424	2.649
2000	29.940	29.561	.222	.403	2.649
2100	29.940	29.561	.222	.382	2.649
2200	29.940	29.561	.222	.361	2.649
2300	29.940	29.561	.222	.340	2.649
2400	29.940	29.561	.222	.319	2.649
2500	29.940	29.561	.222	.298	2.649
2600	29.940	29.561	.222	.277	2.649
2700	29.940	29.561	.222	.256	2.649
2800	29.940	29.561	.222	.235	2.649
2900	29.940	29.561	.222	.214	2.649
3000	29.940	29.561	.222	.193	2.649
3100	29.940	29.561	.222	.172	2.649
3200	29.940	29.561	.222	.151	2.649
3300	29.940	29.561	.222	.130	2.649
3400	29.940	29.561	.222	.109	2.649
3500	29.940	29.561	.222	.088	2.649
3600	29.940	29.561	.222	.067	2.649
3700	29.940	29.561	.222	.046	2.649
3800	29.940	29.561	.222	.025	2.649
3900	29.940	29.561	.222	.004	2.649
4000	29.940	29.561	.222	-.017	2.649

December 31, 1960.

DIMAGNESIUM SILICIDE (Mg₂Si)

(Liquid)

Mol. Wt. = 76.73

 $\Delta H_f^\circ 298.15 = -3.749$ kcal. mole⁻¹ $S_{298.15}^\circ = [30.2]$ cal. deg.⁻¹ mole⁻¹ $T_m = 1375^\circ K$ $\Delta H_m = [15.33]$ kcal. mole⁻¹Heat of Formation. $\Delta H_f^\circ 298.15$ was based on $\Delta H_f^\circ 298.15$ of the crystal and the heat of melting.Heat Capacity and Entropy. C_p was estimated. A glass transition was assumed at 918°K. $S_{298.15}^\circ$ was calculated from the entropy of the crystal and the entropy of melting.

Trimagnesium Dinitride (Mg_3N_2)
(Solid) Mol. Wt. = 100.98

INTERIM TABLE

T, °K	C_p°	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K_p
			cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	
0					
100					
200					
298	24.480	21.000	.000	- 95.820	70.234
300	24.500	21.000	.000	- 95.730	69.736
400	25.000	21.155	.046	- 90.907	69.687
500	26.460	21.990	2.583	- 86.091	37.628
600	28.460	23.842	5.192	- 81.269	29.600
700	27.190	26.031	7.874	- 76.402	19.560
800	24.920	30.215	13.658	- 66.774	16.214
900	22.600	32.441	16.618	- 61.404	13.419
1000	20.600	34.846	19.578	- 55.864	11.009
1100	20.540	37.088	22.796	- 50.749	7.520
1200	20.540	39.500	25.700	- 47.732	5.888
1300	20.540	41.593	28.458	- 43.828	3.713
1400	20.540	43.175	31.612	- 39.105	1.817
1500	20.540	44.678	37.566	- 33.300	0.494
1600	20.540	46.112	40.520	- 27.485	- 0.752
1700	20.540	47.432	43.428	- 20.559	- 1.932
1800	20.540	48.793	49.382	- 13.300	- 3.052
1900	20.540	50.057	52.336	- 6.000	- 4.104
2000	20.540	51.267	55.290	- 2.000	- 5.156
2100	20.540	52.432	58.244	0.000	- 6.208
2200	20.540	53.563	61.198	203.203	- 7.259
2300	20.540	54.633	64.152	202.617	- 8.298
2400	20.540	55.679			

TRIMAGNESIUM DINITRIDE (Mg_3N_2) (Solid)

Mol. Wt. = 100.98

ΔH_f° 298.15 = -110.2 ± 1 kcal. mole⁻¹

$S_{298.15}^\circ$ = [21 ± 2] cal. deg.⁻¹ mole⁻¹

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

Mg_3N_2

Mg_3N_2

Magnesium Orthophosphate (Mg₃P₂O₈)
(Crystal) Mol. Wt. = 262.91

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	cal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0								
100	45.000	45.000			- 895.100	- 839.836		615.586
200	50.850	45.000			- 895.109	- 839.492		611.540
300	51.000	45.315			- 895.413	- 820.800		448.498
400	57.400	60.943			- 895.395	- 802.264		350.652
500	62.700	74.332			- 895.112	- 783.664		285.436
600	67.450	86.191			- 893.700	- 755.302		206.875
700	72.000	96.829			- 893.264	- 735.209		178.524
800	76.300	106.082			- 892.792	- 712.742		155.762
900	80.300	114.735			- 892.281	- 690.313		137.146
1000	84.020	124.735			- 891.722	- 668.949		108.689
1100	86.060	132.844			- 891.126	- 622.565		86.569
1200	87.400	140.395			- 890.493	- 594.192		77.314
1300	88.400	147.497			- 889.829	- 566.038		70.410
1400	89.100	154.135			- 889.133	- 537.897		61.956
1500	90.800	160.384			- 888.410	- 482.708		49.749
1600	91.000	166.222			- 887.661	- 455.286		44.541
1700	91.200	171.647			- 886.889	- 428.010		39.527
1800	91.200	176.658			- 886.093	- 397.043		31.601
1900	91.200	181.347			- 885.172	- 320.321		28.001
2000	91.200	185.595			- 884.126	- 293.707		24.687
2100	91.200	190.445			- 882.959	- 260.435		18.797
2200	91.200	194.858			- 881.679	- 220.635		16.168
2300	91.200	198.892			- 880.281	- 188.370		13.722
2400	91.200	203.223			- 878.766			
2500	91.200	206.946			- 877.126			
2600	91.200	210.523			- 875.363			
2700	91.200	213.785			- 873.479			
2800	91.200	216.728			- 871.479			
2900	91.200	220.482			- 869.363			
3000	91.200	223.573			- 867.126			

Dec. 31, 1960; Mar. 31, 1963

MAGNESIUM ORTHOPHOSPHATE (Mg₃P₂O₈)

(CRYSTAL)

MOL. WT. = 262.91

ΔH_f° = UnknownΔH_f° 298.15 = -895.1 ± 2.5 kcal. mole⁻¹ΔH_m° = [29 ± 10] kcal. mole⁻¹S°_{298.15} = [45] cal. deg.⁻¹ mole⁻¹
T_m = 1621°K.

Heat of Formation.

The selected ΔH_f° 298.15 is a weighted average of a revised calorimetric determination and a third law calculation using equilibrium data.

A calorimetric determination of the heat of formation reported by C. G. Stevens and E. T. Turkdogan, Trans. Faraday Soc. 50, 370 (1954) was revised three ways:

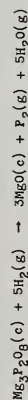
1. The heat of reaction for the reaction 3MgO(c) + P₂O₅(orthorhombic) → Mg₃P₂O₈(c) had been evaluated at 348°K. A small temperature correction to 298.15 was made with thermal data not available to Stevens and Turkdogan (loc. cit.) on MgO (W. F. Glauque, J. Am. Chem. Soc. 71, 3192 (1949)), P₂O₅ (JANAF Table, Dec. 31, 1962) and Mg₃P₂O₈ (this table).

2. A new ΔH_f° 298.15 for P₂O₅(hexagonal) as reported by W. S. Holmen, Trans. Faraday Soc. 58, 1916 (1962) was combined with the heat of reaction, -6.85 ± 1.0 kcal. mole⁻¹, for the reaction: P₂O₅(hexagonal) → P₂O₅(orthorhombic) as reported by W. L. Hill, G. T. Faust, and S. B. Hendricks, J. Am. Chem. Soc. 65, 794 (1943).

3. A correction of +9.35 kcal. mole⁻¹ was made for the change in phosphorus reference state from white (α) → red (V). (The correction is +9.35 kcal./mole of Mg₃P₂O₈ or +4.173 kcal. mole⁻¹ of P.)

This revised ΔH_f° 298.15, -897.60 ± 2.0 kcal. mole⁻¹, would appear to be more reliable than the original value reported by Stevens and Turkdogan (loc. cit.).

For the Reaction



the third law treatment of the equilibrium data of J. B. Boeky, J. Iron Steel Institute (London) 176, 66 (1952) and the JANAF Table free energy functions gave a ΔH_f° 298.15 = -893.11 kcal. mole⁻¹.

The quantity, -895.10 ± 2.50 kcal. mole⁻¹, is taken as the most probable value for the heat of formation of magnesium orthophosphate.

Heat Capacity and Entropy.

The entropy at 298.15 was estimated by considering the additive entropy constants of K. K. Kelley, private communication, June 1960, and E. L. Evans and O. Kubaschewski, "Metallurgical Thermochemistry, 1958. The heat capacity was estimated in a similar manner by considering the heat capacities of the constituent elements and related compounds such as Mg, O₂, MgO, P, P₂O₅, Cr₂P₂O₇, and Ca₃P₂O₈.

Melting Data.

The melting point, 1621°K, as reported by Stevens and Turkdogan (loc. cit.) was selected. There is disagreement on the melting point in the literature. From the work of H. Winter, Dias. Universitäts zu Leipzig 1913, K. K. Kelley, U. S. Bureau of Mines Bulletin 393, (1936) has quoted a melting point of 1457°K and has calculated a "rather uncertain value" of 11,300 kcal./mole for the heat of fusion. J. B. Boeky (loc. cit.) has found a melting point of 1703°K. J. Bereš, Rozniski Chim. 32, 17 (1951) gives 1630°K as the melting point.

Magnesium Orthophosphate ($Mg_3P_2O_8$)

(Liquid) Mol. Wt. = 262.91



MOL. WT. = 262.91

(LIQUID)

MAGNESIUM ORTHOPHOSPHATE ($Mg_3P_2O_8$)

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0								
100								
200								
298	50.850	54.764	54.764	•000	- 876.897	- 824.544	604.378	
300	51.000	55.079	54.764	•004	- 876.906	- 824.218	600.414	
400	62.700	61.017	61.017	11.613	- 877.131	- 788.955	344.635	
500	67.450	66.098	65.894	18.123	- 876.850	- 771.346	280.949	
600	72.000	70.880	70.880	25.097	- 876.333	- 753.797	235.335	
700	76.530	75.167	75.096	32.536	- 875.427	- 746.967	204.052	
800	80.000	78.945	78.845	40.562	- 874.185	- 740.632	178.562	
1000	84.020	134.703	84.062	48.641	- 870.676	- 704.394	155.938	
1100	103.550	143.074	90.658	57.438	- 917.523	- 682.963	135.686	
1200	105.072	152.131	95.591	67.849	- 913.871	- 661.802	120.525	
1300	109.100	160.584	100.271	78.556	- 910.059	- 640.965	107.748	
1400	112.500	168.422	104.742	89.582	- 906.129	- 620.402	96.269	
1500	112.500	176.562	109.405	100.737	- 901.803	- 592.129	86.269	
1600	113.201	182.852	113.832	112.031	- 896.402	- 565.665	77.263	
1700	113.600	189.750	118.155	123.377	- 890.971	- 539.528	69.558	
1800	113.842	197.430	122.369	134.750	- 885.541	- 513.719	62.371	
1900	114.000	204.945	126.473	146.153	- 880.117	- 488.210	56.154	
2000	114.205	209.241	130.466	157.557	- 874.691	- 462.984	50.351	
2100	114.327	214.820	134.351	168.984	- 869.275	- 438.040	45.585	
2200	114.408	220.140	138.131	180.421	- 863.879	- 413.342	41.060	
2300	114.448	225.227	141.808	191.864	- 858.493	- 388.886	36.952	
2400	114.450	230.083	145.386	203.317	- 853.123	- 364.693	33.202	
2500	114.408	234.769	148.868	214.753	- 847.775	- 340.693	29.762	
2600	114.327	239.255	152.259	226.190	- 842.466	- 316.907	26.637	
2700	114.206	243.567	155.561	237.617	- 837.214	- 293.334	23.743	
2800	114.044	247.716	158.779	248.959	- 832.020	- 269.955	21.070	
2900	113.842	251.743	161.915	260.217	- 826.884	- 246.754	18.595	
3000	113.600	255.572	164.973	271.407	- 821.797	- 223.756	16.295	
3100	113.600	259.297	167.956	282.517	- 816.757	- 200.887	14.162	
3200	113.600	262.904	170.867	293.517	- 811.764	- 178.217	12.171	
3300	113.600	266.399	173.709	304.417	- 806.834	- 155.696	10.311	
3400	113.600	269.784	176.484	315.217	- 801.964	- 133.314	8.599	
3500	113.600	273.083	179.199	326.017	- 797.157	- 111.109	7.039	
3600	113.600	276.284	181.851	336.717	- 792.407	- 89.023	5.604	
3700	113.600	279.396	184.446	347.317	- 787.713	- 67.080	3.962	
3800	113.600	282.476	186.984	357.817	- 783.073	- 45.265	2.603	
3900	113.600	285.522	189.467	368.217	- 778.487	- 23.603	1.323	
4000	113.600	288.522	191.903	378.517	- 773.957	- 2.036	•112	
4100	113.600	291.057	194.288	388.717	- 769.487	19.380	1.033	
4200	113.600	293.795	196.624	408.117	- 765.073	40.690	2.117	
4300	113.600	296.468	198.915	427.417	- 760.713	61.893	3.146	
4400	113.600	299.083	201.157	446.617	- 756.407	82.487	4.122	
4500	113.600	301.632	203.367	465.717	- 752.157	103.397	5.049	
4600	113.600	304.129	205.530	484.817	- 748.063	124.892	5.932	
4700	113.600	306.572	207.654	503.917	- 744.023	146.311	6.771	
4800	113.600	308.964	209.740	523.017	- 740.037	167.311	7.572	
4900	113.600	311.304	211.797	542.117	- 736.107	187.811	8.335	
5000	113.600	313.601	213.802	561.217	- 732.232	207.868	9.064	
5100	113.600	315.851	215.781	580.317	- 728.413	227.767	9.760	
5200	113.600	318.057	217.727	600.417	- 724.647	247.467	10.425	
5300	113.600	320.221	219.640	620.517	- 720.937	266.983	11.064	
5400	113.600	322.344	221.517	640.617	- 717.282	286.259	11.673	
5500	113.600	324.428	223.374	660.717	- 713.682	305.257	12.259	
5600	113.600	326.475	225.197	680.817	- 710.137	324.499	12.820	
5700	113.600	328.486	226.992	700.917	- 706.647	343.420	13.358	
5800	113.600	330.462	228.759	721.017	- 703.213	362.259	13.876	
5900	113.600	332.404	230.497	741.117	- 699.832	380.930	14.373	
6000	113.600	334.313	232.213	761.217	- 696.507	400.726	14.851	

S_{298.15}^o = [54.8] cal. deg.⁻¹ mole⁻¹

ΔH_f^o 298.15 = [-877 ± 10] kcal. mole⁻¹

ΔH_m^o = [29 ± 10] kcal. mole⁻¹

ΔH_v^o = Unknown

T_m = 1621°K

T_b = Unknown

Heat of Formation.

The ΔH_f^o 298.15 was calculated from the estimated ΔH_m and the ΔH_f^o 298.15 of the crystal.

Heat Capacity and Entropy.

The heat capacity was estimated as 13/11 of the corresponding heat capacity of Ca₃P₂O₇ as given in K. K.

Kelley, U. S. Bur. Mines Bull. 5841 (1960).

Melting Data.

The heat of melting was estimated by taking 13/11 of the ΔH_m of Ca₃P₂O₇ as given in K. K. Kelley (loc. cit.)



Molybdenum (Mo)
(Reference State)

GF_W = 95.94

T, °K	C _p ^a	S ^b	g/bbs/mol -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH _f ^c	ΔG ^d	Log K _p
0	.000	.000	INFINITE	- 1.096	.000	.000	.000
100	3.232	1.679	11.469	.000	.000	.000	.000
200	5.131	4.655	7.345	.538	.000	.000	.000
298	5.729	6.837	6.837	.000	.000	.000	.000
300	5.737	6.873	6.838	.011	.000	.000	.000
400	6.050	8.569	7.067	.601	.000	.000	.000
500	6.246	9.942	7.509	1.217	.000	.000	.000
600	6.380	11.093	8.013	1.848	.000	.000	.000
700	6.469	12.084	8.441	2.441	.000	.000	.000
800	6.522	12.954	8.794	3.001	.000	.000	.000
900	6.562	13.730	9.064	3.467	.000	.000	.000
1000	6.598	14.431	9.264	3.861	.000	.000	.000
1100	6.794	15.074	10.400	5.141	.000	.000	.000
1200	6.927	15.670	10.814	5.827	.000	.000	.000
1300	7.046	16.232	11.304	6.467	.000	.000	.000
1400	7.154	16.763	11.757	7.066	.000	.000	.000
1500	7.253	17.272	12.184	7.633	.000	.000	.000
1600	7.344	17.761	12.598	8.171	.000	.000	.000
1700	7.428	18.232	12.993	8.684	.000	.000	.000
1800	7.505	18.687	13.371	9.176	.000	.000	.000
1900	7.577	19.138	13.730	9.650	.000	.000	.000
2000	7.643	19.574	14.066	10.109	.000	.000	.000
2100	7.704	19.997	14.389	10.554	.000	.000	.000
2200	7.760	20.408	14.700	10.986	.000	.000	.000
2300	7.812	20.807	15.000	11.406	.000	.000	.000
2400	7.860	21.195	15.289	11.814	.000	.000	.000
2500	7.904	21.566	15.566	12.211	.000	.000	.000
2600	7.944	21.922	15.832	12.597	.000	.000	.000
2700	7.980	22.274	16.088	12.963	.000	.000	.000
2800	8.012	22.622	16.334	13.310	.000	.000	.000
2900	8.041	22.957	16.571	13.639	.000	.000	.000
3000	8.067	23.279	16.799	13.959	.000	.000	.000
3100	8.090	23.589	17.018	14.270	.000	.000	.000
3200	8.110	23.887	17.228	14.573	.000	.000	.000
3300	8.128	24.174	17.429	14.868	.000	.000	.000
3400	8.143	24.449	17.622	15.155	.000	.000	.000
3500	8.156	24.713	17.807	15.434	.000	.000	.000
3600	8.167	24.967	17.978	15.705	.000	.000	.000
3700	8.176	25.212	18.144	15.969	.000	.000	.000
3800	8.183	25.448	18.302	16.226	.000	.000	.000
3900	8.188	25.675	18.452	16.476	.000	.000	.000
4000	8.191	25.893	18.595	16.719	.000	.000	.000
4100	8.192	26.102	18.731	16.955	.000	.000	.000
4200	8.192	26.302	18.860	17.184	.000	.000	.000
4300	8.191	26.493	18.982	17.406	.000	.000	.000
4400	8.188	26.676	19.100	17.621	.000	.000	.000
4500	8.183	26.851	19.213	17.829	.000	.000	.000
4600	8.176	26.999	19.321	18.030	.000	.000	.000
4700	8.167	27.132	19.424	18.224	.000	.000	.000
4800	8.156	27.257	19.521	18.411	.000	.000	.000
4900	8.143	27.375	19.613	18.591	.000	.000	.000
5000	8.128	27.487	19.700	18.764	.000	.000	.000
5100	8.110	27.593	19.782	18.931	.000	.000	.000
5200	8.090	27.693	19.859	19.092	.000	.000	.000
5300	8.067	27.787	19.931	19.247	.000	.000	.000
5400	8.041	27.875	19.999	19.396	.000	.000	.000
5500	8.012	27.957	20.062	19.539	.000	.000	.000
5600	7.980	28.033	20.120	19.676	.000	.000	.000
5700	7.944	28.104	20.173	19.807	.000	.000	.000
5800	7.904	28.170	20.221	19.932	.000	.000	.000
5900	7.860	28.232	20.264	20.052	.000	.000	.000
6000	7.812	28.290	20.302	20.167	.000	.000	.000
6100	7.760	28.344	20.335	20.277	.000	.000	.000
6200	7.704	28.394	20.363	20.381	.000	.000	.000
6300	7.643	28.440	20.387	20.480	.000	.000	.000
6400	7.577	28.482	20.407	20.574	.000	.000	.000
6500	7.505	28.521	20.423	20.663	.000	.000	.000
6600	7.428	28.557	20.436	20.747	.000	.000	.000
6700	7.344	28.589	20.446	20.826	.000	.000	.000
6800	7.253	28.617	20.453	20.900	.000	.000	.000
6900	7.154	28.642	20.457	20.969	.000	.000	.000
7000	7.046	28.664	20.459	21.033	.000	.000	.000
7100	6.927	28.683	20.458	21.092	.000	.000	.000
7200	6.800	28.699	20.454	21.147	.000	.000	.000
7300	6.666	28.712	20.447	21.197	.000	.000	.000
7400	6.522	28.722	20.437	21.242	.000	.000	.000
7500	6.380	28.729	20.423	21.282	.000	.000	.000
7600	6.246	28.733	20.406	21.317	.000	.000	.000
7700	6.110	28.734	20.386	21.347	.000	.000	.000
7800	5.972	28.732	20.363	21.372	.000	.000	.000
7900	5.831	28.727	20.337	21.393	.000	.000	.000
8000	5.688	28.719	20.308	21.410	.000	.000	.000
8100	5.542	28.708	20.276	21.423	.000	.000	.000
8200	5.394	28.694	20.241	21.432	.000	.000	.000
8300	5.243	28.677	20.203	21.437	.000	.000	.000
8400	5.090	28.657	20.162	21.438	.000	.000	.000
8500	4.934	28.634	20.118	21.435	.000	.000	.000
8600	4.776	28.608	20.072	21.428	.000	.000	.000
8700	4.616	28.579	20.023	21.417	.000	.000	.000
8800	4.454	28.547	19.971	21.402	.000	.000	.000
8900	4.290	28.512	19.917	21.383	.000	.000	.000
9000	4.124	28.474	19.861	21.360	.000	.000	.000
9100	3.956	28.433	19.802	21.333	.000	.000	.000
9200	3.787	28.389	19.741	21.302	.000	.000	.000
9300	3.617	28.342	19.678	21.267	.000	.000	.000
9400	3.445	28.292	19.613	21.228	.000	.000	.000
9500	3.272	28.239	19.546	21.185	.000	.000	.000
9600	3.098	28.183	19.477	21.138	.000	.000	.000
9700	2.923	28.124	19.406	21.087	.000	.000	.000
9800	2.747	28.062	19.333	21.032	.000	.000	.000
9900	2.570	28.000	19.258	20.973	.000	.000	.000
10000	2.392	27.934	19.181	20.910	.000	.000	.000

Dec. 31, 1968

See crystal, liquid and monatomic gas tables for details.

(REFERENCE STATE)

0 - 2892°K Crystal
2892 - 4919°K Liquid
4919 - 6000°K Ideal Monatomic gas

MOLYBDENUM (Mo)

GF_W = 95.94

Mo

Mo

Molybdenum (Mo)
(Crystal)

GFW = 95.94

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	kcal/mol ΔH°	ΔG°	Log Kp
0	•000	•000 INFINITE	- 1.096	•000	•000
100	5.131	1.455	•538	•000	•000
200	5.131	1.455	•000	•000	•000
298	5.729	6.837	•000	•000	•000
300	5.737	6.873	•011	•000	•000
400	6.050	8.569	•067	•000	•000
500	6.246	9.942	1.217	•000	•000
600	6.380	11.093	1.848	•000	•000
700	6.476	12.084	2.491	•000	•000
800	6.552	12.954	3.143	•000	•000
900	6.622	13.730	3.801	•000	•000
1000	6.659	14.451	4.467	•000	•000
1100	6.794	15.074	5.141	•000	•000
1200	6.927	15.670	5.827	•000	•000
1300	7.090	16.231	6.528	•000	•000
1400	7.274	16.753	7.246	•000	•000
1500	7.473	17.272	7.983	•000	•000
1600	7.684	17.761	8.741	•000	•000
1700	7.906	18.233	9.520	•000	•000
1800	8.140	18.692	10.323	•000	•000
1900	8.377	19.138	11.148	•000	•000
2000	8.630	19.574	11.999	•000	•000
2100	8.897	20.001	12.875	•000	•000
2200	9.190	20.422	13.779	•000	•000
2300	9.520	20.837	14.714	•000	•000
2400	9.820	21.231	15.684	•000	•000
2500	10.143	21.606	16.693	•000	•000
2600	11.090	22.089	17.740	•000	•000
2700	11.816	22.520	18.924	•000	•000
2800	12.618	22.964	20.145	•000	•000
2900	13.590	23.422	21.400	•019	•001
3000	14.460	23.897	22.690	•240	•017
3100	15.400	24.386	16.534	•450	•032
3200	16.320	24.890	16.787	•5145	•044
3300	17.240	25.406	17.040	•608	•054
3400	18.160	25.934	17.294	•697	•062
3500	19.080	26.474	17.548	•781	•068
3600	20.000	27.025	17.804	•861	•072
3700	20.920	27.585	18.061	•935	•074
3800	21.840	28.155	18.319	•1.009	•076
3900	22.760	28.734	18.579	•1.083	•078
4000	23.680	29.322	18.840	•1.157	•079

GFW = 95.94

(CRYSTAL)

Mo

$$\Delta H^{\circ}_{298,15} = 0 \text{ kcal/mol}$$

$$\Delta H^{\circ}_{298,15} = 0 \text{ kcal/mol}$$

$$\Delta H^{\circ} = [6652 \pm 600] \text{ kcal/mol}$$

$$\Delta H^{\circ}_{298,15} = 157.3 \pm 0.5 \text{ kcal/mol}$$

$$S^{\circ}_{298,15} = 6.837 \pm 0.01 \text{ gibbs/mol}$$

$$T_m = 2892 \pm 10^{\circ}\text{K}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Below 20°K several investigators 1,2,3,4,5,6 have determined the heat capacity, and an average of these determinations was used to obtain a Debye theta = 440 and an electronic gamma = 4.7×10^{-4} gibbs/mol-deg. From these the entropy at 20°K was calculated as 0.024 gibbs/mol and the enthalpy as 0.265 cal. Between 20°K and 271°K the data of Clausius and Franzosini⁷ are the adopted heat capacities. The data of Simon and Zeidler⁵ are as much as 2.5% high below 78°K and as much as 1% low above this.

Both the high temperature enthalpies and heat capacity have been measured by several investigators and there is generally good agreement in the 1000-2000°K range. A smooth curve was drawn through the high temperature enthalpy data of several investigators 7,8,9,10,11,12, which was also joined smoothly to the integrated low temperature data of Clausius and Franzosini. The heat capacity was obtained by fitting the smoothed enthalpy data with a polynomial and differentiating. The heat capacity obtained agreed satisfactorily with that reported in several investigations 13,14,15,16,17,18,19.

References:

1. C. A. Bryant and P. H. Kesom, J. Chem. Phys. **35**, 1149 (1961). Cp 1°-4.5°K.
2. K. Clausius and P. Franzosini, Z. Naturforsch. **14a**, 99 (1959). Cp 13°-270°K.
3. M. Horowitz and J. G. Daunt, Phys. Rev. **91**, 1099 (1953). Cp 1.3°-10.4°K.
4. P. J. Morin and J. P. Maite, Phys. Rev. **123**, 1115 (1963). Cp 1.5°-20°K.
5. F. Simon and M. Zeidler, Z. Phys. Chem. **123**, 383 (1926). Cp 15°-238°K.
6. D. C. Rohrer, D. G. Onn and H. Meyer, Phys. Rev. **139**, A1661, (1965). Cp 0.4°-4°K.
7. P. M. Jaeger and M. A. Veenstra, Rec. Trav. Chim. **53**, 677 (1934). H_m-H₂₇₃ 670°-1827°K.
8. V. A. Kirillin, A. E. Sheindlin and V. Ya. Chekhovskoi, Inter. J. Heat Mass Transfer **5**, 1 (1962). H_m-H₂₇₃ 973°-2810°K.
9. C. W. Kohnen, Ph.D. Dissertation, Ohio State University (1952). H_m-H₂₉₈ 1103°-2623°K.
10. L. S. Lazareva, P. B. Kantor and V. V. Kandyba, Phys. Metals and Metallog. **11**, 133 (1961). H_m-H₂₉₈ 1154°-2462°K.
11. T. A. Redfield and J. H. Hill, U.S.A. Energy Comm., ONR-1087 (1951). H_m-H₂₇₃ 481°-1359°K.
12. F. Kust, A. Meuthen and R. Durrer, Forsch. Gebiete Ingenieurw. **204**, 3 (1918). H_m-H₂₇₃ 375-773°K.
13. H. L. Bronson, H. M. Chisholm and S. M. Docketty, Can. J. Res. **8**, 282 (1933). Cp 254-774°K.
14. D. Cooper and G. O. Longstroth, Phys. Rev. **33**, 243 (1929). Cp 233°-563°K.
15. G. C. Lowenthal, Australian J. Phys. **16**, 47 (1963). Cp 1200° - 2100°K.
16. N. S. Raor and J. D. McClelland, J. Phys. Chem. Solids **15**, 17 (1959). Cp 1400°-2860°K.
17. R. L. Rudkin, W. J. Parker and R. J. Jenkins, "Temperature, Its Measurement and Control in Science and Industry," Ed. A. I. Dahl Vol. 3, Part 2, Reinhold Publishing Corp., New York, 1962.
18. T. E. Stern, Phys. Rev. **32**, 298 (1928). Cp 273°-718°K.
19. R. E. Taylor and R. A. Finch, J. Less-Common Metals **5**, 283 (1964). Cp 200-2860°K.

Sublimation Data.

See Mo(g) for details.

Heat of Formation.

The ΔH_f^{298} was obtained from that of the crystal plus ΔH_m° and the difference between H_{2992}° and H_{2998}° for crystal and liquid.

$$S_{298,15}^\circ = [9.261] \text{ gibbs/mol}$$
$$\Delta H_f^{298,15} = [7.076] \text{ kcal/mol}$$
$$T_m = 2892 \pm 10^\circ \text{K}$$
$$\Delta H_m^\circ = [6652 \pm 600] \text{ kcal/mol}$$
$$T_b = [491.9^\circ \text{K}]$$
$$\Delta H_v^\circ = [140.812] \text{ kcal/mol}$$

The ΔH_{298}° was obtained from that of the crystal plus ΔH_m° and the difference between $H_{2892} - H_{2998}$ for crystal and liquid.

The heat capacity was estimated as 10 gibbs/mol in the real range in order to be comparable with the value in the crystal below the melting point. Below the melting point the heat capacity was assumed constant to a glass transition, assumed to be 2000°K, below which the heat capacity was that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

The heat of melting was obtained from an entropy of melting of 2.3 eu, assumed by comparison with Fe, Cu, Co, Mg and Al. The melting point was reported by E. Rudy and S. Windisch, Aerojet-General Corporation, Report No. AFWT-TN-65-2, Part 1, Vol. III, July 1965. A. O. Worthing, *Phys. Rev.* **25**, 846 (1925), reports a melting point of 2835°K which, corrected to the 1948 International Temperature Scale, is 2882°K.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

OPW = 95.94

(IDEAL GAS)

MOLYBDENUM (Mo)

GFW = 95.94

Molybdenum (Mo)
(Ideal Gas)

T, °K	Cp°	$\frac{G^{\circ}-H^{\circ}_{298}}{T}$	$\frac{H^{\circ}-H^{\circ}_{298}}{T}$	$\frac{H^{\circ}-H^{\circ}_{298}}{T}$	ΔG°	Log Kp
0	-0.00	INFINITE	-1.481	156.915	156.915	INFINITE
100	4.968	39.033	47.677	157.225	157.225	156.915
200	4.968	41.477	43.915	157.350	157.350	156.915
298	4.968	43.460	41.481	157.300	157.300	156.915
300	4.968	43.460	41.481	157.300	157.300	156.915
400	4.968	43.460	41.481	157.300	157.300	156.915
500	4.968	43.460	41.481	157.300	157.300	156.915
600	4.968	43.460	41.481	157.300	157.300	156.915
700	4.968	43.460	41.481	157.300	157.300	156.915
800	4.968	43.460	41.481	157.300	157.300	156.915
900	4.968	43.460	41.481	157.300	157.300	156.915
1000	4.968	43.460	41.481	157.300	157.300	156.915
1100	4.968	43.460	41.481	157.300	157.300	156.915
1200	4.968	43.460	41.481	157.300	157.300	156.915
1300	4.968	43.460	41.481	157.300	157.300	156.915
1400	4.968	43.460	41.481	157.300	157.300	156.915
1500	4.968	43.460	41.481	157.300	157.300	156.915
1600	4.968	43.460	41.481	157.300	157.300	156.915
1700	4.968	43.460	41.481	157.300	157.300	156.915
1800	4.968	43.460	41.481	157.300	157.300	156.915
1900	4.968	43.460	41.481	157.300	157.300	156.915
2000	4.968	43.460	41.481	157.300	157.300	156.915
2100	4.968	43.460	41.481	157.300	157.300	156.915
2200	4.968	43.460	41.481	157.300	157.300	156.915
2300	4.968	43.460	41.481	157.300	157.300	156.915
2400	4.968	43.460	41.481	157.300	157.300	156.915
2500	4.968	43.460	41.481	157.300	157.300	156.915
2600	4.968	43.460	41.481	157.300	157.300	156.915
2700	4.968	43.460	41.481	157.300	157.300	156.915
2800	4.968	43.460	41.481	157.300	157.300	156.915
2900	4.968	43.460	41.481	157.300	157.300	156.915
3000	4.968	43.460	41.481	157.300	157.300	156.915
3100	4.968	43.460	41.481	157.300	157.300	156.915
3200	4.968	43.460	41.481	157.300	157.300	156.915
3300	4.968	43.460	41.481	157.300	157.300	156.915
3400	4.968	43.460	41.481	157.300	157.300	156.915
3500	4.968	43.460	41.481	157.300	157.300	156.915
3600	4.968	43.460	41.481	157.300	157.300	156.915
3700	4.968	43.460	41.481	157.300	157.300	156.915
3800	4.968	43.460	41.481	157.300	157.300	156.915
3900	4.968	43.460	41.481	157.300	157.300	156.915
4000	4.968	43.460	41.481	157.300	157.300	156.915
4100	4.968	43.460	41.481	157.300	157.300	156.915
4200	4.968	43.460	41.481	157.300	157.300	156.915
4300	4.968	43.460	41.481	157.300	157.300	156.915
4400	4.968	43.460	41.481	157.300	157.300	156.915
4500	4.968	43.460	41.481	157.300	157.300	156.915
4600	4.968	43.460	41.481	157.300	157.300	156.915
4700	4.968	43.460	41.481	157.300	157.300	156.915
4800	4.968	43.460	41.481	157.300	157.300	156.915
4900	4.968	43.460	41.481	157.300	157.300	156.915
5000	4.968	43.460	41.481	157.300	157.300	156.915
5100	4.968	43.460	41.481	157.300	157.300	156.915
5200	4.968	43.460	41.481	157.300	157.300	156.915
5300	4.968	43.460	41.481	157.300	157.300	156.915
5400	4.968	43.460	41.481	157.300	157.300	156.915
5500	4.968	43.460	41.481	157.300	157.300	156.915
5600	4.968	43.460	41.481	157.300	157.300	156.915
5700	4.968	43.460	41.481	157.300	157.300	156.915
5800	4.968	43.460	41.481	157.300	157.300	156.915
5900	4.968	43.460	41.481	157.300	157.300	156.915
6000	4.968	43.460	41.481	157.300	157.300	156.915

See 31, 1966

Ground State Configuration $7s_3$
 $\Delta H^{\circ}_f = 43.46 \text{ gibbs/mol}$
 $\Delta H^{\circ}_f = 156.9 \pm 0.5 \text{ kcal/mol}$
 $\Delta H^{\circ}_f = 157.3 \pm 0.5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_1, \text{ cm}^{-1}$	g_1	$\epsilon_1, \text{ cm}^{-1}$	g_1
-------------------------------	-------	-------------------------------	-------

0	7	21206.5	42
---	---	---------	----

10768.3	5	23571.2	21
---------	---	---------	----

10986.0	1	24504.7	34
---------	---	---------	----

11142.8	3	25990.1	152
---------	---	---------	-----

11454.4	5	27548.0	52
---------	---	---------	----

11858.5	7	29551.1	133
---------	---	---------	-----

12346.3	9	31809.1	105
---------	---	---------	-----

18746.8	45	34546.4	109
---------	----	---------	-----

18321.8	15	37024.7	169
---------	----	---------	-----

20240.5	26	29820.1	168
---------	----	---------	-----

22639.0	8	40876.3	124
---------	---	---------	-----

		56851.0	58
--	--	---------	----

Heat of Formation

The heat of formation is simply the heat of sublimation at 298°K; this is obtained by second and third law analysis of several vapor pressure sets. A comparison of the results is tabulated below.

Reference Method Points Range °K $\Delta H_{298} \text{ kcal/mol}$

1. Vozella Langmuir 12 2140-2533 156.4 ± 2.9 157.8 ± 0.9

2. Edwards Langmuir 9 2150-2460 146.7 ± 1.5 158.2 ± 1.2

3. Fries Langmuir 12 2086-2489 156.5 ± 1.6 156.7 ± 0.7

4. Jones Langmuir 9* 2113-2496 161.6 ± 3.8 156.0 ± 1.4

5. Norris Langmuir Equin. 2000-2600 131.1 148.6 ± 4.3

6. Zwicker Langmuir Equin. 1200-2500 159.1 158.2 ± 0.8

7. Babelawsky Mass Spec. 2220-2603 149.6 ± 2.2

* One point rejected due to failure of statistical test

The data of references 1 and 3 show no drift and thus indicate that the accommodation coefficient is essentially unity. A median value of the 3rd law heat is adopted as $157.3 \pm 0.5 \text{ kcal/mol}$.

References

1. P. A. Vozella, A. D. Miller and M. A. DeCrescente, J. Chem. Phys. **41**, 589 (1964).
2. J. W. Edwards, H. L. Johnston and P. E. Blackburn, J. Am. Chem. Soc. **74**, 1539 (1952).
3. R. J. Fries, AEC Accession No. 13023, Rept. No. LA-3423, January 1966.
4. H. A. Jones, I. Langmuir and O. M. J. Mackay, Phys. Rev. **30**, 201 (1927).
5. L. Norris and A. G. Worthing, Phys. Rev. **44**, 323 (1933).
6. C. Zwicker, Physica **7**, 71 (1927).
7. T. P. J. H. Babelawsky, Physica **28**, 1160 (1962).

** Temperatures adjusted to 1946 IFTS according to R. J. Cornucini, J. Natl. Bur. Std. **42**, 133 (1949).

Heat Capacity and Entropy

The electronic energy levels are those listed by C. E. Moore, U. S. Natl. Bur. Std. Circular 467, Washington D. C. (1959). Several individual lines missing from given terms were estimated by analogy with the observed lines in the term. In addition, an estimate of the values of completely missing terms, arising out of low lying multiplets, was made as follows: The $1D$ and $3F$ and $3P$ terms of the $[Kr] 4d^5s^2$ multiplet were estimated at 25000, 30000, 34000 and 36000 cm^{-1} . The triplet P, D, F and G levels and the singlet S, D, F and O levels of the $[Kr] 4d^5$ configuration were estimated at 30000 cm^{-1} and 40000 cm^{-1} respectively.

Higher configurations such as $[Kr] 4d^4s^2$ and $4d^4s^2$ which have many septuplet and quintuplet terms were thought to lie close to the ionization limit. However, upon calculating a table which contains an extra 100 levels at 35000 cm^{-1} and 200 levels each at 40000 and 45000 cm^{-1} , the difference in free energy function at 6000°K is a negligible 0.008 gibbs/mol.

Molybdenum Unipositive Ion (Mo⁺)
(Ideal Gas) GFW = 95.9395

T, °K	Cp	S° -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal/mol	ΔHf° kcal/mol	ΔGF	Log Kp
0						
100						
200	4.968	43.154	0.000	322.823	310.508	- 227.608
298						
300	4.968	43.154	0.009	322.830	310.431	- 226.149
400	4.968	43.154	0.031	322.833	310.403	- 224.689
500	4.968	43.177	1.003	323.612	301.043	- 131.970
600	4.968	46.628	4.4129	323.975	297.576	- 108.392
700	4.968	46.394	4.542	324.324	293.147	- 91.525
800	4.968	48.057	4.941	324.666	288.670	- 78.661
900	4.968	48.413	5.140	325.002	284.151	- 68.001
1000	4.968	49.166	5.487	325.330	279.534	- 61.405
1100	4.968	49.639	6.018	325.650	275.007	- 56.339
1200	4.969	50.072	6.438	325.957	270.388	- 52.444
1300	4.970	50.470	6.841	326.249	265.773	- 48.673
1400	4.971	50.836	7.226	326.527	261.166	- 45.016
1500	4.977	51.181	7.592	326.793	256.557	- 41.357
1600	4.986	51.503	7.947	327.020	251.955	- 37.698
1700	4.999	51.805	8.290	327.237	246.982	- 34.038
1800	5.020	52.091	8.622	327.431	242.255	- 30.414
1900	5.049	52.361	8.945	327.601	237.271	- 26.830
2000	5.091	52.624	9.260	327.759	232.711	- 23.286
2100	5.145	52.873	9.561	327.892	228.018	- 19.780
2200	5.214	53.114	9.847	328.003	223.261	- 16.310
2300	5.290	53.348	10.119	328.089	218.494	- 12.876
2400	5.372	53.576	10.378	328.156	213.666	- 9.478
2500	5.458	53.799	10.625	328.176	208.921	- 6.116
2600	5.545	54.018	10.860	328.156	204.196	- 2.794
2700	5.632	54.235	11.084	328.084	199.429	- 0.514
2800	5.719	54.448	11.297	327.953	194.664	- 1.762
2900	5.806	54.657	11.500	327.766	189.901	- 3.010
3000	5.892	54.860	11.693	327.517	185.140	- 4.258
3100	5.976	55.056	11.876	327.207	180.386	- 5.506
3200	6.059	55.243	12.049	326.836	175.632	- 6.754
3300	6.141	55.425	12.212	326.406	170.878	- 8.002
3400	6.222	55.599	12.365	325.917	166.124	- 9.250
3500	6.302	55.773	12.508	325.369	161.370	- 10.500
3600	6.379	55.942	12.641	324.764	156.616	- 11.750
3700	6.454	56.108	12.764	324.109	151.862	- 13.000
3800	6.528	56.271	12.877	323.404	147.108	- 14.250
3900	6.599	56.431	12.980	322.649	142.354	- 15.500
4000	6.668	56.588	13.073	321.844	137.600	- 16.750
4100	6.735	56.742	13.156	320.989	132.846	- 18.000
4200	6.799	56.892	13.229	320.084	128.092	- 19.250
4300	6.861	57.038	13.292	319.129	123.338	- 20.500
4400	6.921	57.180	13.345	318.124	118.584	- 21.750
4500	6.978	57.318	13.388	317.069	113.830	- 23.000
4600	7.032	57.452	13.421	315.964	109.076	- 24.250
4700	7.084	57.582	13.444	314.809	104.322	- 25.500
4800	7.134	57.708	13.457	313.604	99.568	- 26.750
4900	7.181	57.830	13.460	312.349	94.814	- 28.000
5000	7.226	57.948	13.453	311.044	90.060	- 29.250
5100	7.269	58.062	13.436	309.689	85.306	- 30.500
5200	7.309	58.172	13.409	308.294	80.552	- 31.750
5300	7.346	58.278	13.372	306.854	75.798	- 33.000
5400	7.380	58.379	13.325	305.369	71.044	- 34.250
5500	7.411	58.475	13.268	303.829	66.290	- 35.500
5600	7.439	58.566	13.201	302.234	61.536	- 36.750
5700	7.464	58.652	13.124	300.584	56.782	- 38.000
5800	7.486	58.733	13.037	298.879	52.028	- 39.250
5900	7.506	58.809	12.940	297.119	47.274	- 40.500
6000	7.523	58.880	12.833	295.314	42.520	- 41.750

Dec. 31, 1966

Mo⁺

GFW = 95.9395

(IDEAL GAS)

Ground State Configuration S₂ 1/2
S°_{298.15} = 43.154 gibbs/mol
ΔHf°₀ = 320.957 kcal/mol
ΔHf°_{298.15} = 322.823 kcal/mol

Electronic Levels and Quantum Weights

ε ₁ , cm ⁻¹	g ₁	ε ₁ , cm ⁻¹	g ₁	ε ₁ , cm ⁻¹	g ₁
0	6	22864.4	4	42560	32
11783.4	2	22980.5	12	43976	28
12034.1	4	23248.2	14	47797	54
12417.3	6	23904	28	49426	18
12900.3	8	24879	34	50454	30
13460.7	10	26544	40	52216	28
15199.3	6	27646	40	55208	20
15330.6	8	28975	36	60090	182
15427.7	10	30144	36	62260	44
15447.0	12	32124	2	63143	116
15691.2	4	34419	4	64560	104
15698.2	4	33350	70	65969	110
15890.1	2	35241	26	67971	72
16796.1	2	36547	14	68202	98
17174.1	4	37777	18	71319	52
17344.1	6	39645	10	73794	68
16946.8	8	41537	12	76227	106
22444.4	6			83557	82

Heat of Formation.

The heat of formation is obtained by adding the heat of ionization to the heat of formation of the gas at 0°K. The heat of ionization, 163.742 kcal/mol (7.10 eV), is obtained from C. E. Moore, Natl. Bur. Std. Circular 467, Vol. III, Washington, D. C. (1958).

Heat Capacity and Entropy.

The electronic energy levels are taken from C. E. Moore, loc. cit. The configuration [Kr] 4d⁵s² is completely missing in Mo⁺, while in the isoelectronic Nb(g) this is a very low lying configuration. However, a comparison of Cr⁺ with Mo⁺ and V(g) with Nb(g) indicates that the similarities are much closer down a given group than across a row to an isoelectronic neighbor. Thus, by analogy with Cr⁺, the missing configuration is expected to lie >50,000 cm⁻¹ and thus be negligible.

The enthalpy at 0°K is calculated to be -1.481 kcal/mol.

Molybdenum Monoxide (MoO)

(Ideal Gas) GFW = 111.9394

MoO

GFW = 111.9394

MOLYBDENUM MONOXIDE (MoO)

(IDEAL GAS)

Ground State Configuration [2]

 $S_{298.15}^{\circ} = [56.9 \pm 2] \text{ gibbs/mol}$ $\Delta H_{298.15}^{\circ} = 92.5 \pm 15 \text{ kcal/mol}$ $\Delta H_{298.15}^{\circ} = 92.5 \pm 15 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

E_i, cm^{-1}	g_i
[0]	[3]
[14000]	[1]
[17000]	[2]
[19000]	[6]

 $\omega_e X_e = [3.61] \text{ cm}^{-1}$ $\sigma = 1$ $\omega_e = [955] \text{ cm}^{-1}$ $\tau_e = [1.80] \text{ \AA}$ $B_e = [0.37943] \text{ cm}^{-1}$ $\tau_e = [1.80] \text{ \AA}$

Heat of Formation

The heat of formation, $\Delta H_{298}^{\circ}(\text{MoO}, g) = 92.5 \pm 15 \text{ kcal/mol}$, is derived from the heat of reaction, $\Delta H_{298}^{\circ} = 32.9 \text{ kcal/mol}$ for $\text{Mo}(c) + \text{O}(g) \rightarrow \text{MoO}(g)$ with all JANAF auxiliary data. The value of ΔH_{298}° is calculated by the third law method from the partial pressure data determined mass-spectrometrically in the temperature range from 2262 to 2466°K by G. DeMaria, et al. (1). The drift in the third law analysis is $\pm 11 \text{ eu}$.

Heat Capacity and Entropy

The ground state configuration and the probable electronic levels are assumed to be similar to those for $\text{WO}(g)$ (see JANAF $\text{WO}(g)$ table of Sept. 30, 1966). T. M. Swaminathan and S. G. Krishnamurthy (2) observed ten band systems attributed to molybdenum oxide with lower state values of $\omega_e = 950 \pm 10 \text{ cm}^{-1}$. T. V. Iorns and F. E. Stafford (3) also observed a band with a peak at 969 cm^{-1} in the vapor above $\text{MoO}_3(c)$. It is surprising that the observed vibrational frequency of $\text{MoO}(g)$ is lower than 1055 cm^{-1} observed for $\text{WO}(g)$. The latter comes not only from electronic spectra of the gas but also from infrared observation in matrix isolation; the former comes only from tentative assignments of electronic spectra presumably arising from $\text{MoO}(g)$. It is possible that the observed states could be low lying excited states. We tentatively assume the fundamental vibrational frequency to be 955 cm^{-1} . The bond distance is then calculated by Guggenheimer's relation (4) for multiple bond molecules from the estimated vibrational frequency. The anharmonicity correction x_e is estimated from the relation $x_e^{1/2} = 0.014$ given by R. F. Barrow and A. D. Caunt (5). The constant (0.014) is assumed to be the same as that for $\text{WO}(g)$. The value of τ_e is calculated from the Morse potential function. The rotational constant B_e is calculated from the estimated bond distance.

References

1. G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram, *J. Chem. Phys.* **32**, 1373 (1960).
2. T. M. Swaminathan and S. G. Krishnamurthy, *Current Sci. (India)* **23**, 256 (1954).
3. T. V. Iorns and F. E. Stafford, *J. Am. Chem. Soc.* **88**, 4819 (1966).
4. K. M. Guggenheimer, *Proc. Phys. Soc. (London)* **52**, 456 (1946).
5. R. F. Barrow and A. D. Caunt, *Proc. Roy. Soc. (London)* **219A**, 120 (1953).

T, °K	C_p°	$S^{\circ} - (G^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	ΔH°	ΔG°	Log Kp
100	6.000	1.002	92.531	92.531	92.531	1.002
200	7.059	1.703	92.572	92.572	92.572	1.703
298	7.399	56.872	92.500	92.500	92.500	56.872
300	7.406	56.872	92.496	92.496	92.496	56.872
400	7.782	57.157	92.316	92.316	92.316	57.157
500	8.077	57.737	92.123	92.123	92.123	57.737
600	8.291	58.387	91.933	91.933	91.933	58.387
700	8.444	59.049	91.738	91.738	91.738	59.049
800	8.556	59.697	91.538	91.538	91.538	59.697
900	8.639	60.320	91.333	91.333	91.333	60.320
1000	8.703	60.915	91.120	91.120	91.120	60.915
1100	8.754	61.481	90.900	90.900	90.900	61.481
1200	8.794	62.018	90.677	90.677	90.677	62.018
1300	8.827	62.530	90.451	90.451	90.451	62.530
1400	8.855	63.017	90.219	90.219	90.219	63.017
1500	8.878	63.481	89.983	89.983	89.983	63.481
1600	8.898	63.924	89.740	89.740	89.740	63.924
1700	8.916	64.348	89.491	89.491	89.491	64.348
1800	8.933	64.754	89.236	89.236	89.236	64.754
1900	8.948	65.143	88.977	88.977	88.977	65.143
2000	8.962	65.517	88.714	88.714	88.714	65.517
2100	8.976	65.877	88.446	88.446	88.446	65.877
2200	8.990	66.223	88.173	88.173	88.173	66.223
2300	9.005	66.558	87.895	87.895	87.895	66.558
2400	9.020	66.880	87.612	87.612	87.612	66.880
2500	9.037	67.192	87.324	87.324	87.324	67.192
2600	9.054	67.494	87.031	87.031	87.031	67.494
2700	9.071	67.786	86.734	86.734	86.734	67.786
2800	9.087	68.069	86.432	86.432	86.432	68.069
2900	9.103	68.344	86.125	86.125	86.125	68.344
3000	9.118	68.611	85.812	85.812	85.812	68.611
3100	9.133	68.871	85.494	85.494	85.494	68.871
3200	9.147	69.124	85.171	85.171	85.171	69.124
3300	9.161	69.370	84.843	84.843	84.843	69.370
3400	9.175	69.610	84.510	84.510	84.510	69.610
3500	9.189	69.844	84.172	84.172	84.172	69.844
3600	9.202	70.072	83.830	83.830	83.830	70.072
3700	9.215	70.295	83.483	83.483	83.483	70.295
3800	9.228	70.513	83.131	83.131	83.131	70.513
3900	9.241	70.727	82.774	82.774	82.774	70.727
4000	9.254	70.935	82.412	82.412	82.412	70.935
4100	9.267	71.139	82.045	82.045	82.045	71.139
4200	9.279	71.340	81.673	81.673	81.673	71.340
4300	9.291	71.536	81.296	81.296	81.296	71.536
4400	9.303	71.728	80.914	80.914	80.914	71.728
4500	9.315	71.917	80.527	80.527	80.527	71.917
4600	9.327	72.102	80.135	80.135	80.135	72.102
4700	9.339	72.284	79.738	79.738	79.738	72.284
4800	9.351	72.462	79.336	79.336	79.336	72.462
4900	9.363	72.638	78.929	78.929	78.929	72.638
5000	9.375	72.810	78.517	78.517	78.517	72.810
5100	9.387	72.980	78.100	78.100	78.100	72.980
5200	9.399	73.147	77.678	77.678	77.678	73.147
5300	9.411	73.312	77.251	77.251	77.251	73.312
5400	9.423	73.474	76.819	76.819	76.819	73.474
5500	9.435	73.633	76.382	76.382	76.382	73.633
5600	9.447	73.790	75.940	75.940	75.940	73.790
5700	9.459	73.945	75.493	75.493	75.493	73.945
5800	9.471	74.098	75.041	75.041	75.041	74.098
5900	9.483	74.249	74.584	74.584	74.584	74.249
6000	9.495	74.397	74.122	74.122	74.122	74.397

June 30, 1967

MoO

Molybdenum Dioxide (MoO₂)
(Crystal) GFW = 127.9388

MOLYBDENUM DIOXIDE (MoO₂)

(CRYSTAL)

GFW = 127.9388

MoO₂

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	Log K _p
0	.000	.000	INFINITE	- 1.988	- 139.317	INFINITE
100	3.866	2.534	11.278	- 1.964	- 135.960	297.141
200	9.866	7.534	13.059	- 1.957	- 140.434	133.935
298	13.380	11.254	.000	.000	- 140.500	93.396
300	13.407	12.037	11.954	.025	- 140.499	92.763
400	15.169	15.165	12.505	1.464	- 140.361	122.263
500	16.237	19.674	13.597	3.039	- 140.134	118.439
600	17.011	22.705	14.868	4.702	- 139.856	81.687
700	17.671	25.378	16.192	6.437	- 139.542	110.180
800	18.281	27.777	17.484	8.235	- 139.194	28.968
900	18.873	29.965	18.751	10.092	- 138.809	24.728
1000	19.464	31.984	19.975	12.009	- 138.385	21.362
1100	20.044	33.847	21.153	13.984	- 137.921	93.706
1200	20.577	35.639	22.293	16.022	- 137.419	18.617
1300	21.077	37.319	23.379	18.121	- 136.879	85.707
1400	21.558	38.921	24.433	20.285	- 136.296	85.752
1500	22.029	40.459	25.450	22.514	- 135.675	81.941
1600	22.424	41.942	26.435	24.811	- 135.013	77.972
1700	22.841	43.377	27.389	27.179	- 134.306	74.147
1800	23.282	44.772	28.316	29.620	- 133.557	70.424
1900	23.746	46.132	29.218	32.136	- 132.761	66.824
2000	24.238	47.463	30.094	34.731	- 131.917	59.275
2100	24.753	48.767	30.954	37.405	- 131.028	5.793
2200	25.293	50.050	31.794	40.162	- 130.083	55.664
2300	25.858	51.313	32.616	43.004	- 129.092	46.576
2400	26.449	52.560	33.421	45.934	- 128.054	4.166
2500	27.065	53.793	34.211	48.955	- 126.980	45.093
2600	27.707	55.014	34.989	52.069	- 125.876	41.663
2700	28.367	56.225	35.752	55.277	- 124.749	3.217
2800	29.046	57.427	36.505	58.584	- 123.606	30.659
2900	29.745	58.623	37.247	61.991	- 122.457	31.615
3000	30.469	59.813	37.979	65.502	- 121.305	2.135
					- 127.519	24.883

June 30, 1967

Heat of Formation

The adopted heat of formation, -140.5 kcal/mol, is a weighted average of values derived from calorimetric determinations, emf measurements and equilibrium studies. The results are given below.

Ignition of the bomb products from the calorimetric studies of Stankiewicz et al. indicated that oxidation was only about 70 per cent complete. The authors also digested the products with NH₄OH to remove the trioxide. The residue was the dioxide, as indicated by both oxidation and reduction. This evidence does not necessarily eliminate the possibility of known intermediate oxides in the combustion products. Mah found 72 - 75 per cent conversion to trioxide by weighing the total combustion products; he performed no additional analysis.

Investigator	Method	Reaction	Temp. Range (°K)	No. of Points	ΔH ^c ₂₉₈ (kcal/mol)	Drift (eu)	ΔH ^c ₂₉₈ (kcal/mol)
1. Stankiewicz et al.	Calorimetric	A	-	-	-37.12	-	-140.86±0.13**
2. Mah	Calorimetric	A	-	-	-37.52	-	-140.64±0.13**
3. Rapp	EMF	B	1073-1223	35	-13.18	-13.42	0.1±0.1
		C	1073-1273	22	-25.65	-25.63	0±0.1
		F	873-1073	Equation	-138.66	-140.3	1.7
4. Barbi	EMF	D	1296-1391	9	-5.44	-0.3	-4.4±2.2
5. Gleiser and Chipman	Equilibrium	E	949-1344	Equation	-24.58	-17.7	-6.0
6. Gokcen	Equilibrium	E	973-1173	Equation	-24.57	-22.2	-2.2
7. Collins	Equilibrium	E	981-1096	Equation	-24.0	-18.5	-5.4
8. Tonosaki	Equilibrium	E	-	-	-	-	-139.61*

*Third law value used in the calculation.

**Auxiliary data for Mo₂O₃(c) are taken from corresponding measurements of the same authors. See JANAF MoO₃(c) table for details.

Reaction: A. MoO₂(c) + 1/2 O₂(g) = MoO₃(c).

B. 2Fe₃O₄(c) + Mo(c) = MoO₂(c) + 2Fe(c).

C. 2NiO(c) + Mo(c) = MoO₂(c) + 2Ni(c).

D. Mo(c) + 2CO₂(g) = MoO₂(c) + 2CO(g).

E. Mo(c) + 2H₂O(g) = MoO₂(c) + 2H₂(g).

F. Mo(c) + O₂(g) = MoO₂(c) derived by the author from the cell reaction 2Fe₃O₄(c) + Mo(c) = MoO₂(c) + 2Fe(c) using ΔG^c data for Fe₃O₄(c).

References

1. B. A. Stankiewicz, J. R. Tucker and P. E. Snyder, J. Am. Chem. Soc. **77**, 2987 (1955).
2. A. D. Mah, J. Am. Chem. Soc. **81**, 1572 (1957).
3. R. A. Rapp, Trans. AIME **227**, 371 (1963).
4. G. B. Barbi, J. Phys. Chem. **68**, 1025 (1964).
5. M. Gleiser and J. Chipman, J. Phys. Chem. **66**, 1539 (1962).
6. N. A. Gokcen, Trans. AIME **227**, 1019 (1953).
7. B. T. Collins, Sc. D. Thesis, Massachusetts Institute of Technology, 1949.
8. K. Tonosaki, Bull. Inst. Phys. Chem. Res. (Tokyo) **13**, 126 (1940).

Heat Capacity and Entropy

E. G. King, J. Am. Chem. Soc. **80**, 1799 (1958), measured the low temperature heat capacities from 53.3° to 296°K. E. G. King, W. W. Weller and A. U. Christensen, U. S. Bur. Mines RI 5684, 1960, measured the high temperature enthalpy changes from 399° to 1801°K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that there be a smooth joint at 298°K. Deviations of the enthalpy data from the adopted values are -1.3 to +0.7 percent, excluding the point at 1801°K. This point at the highest temperature deviates by +2.3 percent, which suggests that the apparent heat capacity is rising very rapidly. No explanation for this rapid rise is available.

The entropy S°₂₉₈ = 11.054 eu is obtained from the low temperature heat capacity data, based on S°₂₉₈ = 0.31 eu.

B. N. Figgis and J. Lewis, "Progress in Inorg. Chem.", Vol. 5, page 123, Interscience Publishers, New York, 1964, indicated that MoO₂ is probably antiferromagnetic. Its small susceptibility is presumably due to Mo-Mo interactions. It is possible that at temperatures below 50°K entropy due to spin interactions of the d² electrons will appear, contributing up to 2.2 eu. The drifts in the equilibrium data do suggest that additional entropy may be appropriate; however, only the EMF data of Rapp appear to be sufficiently precise to influence the decision. These data suggest addition of 0.8±0.1 eu and 0.9±0.1 eu based on auxiliary data for Wüstite and NiO(c), respectively. We select the entropy of 11.954 eu from equilibrium data for NiO.

MoO₂

Molybdenum Dioxide (MoO₂)

(Ideal Gas)

GFW = 127.9388

Point Group [C_{2v}]MOLYBDENUM DIOXIDE (MoO₂)

(IDEAL GAS)

GFW = 127.9388

 $\Delta H_f^\circ = -2.6 \pm 5 \text{ kcal/mol}$ $\Delta H_f^\circ_{298.15} = -3.1 \pm 5 \text{ kcal/mol}$ $S^\circ_{298.15} = [66.4 \pm 3] \text{ gibbs/mol}$

Ground State Quantum Weight = [3]

T, °K	Cp°	S°	-(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	ΔH°	Log Kp
0	6.500	0.000	INFINITE	-2.688	-2.613	INFINITE
100	6.557	56.276	75.046	-1.877	-2.617	8.605
200	9.487	62.475	74.359	-1.977	-2.654	5.654
298	10.422	66.436	74.000	-2.000	-3.100	6.259
300	10.430	66.501	74.036	-2.019	-3.105	6.279
400	10.808	69.626	74.856	-1.108	-3.317	7.304
500	11.647	72.221	77.677	-2.272	-3.500	8.319
600	12.410	74.442	80.624	-3.491	-3.667	9.218
700	12.739	76.381	82.596	-4.749	-3.830	10.130
800	12.976	78.039	84.578	-6.032	-4.000	11.050
900	13.122	79.432	86.466	-7.346	-4.159	11.987
1000	13.282	81.030	88.366	-8.664	-4.330	12.737
1100	13.483	82.301	90.212	-9.998	-4.509	13.569
1200	13.462	83.469	92.019	-11.340	-4.701	14.385
1300	13.225	84.245	93.788	-12.685	-4.908	15.185
1400	12.919	84.691	95.522	-14.004	-5.136	15.964
1500	13.619	85.491	97.222	-15.404	-5.385	16.730
1600	13.655	87.371	98.991	-16.748	-5.656	17.477
1700	13.687	88.200	100.732	-18.135	-5.950	18.207
1800	13.717	88.983	102.442	-20.566	-6.218	19.412
1900	13.742	89.721	104.119	-22.944	-6.464	20.269
2000	13.772	90.432	105.764	-25.264	-6.694	20.269
2100	13.800	91.104	107.450	-27.524	-6.911	20.943
2200	13.829	91.747	109.077	-29.724	-7.111	21.578
2300	13.855	92.362	110.644	-31.864	-7.294	22.184
2400	13.877	92.951	112.151	-33.944	-7.461	22.763
2500	13.897	93.521	113.604	-35.964	-7.611	23.319
2600	13.964	94.067	115.009	-37.924	-7.744	23.904
2700	14.004	94.595	116.354	-39.824	-7.861	24.459
2800	14.047	95.105	117.644	-41.664	-7.961	24.994
2900	14.084	95.595	118.884	-43.444	-8.044	25.511
3000	14.138	96.077	120.074	-45.164	-8.111	25.587
3100	14.187	96.542	121.219	-46.824	-8.161	25.763
3200	14.238	96.993	122.319	-48.424	-8.194	25.984
3300	14.291	97.432	123.374	-49.964	-8.211	26.250
3400	14.346	97.851	124.384	-51.444	-8.211	26.470
3500	14.400	98.276	125.349	-52.864	-8.194	26.640
3600	14.457	98.683	126.269	-54.224	-8.156	26.761
3700	14.513	99.079	127.144	-55.524	-8.094	26.831
3800	14.571	99.467	127.974	-56.764	-8.011	26.851
3900	14.628	99.844	128.759	-57.944	-7.911	26.811
4000	14.686	100.218	129.489	-59.064	-7.794	26.711
4100	14.743	100.581	130.164	-60.124	-7.661	26.574
4200	14.800	100.937	130.784	-61.124	-7.511	26.404
4300	14.857	101.286	131.349	-62.064	-7.344	26.204
4400	14.914	101.624	131.859	-62.944	-7.161	26.074
4500	14.967	101.944	132.314	-63.764	-6.961	25.924
4600	15.021	102.293	132.714	-64.524	-6.744	25.754
4700	15.074	102.617	133.059	-65.224	-6.511	25.564
4800	15.125	102.935	133.349	-65.864	-6.261	25.344
4900	15.174	103.244	133.584	-66.444	-6.004	25.094
5000	15.224	103.554	133.764	-66.964	-5.734	24.814
5100	15.272	103.856	133.894	-67.424	-5.454	24.494
5200	15.317	104.153	133.974	-67.824	-5.164	24.144
5300	15.362	104.445	134.004	-68.164	-4.864	23.764
5400	15.405	104.724	134.074	-68.444	-4.554	23.354
5500	15.445	105.016	134.094	-68.664	-4.234	22.914
5600	15.485	105.295	134.054	-68.824	-3.904	22.444
5700	15.522	105.569	133.954	-68.924	-3.564	21.944
5800	15.558	105.839	133.794	-68.964	-3.214	21.414
5900	15.591	106.104	133.574	-68.944	-2.854	20.854
6000	15.625	106.368	133.294	-68.864	-2.484	20.264

June 30, 1968

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i
0	(3)
[13000]	(6)
[25000]	(6)

Vibrational Frequencies and Degeneracies

ω _i , cm ⁻¹	No. of Points
970 (1)	11*
[300](1)	
990 (1)	

Bond Distance: Mo-O = [1.80] Å
 Bond Angle: O-Mo-O = [110°]
 Product of the Moments of Inertia: $I_{A}I_{B}I_{C} = [7.750 \times 10^{-115}] \text{ g}^3 \text{ cm}^6$
 $\sigma = [2]$

Heat of Formation

Burns et al. (1) have investigated mass-spectrometrically the vapor in equilibrium with powdered MoO₂(s) and also reported the partial pressures of MoO₂(g), MoO₃(g), (MoO₂)₂(g), and (MoO₂)₃(g). Second and third analyses of their partial pressure data are given in the table below. The adopted value, $\Delta H_f^\circ(\text{MoO}_2, g) = -3.1 \text{ kcal/mol}$, is calculated from their 3rd law value of $\Delta H_f^\circ = 137.4 \text{ kcal/mol}$ for MoO₂(s) + MoO₂(g), using all JANAF functions.

DeMaria et al. (2) have measured the partial pressures of gaseous oxides MoO, MoO₂, MoO₃ and O(g) in the Mo-Al₂O₃ system by mass spectrometry. Blackburn et al. (3) and Plante (4) have studied the vapor pressures above molybdenum dioxide(c) by the Knudsen effusion method. Second and third law analyses of these three sets of partial pressure data are reported in the following table.

Investigator	Reaction	Temp. °K	No. of Points	ΔH° ₂₉₈ , kcal/mol	ΔHf° ₂₉₈ (MoO ₂ , g)
1. Burns et al.	MoO ₂ (s) + MoO ₂ (g)	1598-1777	11*	137.9±3.1	-3.1
2. DeMaria et al.	Mo(c) + 2O(g) + MoO ₂ (g)	2262-2466	9	-61.8±32.1	-19.9±13.6
3. Blackburn et al.	MoO ₂ (c) + MoO ₂ (g)	1818-2028	7	107.2±6.6	-15.6
4. Plante	MoO ₂ (c) + MoO ₂ (g)	1811-1802	6	149.6±13.0	-0.4

*2 points rejected due to failure of statistical test
 **based on the third law ΔH_f° value

Heat Capacity and Entropy

The MoO₂(g) is assumed to have a C_{2v} symmetry similar to that of TaO₂ reported by Weltner and McLeod (5). The bond angle O-Mo-O is estimated to be 110°. The bond distance Mo-O is estimated to be 1.80 Å, the same as that in MoO(g). The symmetric and asymmetric stretching frequencies were obtained from the infrared spectra of gaseous MoO₂Cl₂ and MoO₂Br₂, reported by Iorns and Stafford (6). The bending vibrational frequency (300 cm⁻¹) is estimated by comparison with other transition metal dioxides. The three principal moments of inertia are: $I_A = 4.2470 \times 10^{-38}$, $I_B = 11.5512 \times 10^{-38}$, and $I_C = 15.7982 \times 10^{-38} \text{ g cm}^2$.

The electronic levels and quantum weights are estimated from the data reported by Weltner and McLeod (2) on MoO₂. The ground state is assumed to be ³A₁ and the first excited level is assumed to lie close to the observed transitions at 7800 Å and 7806 Å in MoO₂. Since both these states are presumed to be triplet, we have assigned a total degeneracy of 6. In addition, we expect from the electronic levels of Mo⁴⁺(g) (g) that other electronic states will also be found and these are arbitrarily estimated in the level at 25000 cm⁻¹.

References

1. R. P. Burns, G. DeMaria, J. Drowart and R. T. Grimley, J. Chem. Phys. **32**, 1363 (1960).
2. G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. **32**, 1373 (1960).
3. P. E. Blackburn, M. Hoch and H. L. Johnston, J. Phys. Chem. **62**, 769 (1958).
4. E. R. Plante, Ph. D. Thesis, Univ. of Kansas, 1960.
5. W. Weltner, Jr., and D. McLeod, Jr., J. Chem. Phys. **42**, 882 (1965).
6. T. V. Iorns and F. E. Stafford, J. Am. Chem. Soc. **88**, 4419 (1966).
7. W. Weltner, Jr., and D. McLeod, Jr., J. Mol. Spectry. **17**, 276 (1965).
8. C. E. Moore, "Atomic Energy Levels," U. S. Natl. Bur. Std., Circ. 467, 1958.

T, °K	C _p ^o	g/bbs/mol S ^o	-(G ^o -H ^o) ₂₉₈ /T	H ^o -H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	+0.00	+0.00	INFINITE	-	3.009	- 176.900	INFINITE
100	7.564	4.673	31.743	- 2.707	- 177.756	- 171.947	375.570
200	14.168	12.184	20.109	- 1.585	- 179.120	- 165.760	191.134
298	17.497	18.585	18.585	-0.000	- 179.100	- 159.687	117.054
300	17.951	18.496	18.585	-0.033	- 178.097	- 159.573	116.249
400	19.460	20.155	19.317	1.935	- 177.952	- 151.431	83.631
500	20.973	20.712	20.753	3.979	- 177.520	- 147.364	64.413
600	21.935	32.621	22.413	6.125	- 177.138	- 141.367	51.493
700	22.900	36.194	24.122	10.307	- 176.706	- 135.426	42.548
800	23.862	39.768	25.443	14.489	- 176.318	- 129.485	35.992
900	24.922	42.074	27.443	13.150	- 175.651	- 123.779	30.058
1000	26.061	44.760	29.060	15.700	- 175.007	- 118.048	25.799
1100	27.197	47.297	30.604	18.363	- 174.277	- 112.387	22.329
1200	28.365	49.744	32.096	21.037	- 173.507	- 106.728	19.020
1300	29.564	52.031	33.457	23.721	- 172.597	- 101.070	15.960
1400	30.779	54.266	34.942	27.034	- 171.545	- 95.433	14.960
1500	32.017	56.432	36.303	30.194	- 170.448	- 90.462	13.180

Heat Capacity and Entropy

Smith et al. (5) measured low temperature heat capacities from 18.3 to 299.8°K. King et al. (8) measured high temperature enthalpy data from 399.3° to 1063.9°K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that there be a smooth joint at 298°K. Deviations of the enthalpy data from the adopted values are -0.65 percent to +0.17 percent. Seitz et al. (2) have also measured low temperature heat capacities from 70° to 298.7°K which are not in agreement with the values adopted. (The discrepancy has been discussed by Smith.) Cosgrove and Snyder (8) have also measured high temperature enthalpy data from 273° to 1068°K by drop calorimetry. Their smooth values are about 2 percent higher than the values adopted in the tabulation.

The entropy, S₂₉₈^o = 18.585 eu, is obtained from the low temperature heat capacity data of Smith (5), based on S₀^o = 0.197 eu. This starting entropy was obtained by the authors from a τ^2 extrapolation of the data. It is surprising that the entropy of MoO₃(c) is larger than that of WO₃(c) by about 0.4 eu. This may be due to the difference in the crystal structures, MoO₃ being orthorhombic and WO₃ monoclinic, and also to uncertainty in the entropy extrapolation below 80°K for WO₃(c).

Melting Data

The adopted melting point is obtained from King (8), and the heat of melting is calculated from the adopted enthalpies of the crystal and liquid based on the enthalpy data of King. Cosgrove and Snyder (8) found the melting point 1068°K by the cooling curve method, and derived ΔH_m^o = 12.54 kcal/mol from their smooth enthalpy values at the melting point.

References

1. A. D. Mah, J. Phys. Chem. **61**, 1572 (1957).
2. B. A. Staskiewicz, J. R. Tucker and P. E. Snyder, J. Am. Chem. Soc. **77**, 2987 (1955).
3. B. Neumann, C. Kroger and H. Kunz, Z. Anorg. Allgem. Chem. **218**, 387 (1934).
4. J. E. Moore and S. W. Parr, J. Am. Chem. Soc. **46**, 2656 (1924).
5. D. F. Smith, D. B. Brown, A. S. Dworkin, D. J. Samor and E. R. Van Artadalen, J. Am. Chem. Soc. **78**, 1533 (1956).
6. E. G. King, W. W. Weller and A. U. Christensen, U. S. Bur. Mines RI 5664, 1960.
7. H. Seitz, F. J. Dunkerley and B. J. Devitt, J. Am. Chem. Soc. **63**, 600 (1943).
8. L. A. Cosgrove and P. E. Snyder, J. Am. Chem. Soc. **75**, 1227 (1953).

Molybdenum Trioxide (MoO₃)
(Liquid) GFW = 143.9382

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K _p
0							
100							
200							
298	17.697	26.971	26.971	.000	-168.555	-152.642	111.890
300	17.951	27.082	26.971	.033	-168.552	-152.584	111.128
400	19.860	32.581	27.701	1.033	-165.466	-148.499	107.019
500	20.973	37.098	29.139	3.079	-167.975	-152.012	92.073
600	21.935	41.007	30.799	6.125	-167.593	-136.853	49.849
700	30.342	48.861	32.508	9.367	-167.161	-131.763	31.138
800	30.342	50.846	34.281	12.609	-165.789	-126.789	38.637
900	30.342	52.086	36.007	14.835	-164.421	-121.816	35.616
1000	30.342	55.283	37.613	17.469	-163.493	-117.257	25.176
1100	30.342	58.175	39.535	20.503	-162.592	-112.667	22.385
1200	30.342	60.815	41.200	23.534	-161.515	-108.177	19.702
1300	30.342	63.143	42.506	26.572	-160.464	-103.774	17.446
1400	30.342	65.192	43.595	29.610	-159.443	-99.453	15.525
1500	30.342	67.565	45.825	32.640	-158.457	-95.280	13.671
1600	30.342	69.584	47.287	35.674	-157.496	-91.014	12.432
1700	30.342	71.303	48.613	38.709	-156.564	-86.888	11.170
1800	30.342	72.757	49.747	41.743	-155.666	-82.816	10.055
1900	30.342	74.758	51.191	44.773	-154.803	-78.813	8.063
2000	30.342	76.314	52.479	47.811	-153.966	-74.813	6.176

MOLYBDENUM TRIOXIDE (MoO₃)
(LIQUID)

S°_{298.15} = 26.971 gibbs/mol
T_m = 1074°

ΔH°_{298.15} = -168.555 ± 0.1 kcal/mol
ΔH_m° = 11.60 kcal/mol

Heat of Formation

The heat of formation is calculated from that of the crystal by adding the heat of melting and the difference between H°₁₀₇₄ - H°₂₉₈ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity between the melting point and 1392.4°K is derived from the enthalpy data measured by E. G. King, W. W. Weller and A. U. Christensen, U. S. Bur. Mines RI 5664 (1960). The heat capacity is assumed constant above and below the measured range. At 700°K, a glass transition is assumed, below which the heat capacity is taken to be the same as that of the crystal. The entropy at 298°K is obtained in a manner analogous to that of the heat of formation. L. A. Cosgrove and P. E. Snyder, J. Am. Chem. Soc. 75, 1227 (1953), also measured the enthalpy changes for MoO₃(l) in the temperature range from 1068° to 1300°K. Their smooth values are ±2.5 percent to ±4.0 percent higher than our tabulated values. They have also found the melting point at 1068°K by the cooling curve method.

Melting Data

See JANAF MoO₃(c) table dated June 30, 1967.

Molybdenum Trioxide (MoO₃)

(Ideal Gas)

GFW = 143.9382

T, °K	Cp	S° —G°—H° ₂₉₈ /T	—H°—H° ₂₉₈	kcal/mol ΔH°	Log Kp
100	9.500	INFINITE	3.225	85.217	INFINITE
200	9.299	54.186	2.401	85.550	184.876
300	12.276	61.618	1.311	85.946	91.215
298	14.347	66.924	.000	86.200	60.254
300	12.380	64.924	.027	86.204	59.846
300	12.390	67.371	1.566	86.341	44.151
300	12.472	75.046	3.194	86.406	34.713
600	17.688	78.208	4.929	86.434	26.417
700	18.162	80.974	6.724	86.449	23.919
800	18.532	82.826	8.557	86.461	20.805
900	18.811	84.161	10.341	86.468	17.920
1000	19.078	85.113	12.316	86.491	15.620
1100	19.123	85.430	14.221	86.519	14.101
1200	19.236	86.099	16.140	86.558	12.669
1300	19.326	86.692	18.068	86.604	11.346
1400	19.407	87.211	20.000	86.658	10.145
1500	19.467	87.658	21.947	86.795	9.0512
1600	19.506	88.035	23.895	86.920	8.0721
1700	19.546	88.346	25.848	87.070	7.2022
1800	19.581	88.597	27.804	87.241	6.4302
1900	19.611	88.797	29.764	87.438	5.7582
2000	19.635	89.043	31.726	87.656	5.1638
2100	19.656	89.240	33.691	87.965	4.6481
2200	19.675	89.391	35.657	88.271	4.2064
2300	19.692	89.506	37.626	88.594	3.8342
2400	19.707	89.588	39.597	88.934	3.5241
2500	19.719	89.640	41.567	89.434	3.2640
2600	19.730	89.668	43.539	89.937	3.0457
2700	19.740	89.672	45.513	90.518	2.8612
2800	19.748	89.665	47.484	91.181	2.7041
2900	19.754	89.648	49.451	91.922	2.5698
3000	19.765	89.618	51.439	92.745	2.4523
3100	19.772	89.582	53.416	93.664	2.3482
3200	19.778	89.541	55.393	94.684	2.2561
3300	19.784	89.496	57.369	95.811	2.1741
3400	19.790	89.448	59.340	97.044	2.0998
3500	19.793	89.403	61.329	98.391	2.0323
3600	19.798	89.355	63.309	101.847	1.947
3700	19.801	89.337	65.289	102.340	1.8799
3800	19.805	89.316	67.269	102.839	1.8164
3900	19.808	89.292	69.250	103.339	1.7568
4000	19.812	89.266	71.231	103.846	1.6993
4100	19.814	89.246	73.212	104.357	1.6442
4200	19.817	89.223	75.193	104.871	1.5914
4300	19.820	89.198	77.174	105.389	1.5404
4400	19.823	89.172	79.157	105.912	1.4915
4500	19.824	89.146	81.140	106.437	1.4442
4600	19.826	89.119	83.122	106.965	1.3987
4700	19.828	89.091	85.105	107.497	1.3544
4800	19.830	89.062	87.088	108.034	1.3114
4900	19.832	89.033	89.072	108.577	1.2697
5000	19.833	89.004	91.054	109.119	1.2293
5100	19.835	88.974	93.037	109.666	1.1898
5200	19.836	88.944	95.021	110.219	1.1514
5300	19.838	88.913	97.006	110.777	1.1142
5400	19.840	88.882	98.992	111.339	1.0781
5500	19.842	88.851	100.978	111.904	1.0431
5600	19.844	88.820	102.966	112.476	1.0092
5700	19.846	88.789	104.951	113.051	0.9764
5800	19.848	88.758	106.936	113.629	0.9447
5900	19.850	88.727	108.921	114.211	0.9141
6000	19.852	88.696	110.906	114.797	0.8845

June 30, 1968

MOLYBDENUM TRIOXIDE (MoO₃)

(IDEAL GAS)

GFW = 143.9382

Point Group [D_{3h}]

ΔHf° = -85.2 ± 5 kcal/mol

S°_{298.15} = [66.9 ± 4] gibbs/molΔHf°_{298.15} = -86.2 ± 5 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_i, cm⁻¹

[800] (1)

[350] (1)

[959] (2)

[300] (2)

σ = [6]

Bond Distance: Mo-O = [1.80] Å

Bond Angle: O-Mo-O = [120°]

Product of the Moments of Inertia: I_AI_BI_C = [4.304 × 10⁻¹¹⁴] g³ cm⁶

Heat of Formation

Burns et al. (1) have determined the partial pressures of gaseous oxides MoO₂, MoO₃, (MoO₃)₂ and (MoO₃)₃ in equilibrium with powdered MoO₃(c) by mass spectrometry. Plante (2) and Blackburn et al. (3) have also investigated the vapor pressures above molybdenum dioxide (c) by the Knudsen effusion method. They all involve the disproportionation of MoO₂(c) to Mo(c) and MoO₃(g). Delahria et al. (4) have reported the partial pressures of MoO(g), MoO₂(g), MoO₃(g) and O(g) in the Mo-Al₂O₃ system by mass spectrometry. Second and third law analyses of these partial pressure data are listed in the following table, using all JANAF functions.

Investigator	Reaction	Temp., °K	No. of Points	ΔHr°, kcal/mol 2nd Law	3rd Law	ΔHf°(MoO ₃ , g) Kcal/mol*
1. Burns et al.	1.5MoO ₂ (c) + MoO ₃ (g) + 0.5 Mo(c)	1481-1777	34	131.611.5	124.5	-86.2
2. Plante	1.5MoO ₂ (c) + MoO ₃ (g) + 0.5Mo(c)	1592-1918	119	134.611.4	120.3	-80.4
3. Blackburn et al.	1.5MoO ₂ (c) + MoO ₃ (g) + 0.5Mo(c)	1818-2028	7	108.746.4	117.2	-93.4
4. Delahria et al.	Mo(c) + 3 O(g) → MoO ₃ (g)	2281-2416	5	-225.1439.9	-255.1	-76.4

*Based on the third law ΔHr°298 value

The selected heat of formation is -86.2 kcal/mol, based on the third law value of ΔHf°298 of Burns et al. The choice is made because there is serious doubt about the data of Blackburn as discussed by Burns et al. In addition the assumption made by Plante that the only vapor species of any importance is MoO₃ may be erroneous. The mass spectrometric work of Burns et al. is thus preferred.

Heat Capacity and Entropy

The MoO₃(g) is assumed to be a planar D_{3h} molecule with a bond angle O-Mo-O = 120°. The three principal moments of inertia are I_A = I_B = 12.9111 × 10⁻³⁹ and I_C = 25.8222 × 10⁻³⁹ g cm².

Irms and Stafford (5) have observed two vibrational frequencies (969 and 715 cm⁻¹) in the infrared spectra of the vapor above MoO₃(c). They assigned the Mo-O stretching frequency at 969 cm⁻¹ and the trimer ring vibration at 815 cm⁻¹, based on their infrared spectrum observations of gaseous molybdenum oxides and oxyhalides. Barraclough et al. (6) have also concluded that the presence of a metal-oxygen double bond can be correlated with a stretching frequency in the range 900-1100 cm⁻¹. For the MoO₃ molecule, they found the stretching frequency at 985 cm⁻¹ in their spectrometric studies.

SO₄²⁻. Based on the vibrational frequencies of MoO₄²⁻ (aq) reported by Nakamoto (7) and Siebert (8), and those of WO₃, WO₄²⁻, SO₃ and SO₄²⁻, we have estimated 800, 350 and 300 cm⁻¹ for MoO₃(g).

References

1. R. P. Burns, G. Delahria, J. Drowart and R. T. Grimley, J. Chem. Phys. **32**, 1363 (1960).
2. E. R. Plante, Ph. D. Thesis, Univ. of Kansas, 1960.
3. P. E. Blackburn, M. Hoch and H. L. Johnston, J. Phys. Chem. **62**, 769 (1958).
4. G. Delahria, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. **32**, 1373 (1960).
5. T. V. Irms and P. E. Stafford, J. Am. Chem. Soc. **88**, 4419 (1966).
6. C. G. Barraclough, J. Lewis and R. S. Nyholm, J. Chem. Soc. **1953**, 3552 (1953).
7. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, 1963.
8. H. Siebert, "Anwendungen Der Schwingungsspektroskopie In Der Anorganischen Chemie," Springer-Verlag, Berlin, 1966.



Nitrogen, Monatomic (N)

(Ideal Gas) At. Wt. = 14.008

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	4.968	31.187	41.031	112.520	INFINITE	INFINITE
100	4.968	31.187	41.031	112.520	111.459	-243.585
200	4.968	31.187	41.031	112.520	111.459	-120.405
298	4.968	31.187	41.031	112.520	111.459	-79.605
300	4.968	31.187	41.031	112.520	111.459	-79.289
400	4.968	31.187	41.031	112.520	111.459	-79.289
500	4.968	31.187	41.031	112.520	111.459	-79.289
600	4.968	31.187	41.031	112.520	111.459	-79.289
700	4.968	31.187	41.031	112.520	111.459	-79.289
800	4.968	31.187	41.031	112.520	111.459	-79.289
900	4.968	31.187	41.031	112.520	111.459	-79.289
1000	4.968	31.187	41.031	112.520	111.459	-79.289
1100	4.968	31.187	41.031	112.520	111.459	-79.289
1200	4.968	31.187	41.031	112.520	111.459	-79.289
1300	4.968	31.187	41.031	112.520	111.459	-79.289
1400	4.968	31.187	41.031	112.520	111.459	-79.289
1500	4.968	31.187	41.031	112.520	111.459	-79.289
1600	4.968	31.187	41.031	112.520	111.459	-79.289
1700	4.968	31.187	41.031	112.520	111.459	-79.289
1800	4.968	31.187	41.031	112.520	111.459	-79.289
1900	4.968	31.187	41.031	112.520	111.459	-79.289
2000	4.968	31.187	41.031	112.520	111.459	-79.289
2100	4.970	42.313	42.050	114.778	81.185	-6.449
2200	4.972	42.313	42.050	114.778	81.185	-6.449
2300	4.974	42.313	42.050	114.778	81.185	-6.449
2400	4.976	42.313	42.050	114.778	81.185	-6.449
2500	4.978	42.313	42.050	114.778	81.185	-6.449
2600	4.982	47.375	42.975	115.088	73.151	-6.149
2700	4.983	47.375	42.975	115.088	73.151	-6.149
2800	4.983	47.375	42.975	115.088	73.151	-6.149
2900	4.983	47.375	42.975	115.088	73.151	-6.149
3000	4.983	47.375	42.975	115.088	73.151	-6.149
3100	4.983	47.375	42.975	115.088	73.151	-6.149
3200	4.983	47.375	42.975	115.088	73.151	-6.149
3300	4.983	47.375	42.975	115.088	73.151	-6.149
3400	4.983	47.375	42.975	115.088	73.151	-6.149
3500	4.983	47.375	42.975	115.088	73.151	-6.149
3600	4.983	47.375	42.975	115.088	73.151	-6.149
3700	4.983	47.375	42.975	115.088	73.151	-6.149
3800	4.983	47.375	42.975	115.088	73.151	-6.149
3900	4.983	47.375	42.975	115.088	73.151	-6.149
4000	4.983	47.375	42.975	115.088	73.151	-6.149
4100	4.983	47.375	42.975	115.088	73.151	-6.149
4200	4.983	47.375	42.975	115.088	73.151	-6.149
4300	4.983	47.375	42.975	115.088	73.151	-6.149
4400	4.983	47.375	42.975	115.088	73.151	-6.149
4500	4.983	47.375	42.975	115.088	73.151	-6.149
4600	4.983	47.375	42.975	115.088	73.151	-6.149
4700	4.983	47.375	42.975	115.088	73.151	-6.149
4800	4.983	47.375	42.975	115.088	73.151	-6.149
4900	4.983	47.375	42.975	115.088	73.151	-6.149
5000	4.983	47.375	42.975	115.088	73.151	-6.149
5100	4.983	47.375	42.975	115.088	73.151	-6.149
5200	4.983	47.375	42.975	115.088	73.151	-6.149
5300	4.983	47.375	42.975	115.088	73.151	-6.149
5400	4.983	47.375	42.975	115.088	73.151	-6.149
5500	4.983	47.375	42.975	115.088	73.151	-6.149
5600	4.983	47.375	42.975	115.088	73.151	-6.149
5700	4.983	47.375	42.975	115.088	73.151	-6.149
5800	4.983	47.375	42.975	115.088	73.151	-6.149
5900	4.983	47.375	42.975	115.088	73.151	-6.149
6000	4.983	47.375	42.975	115.088	73.151	-6.149

March 31, 1961

N

NITROGEN, MONATOMIC (N) (IDEAL GAS) AT. WT. = 14.008

$\Delta H_{f,0}^{\circ} = 112.5 \pm 1 \text{ kcal. mole}^{-1}$
 $\Delta H_{f,298.15}^{\circ} = 113.0 \pm 1 \text{ kcal. mole}^{-1}$
 $S_{298.15}^{\circ} = 36.61 \pm 0.01 \text{ cal. deg. mole}^{-1}$

Ground State Configuration $4s^2$

Electronic Levels and Multiplicities

E_1	E_2	E_3	E_4	E_5	E_6
19,223.9	0	4	4	8	2
19,223.1	19,223.1	4	4	8	2
28,840	28,840	5	4	6	6
83,285.5	83,285.5	2	4	6	8
83,319.3	83,319.3	4	4	6	10
83,366	83,366	6	4	6	6
86,131.4	86,131.4	2	4	6	8
86,223.2	86,223.2	4	4	6	76
88,109.5	88,109.5	6	4	6	90
88,153.4	88,153.4	4	4	6	84
93,582.3	93,582.3	2	4	6	80
94,772.2	94,772.2	2	4	6	102
94,794.8	94,794.8	4	4	6	112
94,832.1	94,832.1	6	4	6	116
88,173	88,173	2	4	6	98
					96

Heat of Formation

The dissociation energy of N_2 has been the subject of considerable controversy and is presented by A. G. Gaydon, "Dissociation Energies", Chapman and Hall, London, 1953. L. Brewer and A. W. Searcy, Ann. Rev. Phys. Chem., 7, 259 (1956), discuss extensive and varied experiments which have now fixed the value of 9.76 e.v. as being highly probable. Additional support for this value is afforded by the recently observed predissociation in the $x^1\Sigma_g$ state by A. Lofthus, Nature 186, 302 (1960).

Heat Capacities and Entropies

The electronic levels noted above are listed by C. E. Moore, Nat. Bur. Standards (U.S.) Circ. 457, Vol. I (1949), Vol. III (1958).

N

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(R°-H° ₂₉₈)/T	h°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	Log K _p
0	.000	INFINITE	- 2.197	21.456	INFINITE
100	7.721	42.286	56.801	21.451	46.453
200	7.271	47.477	51.003	21.558	22.029
298	7.133	50.347	50.347	21.580	15.171
300	7.132	50.392	50.348	21.580	15.073
400	7.157	52.444	50.627	21.590	11.142
500	7.287	54.053	51.157	21.594	8.783
600	7.466	55.387	51.785	21.598	7.230
700	7.682	56.452	52.461	21.601	6.066
800	7.932	57.296	53.176	21.601	5.192
900	8.198	58.528	53.570	21.610	4.587
1000	8.423	59.377	54.064	21.615	4.062
1100	8.608	60.157	54.593	21.620	3.633
1200	8.759	60.882	55.067	21.624	3.262
1300	8.881	61.568	55.500	21.626	2.912
1400	8.981	62.215	55.900	21.631	2.712
1500	9.052	62.763	56.242	21.633	2.487
1600	9.105	63.217	56.545	21.635	2.220
1700	9.142	63.595	56.812	21.635	2.015
1800	9.165	63.935	57.052	21.637	1.823
1900	9.177	64.245	57.267	21.637	1.659
2000	9.179	64.525	57.450	21.626	1.586
2100	9.168	64.788	57.603	21.619	1.586
2200	9.147	65.032	57.732	21.611	1.484
2300	9.117	65.258	57.837	21.601	1.395
2400	9.080	65.468	57.925	21.589	1.305
2500	9.037	65.663	58.000	21.574	1.227
2600	8.989	65.843	58.064	21.558	1.154
2700	8.937	66.008	58.119	21.540	1.095
2800	8.882	66.159	58.166	21.520	1.042
2900	8.824	66.298	58.206	21.498	.987
3000	8.765	66.426	58.240	21.474	.913
3100	8.708	66.543	58.268	21.449	.863
3200	8.650	66.650	58.289	21.421	.815
3300	8.591	66.748	58.303	21.391	.770
3400	8.532	66.837	58.312	21.361	.724
3500	8.472	66.918	58.317	21.329	.690
3600	8.412	66.991	58.319	21.294	.653
3700	8.351	67.057	58.318	21.259	.618
3800	8.290	67.116	58.314	21.224	.584
3900	8.228	67.169	58.308	21.188	.554
4000	8.166	67.216	58.300	21.151	.524
4100	8.104	67.258	58.290	21.114	.496
4200	8.042	67.295	58.278	21.076	.470
4300	7.980	67.328	58.264	21.037	.444
4400	7.918	67.357	58.248	20.997	.420
4500	7.856	67.382	58.230	20.957	.397
4600	7.794	67.404	58.210	20.916	.375
4700	7.732	67.422	58.189	20.874	.354
4800	7.670	67.437	58.166	20.831	.334
4900	7.608	67.449	58.142	20.787	.314
5000	7.546	67.458	58.117	20.742	.296
5100	7.484	67.464	58.090	20.696	.278
5200	7.422	67.468	58.061	20.649	.261
5300	7.360	67.469	58.030	20.601	.246
5400	7.298	67.468	58.000	20.552	.232
5500	7.236	67.464	57.968	20.501	.219
5600	7.174	67.458	57.934	20.451	.207
5700	7.112	67.449	57.898	20.400	.195
5800	7.050	67.437	57.861	20.348	.185
5900	6.988	67.422	57.822	20.295	.176
6000	6.926	67.404	57.781	20.242	.169

Dec. 31, 1960; June 30, 1963

NITRIC OXIDE (NO)

(IDEAL GAS)

MOL. WT. = 30.008

Ground State Configuration 2Π

$$\Delta H_f^{\circ} 0 = 21.46 \pm 0.04 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{\circ} = 50.347 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = 21.58 \pm 0.04 \text{ kcal. mole}^{-1}$$

Electronic Levels and Multiplicities

$$\frac{C_1, \text{ cm.}^{-1}}{g_1}$$

$$0$$

$$2$$

$$121.1$$

$$2$$

$$\omega_e x_e = 13.37 \text{ cm.}^{-1}$$

$$G^- = 1$$

$$\omega_e = 1903.60 \text{ cm.}^{-1}$$

$$\alpha_e = 0.0178 \text{ cm.}^{-1}$$

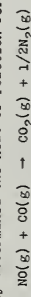
$$r_e = 1.1508 \text{ \AA}$$

Heat of Formation.

O. Herzberg, Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules, D. van Nostrand Co., Inc., New York, 1950, lists two $D_0(\text{NO})$ values, 5.286 and 6.487 e.v. A. O. Onydon, Dissociation Energies and Spectra of Diatomic Molecules, Chapman and Hall, Ltd., London, 1953, lists $D_0(\text{NO}) = 6.49 \pm 0.05$ e.v. A Birge-Sponer extrapolation of the vibrational levels, up to $v = 19$, of the ground state leads to a D_0 of about 6.5 e.v. Onydon's, loc. cit., analysis on the predissociation of NO also leads to the higher value for $D_0(\text{NO})$.

Y. Tanaka, J. Chem. Phys. 22, 2045 (1954), has observed and analyzed the emission bands of NO in the vacuum ultraviolet region. Tanaka's, loc. cit., observation and interpretation of the abrupt cutoff (predissociation) of certain v' values in the β , δ , and ϵ bands and of the complete non appearance of ϵ and β bands strongly favors a $D_0(\text{NO}) = 6.48$ e.v. $\Delta H_f^{\circ} 298.15(\text{NO})/\text{g}$ was calculated on this basis to be 22.033 ± 1 kcal. mole⁻¹.

More recently M. A. Frisch, Diss. Abstr. 23, 1940 (1961), Thesis, University of Wisconsin, Madison, Wisconsin, 1962, has calorimetrically determined the heat of reaction for



at 298.15°K., from which the author derives a $\Delta H_f^{\circ} 298.15 \text{ NO(g)} = 21.58 \pm 0.04$ kcal. mole⁻¹. The auxiliary values used by Frisch to calculate the heat of formation of nitric oxide were based upon the 1961 atomic weight scale. Recalculating $\Delta H_f^{\circ} 298.15 \text{ NO(g)}$ using auxiliary functions based on the 1956 atomic weight scale had a negligible effect on the final result.

The calorimetrically determined heat of formation for nitric oxide, 21.58 ± 0.04 kcal. mole⁻¹, was selected as the best value.

Heat Capacity and Entropy.

The spectroscopic constants were taken from R. H. Ollivette and E. H. Eyster, Phys. Rev. 56, 1113 (1939), who measured and analyzed the fundamental rotation-vibration band of nitric oxide using a grating spectrometer. The constants used in this calculation were adjusted to correspond to the naturally occurring isotopic mixture.

Nitric Oxide Unipositive Ion (NO⁺)

(Ideal Gas) GFW = 30.00555

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	6.961	47.349	47.349	•000	236.660	235.184	-172.395
300							
350	6.961	47.392	47.392	•013	236.660	235.175	-171.324
400	6.983	49.397	47.632	710	237.159	235.603	-128.681
500	7.067	50.964	48.159	1.412	237.641	233.908	-102.241
600	7.191	52.263	48.721	2.125	238.117	233.117	-84.913
700	7.344	53.383	49.309	2.952	238.587	232.245	-72.510
800	7.516	54.354	50.001	3.884	239.057	231.311	-63.090
900	7.662	55.267	50.793	4.913	239.526	230.321	-55.647
1000	7.807	56.082	50.956	5.126	239.995	229.262	-50.105
1100	7.938	56.832	51.456	5.913	240.466	228.166	-45.332
1200	8.054	57.528	51.934	6.713	240.938	227.028	-41.347
1300	8.156	58.177	52.389	7.524	241.411	225.848	-37.968
1400	8.246	58.787	52.824	8.345	241.884	224.628	-35.068
1500	8.323	59.356	53.241	9.172	242.361	223.384	-32.547
1600	8.392	59.895	53.640	10.008	242.837	222.104	-30.338
1700	8.452	60.406	54.023	10.850	243.314	220.794	-28.385
1800	8.503	60.891	54.391	11.697	243.791	219.451	-26.645
1900	8.545	61.352	54.746	12.551	244.268	218.081	-25.101
2000	8.595	61.792	55.087	13.409	244.740	216.700	-23.680
2100	8.633	62.212	55.417	14.270	245.215	215.286	-22.405
2200	8.667	62.614	55.735	15.135	245.688	213.851	-21.244
2300	8.695	62.999	56.042	16.004	246.159	212.382	-20.182
2400	8.723	63.371	56.340	16.875	246.630	210.915	-19.220
2500	8.750	63.728	56.628	17.749	247.101	209.415	-18.307
2600	8.774	64.071	56.908	18.625	247.570	207.900	-17.476
2700	8.795	64.403	57.190	19.503	248.037	206.366	-16.704
2800	8.814	64.723	57.463	20.384	248.502	204.814	-15.986
2900	8.833	65.033	57.728	21.267	248.967	203.246	-15.311
3000	8.849	65.332	57.989	22.150	249.428	201.662	-14.691
3100	8.865	65.623	58.192	23.036	249.889	200.059	-14.104
3200	8.879	65.905	58.429	23.923	250.348	198.446	-13.553
3300	8.893	66.178	58.659	24.812	250.806	196.818	-13.035
3400	8.906	66.444	58.884	25.702	251.261	195.171	-12.546
3500	8.918	66.702	59.104	26.593	251.716	193.518	-12.084
3600	8.929	66.953	59.319	27.485	252.170	191.852	-11.647
3700	8.940	67.198	59.528	28.379	252.622	190.166	-11.233
3800	8.951	67.437	59.733	29.273	253.073	188.473	-10.840
3900	8.961	67.670	59.934	30.168	253.524	186.768	-10.466
4000	8.970	67.896	60.130	31.065	253.971	185.049	-10.111
4100	8.979	68.118	60.322	31.963	254.419	183.319	-9.772
4200	8.988	68.334	60.510	32.861	254.866	181.584	-9.449
4300	8.996	68.546	60.695	33.760	255.312	179.834	-9.140
4400	9.002	68.753	60.876	34.660	255.756	178.066	-8.845
4500	9.012	68.953	61.053	35.560	256.199	176.292	-8.562
4600	9.019	69.154	61.227	36.463	256.643	174.521	-8.292
4700	9.026	69.348	61.398	37.365	257.085	172.729	-8.032
4800	9.033	69.538	61.565	38.268	257.526	170.930	-7.783
4900	9.039	69.723	61.729	39.172	257.966	169.121	-7.543
5000	9.047	69.907	61.892	40.076	258.407	167.304	-7.313
5100	9.053	70.086	62.050	40.981	258.846	165.476	-7.091
5200	9.060	70.262	62.207	41.887	259.286	163.642	-6.878
5300	9.066	70.434	62.360	42.793	259.725	161.802	-6.672
5400	9.072	70.601	62.511	43.699	260.163	159.953	-6.473
5500	9.078	70.770	62.660	44.607	260.601	158.092	-6.282
5600	9.084	70.934	62.806	45.515	261.037	156.216	-6.097
5700	9.089	71.095	62.950	46.424	261.474	154.346	-5.918
5800	9.095	71.253	63.092	47.333	261.911	152.462	-5.745
5900	9.100	71.408	63.233	48.242	262.348	150.577	-5.577
6000	9.106	71.562	63.369	49.153	262.783	148.672	-5.415

June 30, 1966

NITRIC OXIDE UNIPOSITIVE ION (NO⁺) (IDEAL GAS) GFW = 30.00555

Ground State 1Σ⁺

S_{298.15} = 47.35 gibbs/mol

ΔHf₀⁰ = 235.18 ± 0.2 kcal/mol

ΔHf_{298.15} = 236.66 ± 0.2 kcal/mol

Electronic Levels and Quantum Weights

$\frac{E_1}{E_0}, \text{ cm}^{-1}$ g_1

0 1

$\omega_e x_e = 16.35 \text{ cm}^{-1}$

$\sigma = 1$

$\alpha'_e = 0.0202 \text{ cm}^{-1}$

$r_e = 1.0619 \text{ Å}$

B_e = 2.002 cm⁻¹

Heat of Formation

K. Vatanabe, J. Chem. Phys. 22, 1564 (1954), and W. C. Walker and O. L. Weisler, J. Chem. Phys. 23, 1962 (1955), have measured the ionization potential of NO(g) by photoionization, yielding I.P. = 9.25 ± 0.02 and 9.20 ± 0.03 eV, respectively. H. D. Hagstrum, J. Chem. Phys. 23, 1178 (1955), reported I.P. = 9.4 ± 0.2 eV by electron impact. K. P. Huber, Helv. Phys. Acta 34, 929 (1961), determined spectroscopically the ionization potential for NO(g), I.P. = 9.267 ± 0.005 eV (213.72 ± 0.1 kcal/mol). The last value has been selected, and yields the heat of formation of NO⁺(g), ΔHf₀⁰ (NO⁺, g) = 235.18 kcal/mol, using ΔHf₀⁰ (NO, g) = 21.46 ± 0.04 kcal/mol.

Heat Capacity and Entropy

The selected molecular constants were obtained from the ultraviolet spectra by E. Miescher, Can. J. Phys. 33, 355 (1955), Helv. Phys. Acta 29, 135 (1956).

The tabulated thermodynamic functions are in reasonable agreement with those calculated by J. Hilsenrath and Carla G. Messias, NBS Report 8504, July 1, 1964, who have used slightly different molecular constants.

Nitrogen Dioxide (NO₂)

(Ideal Gas) Mol. Wt. = 46.008

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	Log K _p
0	-	∞	∞	∞	∞	∞
100	7.053	48.387	64.785	2.435	8.586	INFINITE
200	8.218	53.954	58.130	1.640	8.326	20.859
298	8.637	57.343	53.343	.835	8.099	11.659
300	8.650	57.398	53.344	.816	8.097	12.974
400	9.601	60.046	57.700	.939	7.770	8.961
500	10.327	62.268	58.397	1.936	7.684	7.513
600	10.955	64.208	59.207	3.001	7.638	6.669
700	11.469	65.937	60.087	4.123	7.618	6.111
800	11.900	67.461	60.882	5.297	7.618	5.714
900	12.268	68.915	61.591	6.547	7.620	5.447
1000	12.668	70.215	62.245	7.730	7.649	5.255
1100	12.677	71.414	63.243	8.988	7.674	5.085
1200	12.687	72.524	64.091	10.265	7.702	4.921
1300	12.698	73.556	64.869	11.566	7.731	4.762
1400	12.709	74.526	65.582	12.861	7.760	4.608
1500	13.193	75.432	65.082	14.176	7.790	4.458
1600	13.273	76.286	66.599	15.499	7.818	4.307
1700	13.340	77.093	67.193	16.830	7.846	4.157
1800	13.398	77.857	67.764	18.167	7.860	4.004
1900	13.447	78.583	68.312	19.507	7.870	3.850
2000	13.490	79.274	68.846	20.856	7.808	3.697
2100	13.527	79.933	69.358	22.207	7.923	3.543
2200	13.560	80.563	69.853	23.561	7.932	3.389
2300	13.589	81.166	70.326	24.919	7.939	3.235
2400	13.614	81.746	70.781	26.186	7.939	3.081
2500	13.636	82.301	71.245	27.641	7.939	2.927
2600	13.656	82.836	71.680	29.006	7.933	2.773
2700	13.674	83.352	72.103	30.373	7.922	2.619
2800	13.690	83.850	72.513	31.741	7.907	2.465
2900	13.705	84.330	72.913	33.111	7.887	2.311
3000	13.718	84.795	73.301	34.482	7.863	2.157
3100	13.730	85.245	73.679	35.854	7.836	2.003
3200	13.741	85.681	74.048	37.228	7.803	1.849
3300	13.750	86.104	74.407	38.602	7.767	1.695
3400	13.758	86.515	74.757	39.976	7.729	1.541
3500	13.768	86.914	75.099	41.354	7.683	1.387
3600	13.776	87.302	75.432	42.731	7.635	1.233
3700	13.783	87.679	75.756	44.109	7.584	1.079
3800	13.789	88.047	76.071	45.486	7.530	0.925
3900	13.796	88.405	76.388	46.861	7.474	0.771
4000	13.801	88.755	76.693	48.247	7.412	0.617
4100	13.806	89.096	76.991	49.627	7.347	0.463
4200	13.811	89.428	77.284	51.008	7.281	0.309
4300	13.816	89.753	77.570	52.389	7.213	0.155
4400	13.820	90.071	77.850	53.770	7.145	0.001
4500	13.824	90.382	78.125	55.154	7.066	-0.153
4600	13.828	90.686	78.395	56.536	6.990	-0.309
4700	13.831	90.983	78.660	57.919	6.911	-0.463
4800	13.834	91.273	78.919	59.300	6.830	-0.617
4900	13.837	91.559	79.175	60.682	6.746	-0.771
5000	13.840	91.839	79.425	62.070	6.663	-0.925
5100	13.843	92.113	79.671	63.454	6.577	-1.079
5200	13.846	92.382	79.913	64.838	6.489	-1.233
5300	13.849	92.648	80.151	66.220	6.400	-1.387
5400	13.850	92.906	80.385	67.608	6.310	-1.541
5500	13.852	93.159	80.615	68.993	6.217	-1.695
5600	13.854	93.408	80.841	70.379	6.122	-1.849
5700	13.856	93.654	81.063	71.764	6.027	-2.003
5800	13.858	93.895	81.281	73.150	5.931	-2.157
5900	13.860	94.132	81.498	74.536	5.831	-2.311
6000	13.862	94.365	81.711	75.922	5.734	-2.465

Dec. 31, 1950; June 30, 1953; Sept. 30, 1964

NITROGEN DIOXIDE (NO₂)

(IDEAL GAS)

MOL. WT. = 46.008

Point Group C_{2v}ΔH_f⁰ = 8.59 ± 0.2 kcal. mole⁻¹ΔH_f⁰ 298.15 = 57.34 ± 0.03 cal. deg.⁻¹ mole⁻¹S_{298.15} = 57.34 ± 0.03 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹
1357.8 (1)
756.8 (1)
1665.5 (1)

Bond Distance: N-O = 1.197 Å

Bond Angle: O-N-O = 134° 15'

Product of the Moments of Inertia: I_AI_BI_C = 15.3993 X 10⁻¹¹⁷ g.³ cm.⁶

σ = 2

Heat of Formation.

The equilibrium constants for NO(g) + 1/2 O₂ → NO₂(g) of Bodenstein and Lindner, Zeits. fur Physik. Chem. 100, 82 (1922) as given by W. F. Glauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938) were subjected to 2nd and 3rd law analysis. Third law analysis gave ΔH₂₉₈ = -13.67 kcal. and 2nd law ΔH₂₉₈ = -13.52 ± 0.01 kcal. The third law value had a very slight trend with temperature which was consistent with an entropy error of 0.25 cal. deg.⁻¹ mole⁻¹, the second law entropy was also consistent with an entropy error of 0.25 cal. deg.⁻¹ mole⁻¹. However the functions for all three gases are well established to about 0.03 cal. deg.⁻¹ mole⁻¹ or better and so this must be interpreted as due to errors in the data. On this basis the 3rd law value of the heat was chosen and combined with JANAF auxiliary data to give ΔH_f 298 = 7.91 ± 0.2 kcal. mole⁻¹, where the uncertainty includes that due to the possible error in the equilibrium constants.

Heat Capacity and Entropy.

O. R. Bird, J. C. Baird, A. W. Jache, J. A. Hodgeson, R. F. Curl Jr., A. C. Kunkle, J. W. Evansford, J. Bastrup-Andersen and J. Rosenthal, J. Chem. Phys. 40, 3378 (1964) have given a complete review of the microwave spectrum of NO₂. They also give a corrected infra-red vibrational assignment, adopted here, which is in excellent agreement with calculations from the microwave data. They report I_A = 0.34981 X 10⁻³⁹ g. cm.² and I_B = 6.45446 X 10⁻³⁹ g. cm.² and I_C = 6.81994 X 10⁻³⁹ g. cm.². The bond length and angle were chosen to give the best fit of the moments of inertia.

Nitrogen Dioxide Uninegative Ion (NO_2^-)
(Ideal Gas) Mol. wt. = 46.00605

T, °K.	C_p^0	S^0	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K _p
0							
100							
200							
298	9.016	56.517	56.517	0.000	- 85.850	- 79.780	58.477
300	9.033	56.573	56.517	.017	- 85.862	- 79.742	58.089
400	9.951	59.288	56.882	.566	- 86.469	- 77.609	42.401
500	10.766	61.604	57.602	2.003	- 87.011	- 75.330	32.925
600	11.412	63.631	58.442	3.114	- 87.509	- 72.945	26.569
700	11.905	65.429	59.314	4.281	- 87.980	- 70.480	22.004
800	12.279	67.044	60.181	5.491	- 88.436	- 67.950	18.562
900	12.564	68.508	61.026	6.733	- 88.884	- 65.363	15.871
1000	12.785	69.844	61.842	8.001	- 89.327	- 62.725	13.708
1100	12.958	71.071	62.626	9.289	- 89.770	- 60.044	11.929
1200	13.095	72.204	63.378	10.592	- 90.212	- 57.322	10.439
1300	13.206	73.257	64.098	11.907	- 90.656	- 54.562	9.172
1400	13.296	74.239	64.787	13.232	- 91.102	- 51.770	8.091
1500	13.370	75.159	65.448	14.566	- 91.551	- 48.945	7.131
1600	13.432	76.024	66.083	15.906	- 92.003	- 46.089	6.295
1700	13.483	76.840	66.692	17.251	- 92.458	- 43.206	5.554
1800	13.528	77.612	67.277	18.602	- 92.916	- 40.295	4.892
1900	13.565	78.344	67.840	19.957	- 93.380	- 37.359	4.297
2000	13.598	79.041	68.383	21.315	- 93.848	- 34.400	3.759
2100	13.626	79.705	68.907	22.676	- 94.320	- 31.414	3.269
2200	13.650	80.339	69.412	24.040	- 94.798	- 28.408	2.822
2300	13.672	80.946	69.900	25.406	- 95.278	- 25.378	2.411
2400	13.691	81.529	70.373	26.774	- 95.765	- 22.330	2.033
2500	13.708	82.088	70.830	28.144	- 96.257	- 19.261	1.684
2600	13.723	82.626	71.274	29.516	- 96.753	- 16.170	1.359
2700	13.736	83.144	71.704	30.889	- 97.255	- 13.062	1.057
2800	13.748	83.644	72.121	32.263	- 97.761	- 9.935	.775
2900	13.759	84.126	72.527	33.638	- 98.271	- 6.786	.511
3000	13.769	84.593	72.922	35.015	- 98.787	- 3.622	.264
3100	13.778	85.045	73.305	36.392	- 99.306	- .443	.031
3200	13.786	85.482	73.679	37.770	- 99.831	2.753	.188
3300	13.793	85.907	74.043	39.149	- 100.360	5.964	.395
3400	13.800	86.318	74.398	40.529	- 100.893	9.198	.591
3500	13.806	86.715	74.745	41.908	- 101.429	12.458	.777
3600	13.812	87.108	75.083	43.290	- 101.971	15.701	.953
3700	13.817	87.486	75.413	44.671	- 102.515	18.982	1.121
3800	13.822	87.855	75.735	46.053	- 103.063	22.270	1.281
3900	13.826	88.214	76.051	47.436	- 103.614	25.574	1.433
4000	13.830	88.564	76.359	48.819	- 104.168	28.894	1.579
4100	13.834	88.905	76.661	50.202	- 104.726	32.232	1.718
4200	13.838	89.239	76.956	51.585	- 105.287	35.573	1.851
4300	13.841	89.564	77.246	52.969	- 105.850	38.940	1.979
4400	13.844	89.883	77.530	54.354	- 106.416	42.306	2.101
4500	13.847	90.194	77.808	55.738	- 106.984	45.696	2.219
4600	13.850	90.498	78.080	57.123	- 107.555	49.100	2.333
4700	13.852	90.796	78.347	58.508	- 108.129	52.510	2.442
4800	13.855	91.088	78.610	59.893	- 108.705	55.935	2.547
4900	13.857	91.373	78.867	61.279	- 109.282	59.366	2.648
5000	13.859	91.653	79.120	62.665	- 109.861	62.814	2.745
5100	13.861	91.928	79.369	64.051	- 110.443	66.275	2.840
5200	13.863	92.197	79.613	65.437	- 111.025	69.742	2.931
5300	13.865	92.461	79.853	66.823	- 111.610	73.230	3.020
5400	13.866	92.720	80.089	68.210	- 112.197	76.720	3.105
5500	13.868	92.975	80.321	69.597	- 112.784	80.225	3.188
5600	13.870	93.225	80.549	70.984	- 113.373	83.739	3.268
5700	13.871	93.470	80.773	72.371	- 113.963	87.261	3.346
5800	13.872	93.711	80.994	73.758	- 114.555	90.805	3.421
5900	13.874	93.948	81.212	75.145	- 115.148	94.349	3.495
6000	13.875	94.182	81.426	76.533	- 115.743	97.899	3.566

Dec. 31, 1965

NITROGEN DIOXIDE UNINEGATIVE ION (NO_2^-) (IDEAL GAS) MOL. WT. = 46.00605

Point Group C_{2v}
 $\Delta H_f^0 = -85.7 \pm 12 \text{ kcal. mole}^{-1}$
 $\Delta F_f^0 = -85.9 \pm 12 \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = [56.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm.^{-1}
(1350) (1)
(750) (1)
(1220) (1)

Bond Distances: N-O = $[1.23] \text{ \AA}$
 Bond Angle: O-N-O = $[116]^\circ$
 $\sigma = 2$

Product of the Moments of Inertia: $I_A I_B I_C = [25.6905] \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation

The heat of formation of $\text{NO}_2^-(g)$ was calculated from the electron affinity of $\text{NO}_2(g)$ and the JANAF value of ΔH_f^0 for $\text{NO}_2(g)$, $4.0 \pm 0.5 \text{ ev}$ and $8.6 \pm 0.2 \text{ kcal. mole}^{-1}$, respectively. The former was obtained from the National Bureau of Standards Report 8628, "Preliminary Report on the Thermodynamic Properties of Selected Light Element and Some Related Compounds", January 1965.

Heat Capacity and Entropy

The bond distance N-O and the angle O-N-O of $\text{NO}_2^-(g)$ were estimated to be the same as those in $\text{NaNO}_2(c)$ which have been determined by G. B. Carpenter, Acta Cryst. 5, 132(1952). The three individual moments of inertia are $I_A = [0.6872] \times 10^{-39} \text{ g. cm.}^2$, $I_B = [5.7804] \times 10^{-39} \text{ g. cm.}^2$ and $I_C = [6.4676] \times 10^{-39} \text{ g. cm.}^2$.

The vibrational frequencies of $\text{NO}_2^-(g)$ were assumed to be the same as those for nitrite ion in solution which have been measured by D. Williams, J. Am. Chem. Soc. 61, 298(1939). These measured frequencies in nitrite solution are comparable to those in $\text{NO}_2(g)$ (1357.8, 756.8 and 1665.5 cm.^{-1}), reported by G. R. Bird et al., J. Chem. Phys. 40, 3378 (1964).

Nitrogen Trioxide (NO₃)
(Ideal Gas) Mol. Wt. = 62.008

NO₃

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	INFINITE	-	2.619	18.529	INFINITE	INFINITE
100	7.970	50.613	68.855	1.824	20.985	45.860	-
200	9.050	56.354	61.305	4.980	24.272	26.522	-
298	11.218	60.352	60.352	∞	27.745	20.157	-
300	11.260	60.422	60.353	∞	27.811	20.260	-
400	13.368	63.961	60.821	1.256	16.815	17.182	-
500	14.962	67.125	61.771	2.677	15.449	15.347	-
600	16.105	69.966	62.904	4.233	15.955	14.123	-
700	16.920	72.507	64.097	5.687	16.078	13.243	-
800	17.511	74.807	65.294	7.010	17.133	12.577	-
900	17.949	76.896	66.469	8.184	17.307	12.055	-
1000	18.279	78.805	67.609	11.156	17.491	11.632	-
1100	18.533	80.559	68.707	13.037	17.680	11.293	-
1200	18.732	82.181	69.763	14.901	17.871	10.989	-
1300	18.891	83.687	70.777	16.782	18.061	10.737	-
1400	19.019	85.092	71.750	18.678	18.251	10.519	-
1500	19.124	86.407	72.684	20.585	18.437	10.328	-
1600	19.211	87.644	73.581	22.502	18.620	10.160	-
1700	19.284	88.811	74.443	24.427	18.801	10.009	-
1800	19.346	89.915	75.272	26.359	18.974	9.874	-
1900	19.398	90.963	76.076	28.296	19.142	9.753	-
2000	19.443	91.959	76.840	30.238	19.306	9.642	-
2100	19.482	92.909	77.583	32.184	19.463	9.541	-
2200	19.516	93.816	78.300	34.134	19.612	9.449	-
2300	19.546	94.684	78.994	36.087	19.757	9.364	-
2400	19.572	95.516	79.665	38.043	19.894	9.285	-
2500	19.595	96.316	80.315	40.002	20.023	9.212	-
2600	19.616	97.085	80.945	41.962	20.147	9.145	-
2700	19.634	97.825	81.557	43.925	20.263	9.082	-
2800	19.651	98.540	82.151	45.889	20.373	9.023	-
2900	19.666	99.230	82.728	47.855	20.475	8.968	-
3000	19.679	99.897	83.289	49.822	20.571	8.917	-
3100	19.691	100.542	83.835	51.791	20.661	8.868	-
3200	19.702	101.167	84.367	53.760	20.743	8.823	-
3300	19.712	101.774	84.886	55.731	20.820	8.780	-
3400	19.721	102.362	85.391	57.703	20.890	8.739	-
3500	19.730	102.934	85.884	59.675	20.956	8.701	-
3600	19.738	103.490	86.365	61.649	21.015	8.664	-
3700	19.745	104.031	86.830	63.623	21.069	8.630	-
3800	19.751	104.558	87.295	65.598	21.119	8.597	-
3900	19.757	105.071	87.744	67.573	21.164	8.566	-
4000	19.763	105.571	88.184	69.549	21.203	8.536	-
4100	19.768	106.059	88.614	71.526	21.238	8.508	-
4200	19.773	106.536	89.035	73.503	21.269	8.485	-
4300	19.778	107.001	89.447	75.480	21.297	8.465	-
4400	19.782	107.456	89.851	77.458	21.319	8.440	-
4500	19.786	107.900	90.248	79.437	21.339	8.417	-
4600	19.790	108.335	90.636	81.414	21.356	8.395	-
4700	19.793	108.761	91.017	83.395	21.368	8.374	-
4800	19.796	109.177	91.391	85.374	21.378	8.352	-
4900	19.799	109.586	91.758	87.354	21.385	8.332	-
5000	19.802	109.986	92.119	89.334	21.389	8.313	-
5100	19.805	110.378	92.473	91.316	21.390	8.295	-
5200	19.808	110.763	92.821	93.295	21.390	8.280	-
5300	19.810	111.140	93.161	95.276	21.387	8.265	-
5400	19.812	111.510	93.500	97.257	21.382	8.254	-
5500	19.815	111.874	93.830	99.236	21.375	8.248	-
5600	19.817	112.231	94.156	101.220	21.365	8.239	-
5700	19.819	112.582	94.479	103.202	21.354	8.233	-
5800	19.820	112.926	94.791	105.184	21.342	8.228	-
5900	19.822	113.265	95.101	107.166	21.327	8.224	-
6000	19.824	113.598	95.407	109.148	21.311	8.218	-

Dec. 31, 1964

NITROGEN TRIOXIDE (NO₃) (IDEAL GAS)

Point Group [D_{3h}]
S_{298.15}⁰ = [60.4] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 2
ΔH_f⁰ = 18.5 ± 5 kcal. mole⁻¹
ΔH_f⁰ 298.15 = 17.0 ± 5 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

W _e , cm. ⁻¹	g
[1158] (2)	[940] (1)
[704] (2)	[765] (1)

Bond Distance: O-N = [1.27] Å
Bond Angle: O-N-O = [120°]
Product of the Moments of Inertia: I_AI_BI_C = [5.309 × 10⁻¹¹⁵] g.³ cm.⁶
σ = [6]

Heat of Formation.

The heat of formation is based on equilibrium constants for the reaction N₂O₅(g) → NO₂(g) + NO₃(g) obtained from shock wave studies by Schott and Davidson, J. Am. Chem. Soc. 80, 1941 (1958). These equilibria give a second law value of ΔH_f⁰ 495 = 21.5 ± 1.4 kcal., corresponding to ΔH_f⁰ 298.15 = 22.2 kcal., and a third law value of ΔH_f⁰ 298.15 = 22.2 kcal. The resulting heat of formation is 17.0 kcal. mole⁻¹.

Quillory and Johnston, J. Am. Chem. Soc. 85, 1695 (1963) report an equilibrium constant based on estimated Beer's law constants for NO₃ and attributed to the reaction O₂ + NO → NO₃. This gives a third law heat of formation of 12 ± 2 kcal. mole⁻¹, which was not considered. A tentative value of 23 kcal. mole⁻¹ (or greater) may be derived from the D₀ given by D. A. Ramsay, Proc. 10th Colloq. Spect. Intern. (1962), Univ. Maryland, pp. 583-596, 1963.

Heat Capacity and Entropy.

The structure and frequencies are those estimated by I. C. Haataine, J. Phys. Chem. 65, 2249 (1961). A symmetry of D_{3h} was chosen on the basis of Valah's correlation, J. Chem. Soc. 1953, 2301 (1953) and the bond distance was taken as 2% longer than in the nitrate ion. The planar mode frequencies were calculated from estimated Urey-Bradley force constants, while the out-of-plane wagging frequency (765 cm.⁻¹) was assumed the same as in HNO₃(g).

There are several conflicting bits of information concerning NO₃ radicals. Chantry, Horaeffeld, Horton and Whiffen, Mol. Phys. 5, 589 (1962) studied the electron resonance and optical absorption spectra of what appear to be NO₃ radicals trapped in crystals of urea nitrate. The authors suggest a planar structure without a threefold axis (thus C_{2v} symmetry), at least for the trapped radicals. Quillory and Johnston, loc. cit., report for gaseous NO₃ radicals an infrared frequency at 1840 cm.⁻¹ which they assign as the N-O stretch. The similarity of this frequency to those in N-O and X-N-O molecules led the authors to suggest an OONO structure (thus C_{2v} symmetry) rather than the nitrate structure. The remaining frequencies for such a structure may be crudely estimated by analogy with those measured for (NO₂)₂ by Smith, Keller & Johnston, J. Chem. Phys. 19, 189 (1951). Based on such frequencies and reasonable bond distances, the room temperature entropy for the OONO structure would be 68-72 cal. deg.⁻¹ mole⁻¹. Such an entropy is quite inconsistent with the second law ΔS_f⁰ 495 = 33.2 ± 3 cal. deg.⁻¹ mole⁻¹ for N₂O₅(g) → NO₂(g) + NO₃(g) obtained from the shock wave studies of Schott and Davidson. The Haataine functions based on the nitrate structure were selected because they are consistent with the experimental entropy. The principal moments of inertia for this structure are I_A = 6.427 × 10⁻³⁹, I_B = 6.427 × 10⁻³⁹ and I_C = 12.853 × 10⁻³⁹ g. cm.². A structure of C_{2v} symmetry would result if the nitrate structure were distorted to give one non-equivalent oxygen. Ramsay, loc. cit., suggests that such distortion can only be small, based on the high dispersion optical spectra of the gas phase.

NO₃

Monophosphorus Mononitride (PN)

(Ideal Gas) Mol. Wt. = 44.983

NP

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	INFINITE	2.080	24.861	INFINITE	INFINITE
100	6.956	49.812	50.565	22.896	- 50.038	- 1.286
200	6.971	47.255	51.231	20.644	- 22.558	- 1.689
298	7.026	50.437	50.437	25.043	- 13.526	- 2.000
300	7.100	50.431	50.437	25.041	- 13.413	- 2.013
400	7.253	52.526	50.718	24.351	- 16.257	- 2.455
500	7.429	54.423	51.250	24.758	- 18.685	- 2.865
600	7.625	56.043	51.874	24.528	- 21.974	- 3.261
700	7.835	57.474	52.502	24.330	- 24.539	- 3.639
800	8.055	58.755	53.118	24.098	- 27.294	- 3.994
900	8.285	59.912	53.712	23.794	- 30.139	- 4.339
1000	8.525	60.952	54.281	23.436	- 33.069	- 4.675
1100	8.775	61.884	54.823	22.998	- 36.084	- 4.994
1200	9.035	62.712	55.339	22.486	- 39.284	- 5.299
1300	9.305	63.442	55.832	21.908	- 42.669	- 5.592
1400	9.585	64.078	56.302	21.266	- 46.240	- 5.875
1500	9.875	64.625	56.751	20.562	- 50.006	- 6.148
1600	10.175	65.084	57.180	19.808	- 53.969	- 6.412
1700	10.485	65.455	57.591	19.006	- 58.129	- 6.667
1800	10.805	65.738	57.984	18.158	- 62.494	- 6.912
1900	11.135	65.935	58.360	17.268	- 67.065	- 7.148
2000	11.475	66.048	58.720	16.340	- 71.842	- 7.375
2100	11.825	66.078	59.078	15.378	- 76.826	- 7.594
2200	12.185	66.024	59.416	14.386	- 82.016	- 7.805
2300	12.555	65.888	59.743	13.366	- 87.412	- 8.008
2400	12.935	65.672	60.058	12.322	- 93.014	- 8.203
2500	13.325	65.378	60.363	11.258	- 98.828	- 8.390
2600	13.725	64.998	60.658	10.178	- 104.854	- 8.569
2700	14.135	64.535	60.945	9.088	- 111.092	- 8.740
2800	14.555	63.988	61.222	7.988	- 117.542	- 8.903
2900	14.985	63.358	61.492	6.878	- 124.202	- 9.058
3000	15.425	62.645	61.754	5.758	- 131.072	- 9.205
3100	15.875	61.848	62.000	4.628	- 138.152	- 9.345
3200	16.335	60.968	62.232	3.488	- 145.442	- 9.478
3300	16.805	60.005	62.452	2.338	- 152.942	- 9.603
3400	17.285	58.958	62.662	1.178	- 160.652	- 9.720
3500	17.775	57.828	62.862	0.008	- 168.572	- 9.829
3600	18.275	56.615	63.052	- 1.152	- 176.702	- 9.930
3700	18.785	55.318	63.232	- 2.282	- 185.042	- 10.023
3800	19.305	53.938	63.402	- 3.392	- 193.592	- 10.108
3900	19.835	52.478	63.562	- 4.482	- 202.352	- 10.185
4000	20.375	51.038	63.712	- 5.552	- 211.322	- 10.255
4100	20.925	49.618	63.852	- 6.602	- 220.502	- 10.318
4200	21.485	48.218	63.982	- 7.632	- 230.002	- 10.375
4300	22.055	46.838	64.102	- 8.642	- 239.822	- 10.426
4400	22.635	45.478	64.212	- 9.632	- 249.952	- 10.472
4500	23.225	44.138	64.312	- 10.602	- 260.392	- 10.513
4600	23.825	42.818	64.402	- 11.552	- 271.142	- 10.550
4700	24.435	41.518	64.482	- 12.482	- 282.202	- 10.583
4800	25.055	40.238	64.552	- 13.392	- 293.572	- 10.612
4900	25.685	38.978	64.612	- 14.282	- 305.252	- 10.637
5000	26.325	37.738	64.662	- 15.152	- 317.242	- 10.658
5100	26.975	36.518	64.702	- 16.002	- 329.542	- 10.675
5200	27.635	35.318	64.732	- 16.832	- 342.152	- 10.689
5300	28.305	34.138	64.752	- 17.642	- 355.072	- 10.700
5400	28.985	32.978	64.762	- 18.432	- 368.302	- 10.708
5500	29.675	31.838	64.762	- 19.202	- 381.842	- 10.713
5600	30.375	30.718	64.752	- 19.952	- 395.692	- 10.715
5700	31.085	29.618	64.732	- 20.682	- 409.852	- 10.715
5800	31.805	28.538	64.692	- 21.392	- 424.322	- 10.712
5900	32.535	27.478	64.642	- 22.082	- 439.102	- 10.707
6000	33.275	26.438	64.582	- 22.752	- 454.192	- 10.699

Dec. 31, 1960; Sept. 30, 1962

MONOPHOSPHORUS MONONITRIDE (PN) (IDEAL GAS) MOL. WT. = 44.983

ΔH_f^o 0 = 24.9 ± 1.2 kcal. mole⁻¹ ΔH_f^o 298.15 = 25.0 ± 1.2 kcal. mole⁻¹
 Ground State Configuration 1⁺ S_{298.15} = 50.437 cal. deg.⁻¹ mole⁻¹

Electronic Level and Multiplicity

$$\frac{\epsilon, \text{ cm.}^{-1}}{0} \frac{g_i}{1}$$

ω_e = 1337.24 cm.⁻¹ ω_ex_e = 6.983 cm.⁻¹

B_e = 0.7862 cm.⁻¹ α_e = 0.00557 cm.⁻¹

D_e = 1.09 × 10⁻⁶ cm.⁻¹

r_e = 1.4910 Å σ = 1

Heat of Formation.

The selected ΔH_f^o 298.15 was calculated from the D₀^o = 165.8 ± 1.2 kcal. mole⁻¹ reported by R. L. Potter and V. M. Distefano, J. Phys. Chem., **65**, 849 (1961). A D₀^o = 163.7 ± 1.2 kcal. mole⁻¹ was experimentally determined by E. O. Huffman, G. Turbation, K. L. Elmore, W. E. Cate, H. K. Walters, Jr., and G. V. Elmore, J. Am. Chem. Soc., **76**, 6239 (1954). The D₀^o reported by Huffman et. al was derived using a pressure-composition method i.e. measurement of equilibrium vapor pressure at 1173°K for the reaction [PN(g) → P₂(g) + N₂(g)]. Potter and Distefano (loc. cit.) recalculated Huffman's results to obtain their D₀^o value. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall (1953), lists a D₀^o = 138.4 ± 19 kcal. mole⁻¹. The corresponding heats of formation are:

ΔH_f^o 298.15
 25.0 ± 1.2 kcal. mole⁻¹ Potter and Distefano (loc. cit.)
 27.1 ± 1.2 kcal. mole⁻¹ Huffman et al. (loc. cit.)
 53 ± 19 kcal. mole⁻¹ Gaydon (loc. cit.)

Heat Capacity and Entropy.

The molecular constants are taken from G. Herzburg, "Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., (1960) 2nd Ed.

NP

MONOSULFUR MONONITRIDE (SN) (IDEAL GAS) MOL. WT. = 46.074

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.000	145.1041E	-2.924	42.843	42.843	-19.101E
100	7.720	44.614	1.526	42.843	42.843	-19.101E
200	7.687	30.011	3.751	42.843	42.843	-19.101E
298	7.599	23.055	5.278	42.843	42.843	-19.101E
300	7.599	23.055	5.278	42.843	42.843	-19.101E
400	7.599	23.055	5.278	42.843	42.843	-19.101E
500	7.599	23.055	5.278	42.843	42.843	-19.101E
600	7.599	23.055	5.278	42.843	42.843	-19.101E
700	7.599	23.055	5.278	42.843	42.843	-19.101E
800	7.599	23.055	5.278	42.843	42.843	-19.101E
900	7.599	23.055	5.278	42.843	42.843	-19.101E
1000	7.599	23.055	5.278	42.843	42.843	-19.101E
1100	7.599	23.055	5.278	42.843	42.843	-19.101E
1200	7.599	23.055	5.278	42.843	42.843	-19.101E
1300	7.599	23.055	5.278	42.843	42.843	-19.101E
1400	7.599	23.055	5.278	42.843	42.843	-19.101E
1500	7.599	23.055	5.278	42.843	42.843	-19.101E
1600	7.599	23.055	5.278	42.843	42.843	-19.101E
1700	7.599	23.055	5.278	42.843	42.843	-19.101E
1800	7.599	23.055	5.278	42.843	42.843	-19.101E
1900	7.599	23.055	5.278	42.843	42.843	-19.101E
2000	7.599	23.055	5.278	42.843	42.843	-19.101E
2100	7.599	23.055	5.278	42.843	42.843	-19.101E
2200	7.599	23.055	5.278	42.843	42.843	-19.101E
2300	7.599	23.055	5.278	42.843	42.843	-19.101E
2400	7.599	23.055	5.278	42.843	42.843	-19.101E
2500	7.599	23.055	5.278	42.843	42.843	-19.101E
2600	7.599	23.055	5.278	42.843	42.843	-19.101E
2700	7.599	23.055	5.278	42.843	42.843	-19.101E
2800	7.599	23.055	5.278	42.843	42.843	-19.101E
2900	7.599	23.055	5.278	42.843	42.843	-19.101E
3000	7.599	23.055	5.278	42.843	42.843	-19.101E
3100	7.599	23.055	5.278	42.843	42.843	-19.101E
3200	7.599	23.055	5.278	42.843	42.843	-19.101E
3300	7.599	23.055	5.278	42.843	42.843	-19.101E
3400	7.599	23.055	5.278	42.843	42.843	-19.101E
3500	7.599	23.055	5.278	42.843	42.843	-19.101E
3600	7.599	23.055	5.278	42.843	42.843	-19.101E
3700	7.599	23.055	5.278	42.843	42.843	-19.101E
3800	7.599	23.055	5.278	42.843	42.843	-19.101E
3900	7.599	23.055	5.278	42.843	42.843	-19.101E
4000	7.599	23.055	5.278	42.843	42.843	-19.101E
4100	7.599	23.055	5.278	42.843	42.843	-19.101E
4200	7.599	23.055	5.278	42.843	42.843	-19.101E
4300	7.599	23.055	5.278	42.843	42.843	-19.101E
4400	7.599	23.055	5.278	42.843	42.843	-19.101E
4500	7.599	23.055	5.278	42.843	42.843	-19.101E
4600	7.599	23.055	5.278	42.843	42.843	-19.101E
4700	7.599	23.055	5.278	42.843	42.843	-19.101E
4800	7.599	23.055	5.278	42.843	42.843	-19.101E
4900	7.599	23.055	5.278	42.843	42.843	-19.101E
5000	7.599	23.055	5.278	42.843	42.843	-19.101E
5100	7.599	23.055	5.278	42.843	42.843	-19.101E
5200	7.599	23.055	5.278	42.843	42.843	-19.101E
5300	7.599	23.055	5.278	42.843	42.843	-19.101E
5400	7.599	23.055	5.278	42.843	42.843	-19.101E
5500	7.599	23.055	5.278	42.843	42.843	-19.101E
5600	7.599	23.055	5.278	42.843	42.843	-19.101E
5700	7.599	23.055	5.278	42.843	42.843	-19.101E
5800	7.599	23.055	5.278	42.843	42.843	-19.101E
5900	7.599	23.055	5.278	42.843	42.843	-19.101E
6000	7.599	23.055	5.278	42.843	42.843	-19.101E

June 30, 1961

D₀ = 115 ± 25 kcal. mole⁻¹
 Ground State Configuration 2Π_r
 ΔI_f^o 298.15 = 63 ± 25 kcal. mole⁻¹
 S_{298.15}^o = 53.055 cal. deg.⁻¹ mole⁻¹

Electronic Levels and Multiplicities

E ₁ , cm. ⁻¹	E ₁
0	2
223	2

(*u*) x_g = 7.75 cm.⁻¹
 α_g = [0.0064] cm.⁻¹
 σ = 1
 r_g = 1.495(7) Å

Heat of Formation

(*u*) = 1220.0 cm.⁻¹
 B₀ = [0.7762] cm.⁻¹
 The dissociation energy is listed by A. O. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 2nd Edn., Chapman and Hall, London (1965).

Heat Capacity and Entropy

The spectroscopic constants other than B₀ and α_g are from O. Herzberg "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Company, New York (1950). r_g is from "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London (1959), and has been used, together with the equation
 α_g = ε ([0.0064] B₀³ - 6B₀²)/ω_e (Herzberg, op. cit., p. 108)
 to calculate B₀ and α_g.

Silicon Nitride (SiN)

(Ideal Gas) GFW = 42.0927

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ^o - 298.15)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	.000	INFINITE	- 2.087	88.718	88.718	INFINITE
100	6.956	42.138	- 1.352	89.002	89.002	18.239
200	11.15	48.423	- .900	89.000	89.000	59.904
298	12.10	51.792	.000		81.722	
300	7.216	51.837	.013	88.998	81.677	59.502
400	7.541	53.957	.751	88.860	79.254	43.302
500	7.843	55.673	1.521	88.754	76.163	31.597
600	8.086	57.125	2.314	88.627	74.496	27.135
700	8.273	58.387	3.136	88.496	72.151	22.526
800	8.421	59.501	3.971	88.360	69.425	19.075
900	8.545	60.501	4.819	88.217	67.517	16.395
1000	8.657	61.407	5.680	88.066	65.225	14.255
1100	8.767	62.237	6.551	87.908	62.949	12.507
1200	8.860	63.005	7.433	87.745	60.694	11.052
1300	8.949	63.720	8.327	87.579	58.435	9.824
1400	9.123	64.392	9.233	87.409	56.202	8.773
1500	9.253	65.025	10.152	87.238	53.980	7.865
1600	9.384	65.627	11.084	87.067	51.768	7.071
1700	9.516	66.200	12.029	86.892	49.572	6.386
1800	9.645	66.747	12.987	86.716	47.393	5.801
1900	9.770	67.272	13.955	86.541	45.231	5.318
2000	9.888	67.776	14.941	86.365	43.085	4.945
2100	9.998	68.261	15.935	86.189	40.955	4.657
2200	10.100	68.729	16.940	86.014	38.832	4.420
2300	10.192	69.180	17.955	85.839	36.716	4.233
2400	10.273	69.615	18.978	85.664	34.607	4.083
2500	10.345	70.036	20.009	85.489	32.502	3.960
2600	10.407	70.443	21.047	85.314	30.401	3.869
2700	10.460	70.837	22.090	85.139	28.304	3.798
2800	10.504	71.218	23.138	84.964	26.211	3.743
2900	10.539	71.587	24.191	84.789	24.121	3.693
3000	10.567	71.945	25.246	84.614	22.034	3.647
3100	10.589	72.292	26.304	84.439	20.000	3.605
3200	10.604	72.629	27.363	84.264	18.025	3.567
3300	10.614	72.955	28.424	84.089	16.100	3.533
3400	10.619	73.272	29.486	83.914	14.225	3.502
3500	10.620	73.580	30.548	83.739	12.400	3.473
3600	10.618	73.879	31.610	83.564	10.625	3.446
3700	10.612	74.170	32.672	83.389	8.900	3.421
3800	10.605	74.453	33.732	83.214	7.225	3.397
3900	10.595	74.728	34.792	83.039	5.600	3.373
4000	10.584	74.996	35.851	82.864	4.025	3.350
4100	10.571	75.257	36.909	82.689	2.500	3.327
4200	10.558	75.512	37.966	82.514	1.025	3.303
4300	10.544	75.760	39.021	82.339	- .450	3.279
4400	10.530	76.002	40.074	82.164	- 1.975	3.255
4500	10.516	76.239	41.127	81.989	- 3.500	3.231
4600	10.502	76.470	42.174	81.814	- 5.025	3.207
4700	10.488	76.696	43.227	81.639	- 6.550	3.183
4800	10.475	76.916	44.275	81.464	- 8.075	3.159
4900	10.462	77.132	45.322	81.289	- 9.600	3.135
5000	10.449	77.343	46.366	81.114	- 11.125	3.111
5100	10.436	77.550	47.412	80.939	- 12.650	3.087
5200	10.427	77.753	48.455	80.764	- 14.175	3.063
5300	10.417	77.951	49.497	80.589	- 15.700	3.039
5400	10.407	78.146	50.539	80.414	- 17.225	3.015
5500	10.399	78.337	51.579	80.239	- 18.750	2.991
5600	10.391	78.524	52.619	80.064	- 20.275	2.967
5700	10.384	78.708	53.657	79.889	- 21.800	2.943
5800	10.376	78.888	54.695	79.714	- 23.325	2.919
5900	10.373	79.066	55.733	79.539	- 24.850	2.895
6000	10.366	79.240	56.770	79.364	- 26.375	2.871

Dec. 31, 1960; Mar. 31, 1967

SILICON NITRIDE (SiN)

(IDEAL GAS)

OPW = 42.0927

Ground State Configuration 2 Σ⁺ΔH_f^o = 89.7 ± 15 kcal/molΔH_f^o = 89.15 ± 15 kcal/mol

Electronic Levels and Quantum Weights

E _l , cm ⁻¹	K _l
0	2
[6000]	4
24299.4	2
[31000]	4

ω_eX_e = 6.55 cm⁻¹

O = 1

ω_e = 1150.8 cm⁻¹B_e = 0.7299 cm⁻¹r_e = 1.578 Åα_e = 0.00557

Heat of Formation

A linear Birge-Spencer extrapolation of the ground state gives a dissociation energy of 142.9 kcal. The ground state can correlate with normal atoms Si(³P) + N(²D); in this latter case D₀ would be 88 kcal. The uncertainty in the extrapolation is quite large, ± 30 kcal, since only 6 levels, of the estimated total of 87 levels, are observed.

A dissociation energy can also be calculated from the B²Σ⁺ state by a much shorter extrapolation. This extrapolation is done graphically since some curvature is evident in the first six levels. A value of D₀(B²Σ⁺) = 50.4 kcal is obtained. This corresponds to D₀(X²Σ⁺) = 119.9 kcal for normal products or D₀(X²Σ⁺) = 85 kcal for excited nitrogen as a product. The uncertainty in this extrapolation is less than the ground state and is probably ± 20 kcal.

An estimate of D₀(SiN) may be obtained by equating D₀(SiN)/D₀(SiO) = D₀(CN)/D₀(CO); this yields D₀(SiN) = 135 kcal.

A comparison of the isoelectronic molecules CP, BS and BeCl and the related molecules CN, BO, BeF indicates D₀(SiN) > 115 kcal.

A value of D₀(SiN) = 130 ± 15 kcal/mol is in agreement within the uncertainties of both ground state and B state extrapolations assuming normal atoms as products, and is in agreement with the other estimates. This value is adopted and yields ΔH_f^o(SiN,g) = 89 kcal/mol.

Heat Capacity and Entropy

The B-X transition has been reported by F. A. Jenkins and H. de Laezy, Proc. Roy. Soc. (London) 122, 103 (1929). The rotational and vibrational constants are derived from their work and adjusted to normal isotopic abundance. The A²Π-²Σ⁺ transition has been observed by M. D. Shetlar, Ph.D. Thesis, Univ. of California, Berkeley (1965). The height of the A state is estimated by correlation with CP(g). The level of the B state is taken from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., 2nd Edition, New York, 1950.

NSI

Disilicon Nitride (Si₂N)

(Ideal Gas) GFW = 70.1787

T, °K	Cp°	S°	-(Cp°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	∞	∞	∞	∞	94.749	94.749	INFINITE
100	10.581	50.108	20.956	- 2.095	95.015	92.094	- 201.275
200	10.659	54.767	20.577	- 1.112	95.007	94.134	- 97.406
298	11.722	61.275	21.275	- .000	95.000	94.134	- 93.213
300	11.942	61.349	21.275	.022	94.999	86.182	- 62.783
400	12.803	68.910	21.755	1.262	94.875	83.261	- 45.092
500	13.374	67.833	22.687	2.571	94.747	80.374	- 35.131
600	13.755	70.307	23.756	3.931	94.612	77.511	- 28.233
700	14.017	72.449	24.848	5.320	94.468	74.672	- 23.314
800	14.202	74.333	25.919	6.732	94.308	71.853	- 19.629
900	14.336	76.014	26.949	8.159	94.131	69.059	- 16.770
1000	14.435	77.530	27.935	9.594	93.935	66.283	- 14.486
1100	14.512	78.909	28.868	11.045	93.719	63.529	- 12.472
1200	14.571	80.175	29.759	12.499	93.482	60.793	- 11.072
1300	14.618	81.343	30.605	13.959	93.226	58.075	- 9.764
1400	14.656	82.428	31.411	15.421	92.950	55.385	- 8.646
1500	14.687	83.440	32.180	16.890	92.652	52.713	- 7.680
1600	14.712	84.389	32.914	18.360	92.334	50.041	- 6.830
1700	14.733	85.281	33.615	19.832	91.997	47.461	- 6.125
1800	14.751	86.124	34.287	21.306	91.759	44.851	- 5.640
1900	14.767	86.922	34.931	22.782	91.508	42.213	- 5.208
2000	14.780	87.680	35.550	24.260	91.257	39.576	- 4.820
2100	14.791	88.401	36.145	25.734	91.004	36.949	- 4.471
2200	14.801	89.089	36.714	27.214	90.751	34.319	- 4.154
2300	14.810	89.747	37.270	28.694	90.497	31.682	- 3.867
2400	14.817	90.378	37.803	30.180	90.243	29.056	- 3.604
2500	14.824	90.983	38.314	31.662	90.000	26.429	- 3.363
2600	14.830	91.564	38.817	33.145	89.752	23.802	- 3.142
2700	14.836	92.124	39.299	34.624	89.507	21.177	- 2.937
2800	14.841	92.664	39.767	36.112	89.257	18.551	- 2.748
2900	14.846	93.185	40.221	37.596	89.002	15.924	- 2.573
3000	14.851	93.688	40.661	39.081	88.752	13.297	- 2.410
3100	14.856	94.175	41.089	40.564	88.507	10.670	- 2.258
3200	14.860	94.647	41.506	42.052	88.257	8.043	- 2.117
3300	14.865	95.104	41.911	43.534	88.002	5.416	- 1.994
3400	14.869	95.548	42.305	45.025	87.752	2.789	- 1.880
3500	14.874	95.979	42.690	46.512	87.507	0.162	- 1.783
3600	14.879	96.398	43.065	48.000	87.257	- 2.465	- 1.708
3700	14.885	96.806	43.431	49.489	87.002	- 5.092	- 1.656
3800	14.890	97.203	43.788	50.977	86.752	- 7.719	- 1.624
3900	14.896	97.590	44.137	52.466	86.507	- 10.346	- 1.606
4000	14.903	97.967	44.478	53.956	86.257	- 12.973	- 1.600
4100	14.910	98.335	44.812	55.447	86.002	- 15.600	- 1.603
4200	14.918	98.695	45.138	56.934	85.752	- 18.227	- 1.620
4300	14.926	99.046	45.457	58.420	85.507	- 20.854	- 1.656
4400	14.934	99.389	45.775	59.921	85.257	- 23.481	- 1.703
4500	14.944	99.725	46.076	61.417	85.002	- 26.108	- 1.761
4600	14.953	100.053	46.377	62.912	84.752	- 28.735	- 1.830
4700	14.964	100.375	46.671	64.409	84.507	- 31.362	- 1.908
4800	14.975	100.690	46.960	65.905	84.257	- 33.989	- 1.994
4900	14.986	100.999	47.243	67.403	84.002	- 36.616	- 2.094
5000	14.999	101.302	47.521	68.902	83.752	- 39.243	- 2.206
5100	15.011	101.599	47.795	70.401	83.507	- 41.870	- 2.330
5200	15.025	101.891	48.063	71.904	83.257	- 44.497	- 2.466
5300	15.039	102.177	48.326	73.404	83.002	- 47.124	- 2.614
5400	15.053	102.458	48.586	74.912	82.752	- 49.751	- 2.774
5500	15.068	102.735	48.840	76.414	82.507	- 52.378	- 2.944
5600	15.084	103.006	49.091	77.924	82.257	- 55.005	- 3.124
5700	15.100	103.273	49.337	79.435	82.002	- 57.632	- 3.314
5800	15.116	103.536	49.580	80.944	81.752	- 60.259	- 3.514
5900	15.133	103.795	49.819	82.454	81.507	- 62.886	- 3.724
6000	15.151	104.049	50.054	83.964	81.257	- 65.513	- 3.944

Mar. 31, 1967

DISILICON NITRIDE (Si₂N)

OPW = 70.1787

(IDEAL GAS)

Point Group[D_{2h}h]
S_{298.15} = {61.3 ± 2} gibbs/mol
ΔH_f° = 94.6 ± 5 kcal/mol
ΔH_f°_{298.15} = 95 ± 5 kcal/mol

Electronic Levels and Quantum Weights

ε ₁ , cm ⁻¹	g ₁
0	[4]
[24000]	[4]
[28000]	[2]

Vibrational Frequencies and Degeneracies

ω _j , cm ⁻¹	g _j
[600]	(1)
[240]	(2)
[1000]	(1)

Bond Distance: Si-N = [170] Å

Bond Angle: Si-N-Si = [180]°

Rotational Constant: B₀ = [0.10384] cm⁻¹

Heat of Formation

K. P. Zmbov and J. L. Margrave, Rice University, private communication, March 1967, have identified Si₂N(g) in a mass spectrometer. They also determined partial pressures of Si₂N(g) in equilibrium with Si(g) and N₂(g). From four of these measurements, in the temperature range 1742° - 1846°K, we obtain a second law ΔH_f°₂₉₈ = 99.6 ± 6 kcal/mol for the reaction Si₂N(g) = 2 Si(g) + 0.5 N₂(g) and a third law ΔH_f°₂₉₈ = 120.2 kcal/mol with a drift of -11.4 ± 3.4 eu. Considering the small temperature range and the uncertainties in the free energy functions, the data appear consistent. We adopt the 3rd law heat of reaction which yields ΔH_f°₂₉₈(Si₂N,g) = 95 kcal/mol.

Heat Capacity and Entropy

Si₂N(g) is considered to be closely related to C₂N(g), and its structure and electronic configuration are adopted by analogy to this species. The bond length was obtained by adding the difference between the bond distances of SiN(g) and CN(g) to the bond length in CN(g). The vibrational frequencies were estimated by comparison with several molecules, CN(g); 1/4 state of C₂(g); NCN(g); and SiC(g). It should be noted that there is a wide variation in observed frequencies for these molecules and ω₁ and ω₃ may be significantly different from the chosen values.

The electronic ground state is considered to be ¹Σ_g⁺ with excited states of ²Δ_g and ²Σ_g⁺ as in the case of CN(g). The levels are obtained from those in CN(g) by use of the shift between C₂(g) and SiC(g).

Titanium Nitride (TiN)

(Crystal) GFW = 61.9067

NTi

T, °K	Cp ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	2.672	1.057	1.234	1.311	79.823	79.823	INFINITE
200	6.532	4.144	7.971	1.234	80.226	78.227	170.944
298	8.862	7.226	11.006	1.234	80.564	76.080	43.136
				0.000	80.700	73.847	53.132
300	8.900	7.281	11.066	0.016	80.701	73.805	53.767
400	10.471	10.079	12.509	0.993	80.691	71.504	39.068
500	11.247	12.509	14.526	2.083	80.598	69.217	30.295
600	11.645	14.597	16.261	3.229	80.475	66.953	24.387
700	11.998	16.012	17.780	4.406	80.329	64.710	20.203
800	12.308	17.449	19.066	5.606	80.166	62.484	17.070
900	12.581	18.888	20.153	6.825	80.000	60.271	14.636
1000	12.823	20.336	21.066	8.063	79.823	58.071	12.691
1100	13.035	21.799	21.823	9.318	79.636	55.877	11.102
1200	13.215	23.276	22.450	10.586	79.445	53.692	9.771
1300	13.367	24.763	22.950	11.866	79.250	51.516	8.600
1400	13.497	26.261	23.423	13.153	79.051	49.345	7.672
1500	13.603	27.768	23.876	14.450	78.848	47.180	6.836
1600	13.684	29.292	24.312	15.756	78.641	45.021	6.105
1700	13.742	30.833	24.732	17.071	78.430	42.868	5.462
1800	13.778	32.390	25.137	18.396	78.215	40.721	4.891
1900	13.794	33.962	25.528	19.731	78.000	38.580	4.381
2000	13.792	35.549	25.906	21.076	77.785	36.445	3.907
2100	13.773	37.151	26.272	22.431	77.568	34.316	3.471
2200	13.738	38.768	26.625	23.796	77.349	32.193	3.075
2300	13.688	40.400	26.966	25.171	77.128	30.076	2.715
2400	13.624	42.047	27.295	26.556	76.905	27.965	2.395
2500	13.547	43.709	27.612	27.951	76.680	25.859	2.083
2600	13.458	45.386	27.917	29.356	76.453	23.757	1.805
2700	13.358	47.078	28.211	30.771	76.225	21.659	1.549
2800	13.248	48.785	28.495	32.196	75.995	19.566	1.312
2900	13.128	50.507	28.768	33.631	75.762	17.479	1.092
3000	12.998	52.244	29.030	35.076	75.526	15.396	0.887
3100	12.859	54.000	29.282	36.531	75.288	13.316	0.697
3200	12.712	55.768	29.525	37.996	75.048	11.241	0.520
3300	12.558	57.547	29.758	39.471	74.805	9.171	0.357
3400	12.398	59.336	29.981	40.956	74.559	7.106	0.205
3500	12.233	61.136	30.195	42.451	74.311	5.045	0.064
3600	12.063	62.947	30.399	43.956	74.061	2.989	0.000
3700	11.888	64.768	30.594	45.471	73.808	0.936	-0.134
3800	11.709	66.599	30.780	46.996	73.552	-1.116	-0.266
3900	11.525	68.440	30.957	48.531	73.294	-3.161	-0.394
4000	11.337	70.291	31.125	50.076	73.033	-5.206	-0.516
4100	11.145	72.152	31.284	51.631	72.769	-7.251	-0.631
4200	10.949	74.023	31.434	53.196	72.502	-9.296	-0.741
4300	10.749	75.904	31.576	54.771	72.232	-11.341	-0.846
4400	10.545	77.795	31.711	56.356	71.959	-13.386	-0.946
4500	10.337	79.696	31.838	57.951	71.683	-15.431	-1.041
4600	10.125	81.607	31.958	59.556	71.405	-17.476	-1.136
4700	9.909	83.528	32.075	61.171	71.125	-19.521	-1.226
4800	9.689	85.459	32.184	62.796	70.842	-21.566	-1.311
4900	9.464	87.399	32.284	64.431	70.557	-23.611	-1.391
5000	9.235	89.349	32.376	66.076	70.270	-25.656	-1.466

TITANIUM NITRIDE (TiN)

(CRYSTAL)

GFW = 61.9067

NTi

$\Delta H_f^\circ = -79.8 \pm 1 \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = -80.7 \pm 1 \text{ kcal/mol}$
 $\Delta H_m^\circ = [16] \text{ kcal/mol}$

$S^\circ_{298.15} = 7.23 \pm 0.05 \text{ gibbs/mol}$
 $T_m = 3220 \pm 50^\circ \text{K}$

Heat of Formation

Humphrey (1) and Neumann et al. (2) determined the heat of combustion of titanium nitride by burning the material in an oxygen bomb calorimeter. For reaction (a) Humphrey obtained $\Delta H_{298}^\circ = -145.05 \pm 0.14 \text{ kcal/mol}$ and Neumann et al. $\Delta H_{298}^\circ = -145.0 \text{ kcal/mol}$. From an examination of the combustion products Humphrey reported that the TiO_2 was 95 per cent rutile and <5 per cent anatase, but made no correction for the anatase. The adopted $\Delta H_{298}^\circ = -80.7 \text{ kcal/mol}$ is the average of three values, two from Humphrey (-80.75, -80.61), one as reported and one corrected for anatase, and one from Neumann et al. (-80.8). The uncertainty in the adopted heat is due mainly to the uncertainty in the heat of formation of rutile. Hoch et al. (3) determined the vapor pressure of reaction (b), in the temperature range 1987-2241°K, using a Knudsen effusion method. Third law analysis of the data yields a $\Delta H_{298}^\circ = -79.5 \pm 9 \text{ kcal/mol}$. Linevsky (4) obtained the titanium partial pressures of reaction (c) (2088-2141°K) at fixed nitrogen pressures using atomic absorption spectroscopy. Third law analysis of the data gives a $\Delta H_{298}^\circ = -81 \pm 10 \text{ kcal/mol}$. These equilibrium measurements were not considered in deriving the heat of formation due to their large uncertainties in comparison to the calorimetric data.

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52-296°K) of Shomate (5). Naylor (6) measured high temperature heat contents (388-1738°K). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. Above 1738°K the heat capacity is graphically extrapolated. The entropy is based on $S^\circ_{50} - S^\circ_0 = 0.138 \text{ eu}$.

Melting Data

See liquid table.

Reference	Method	Reaction	T°K	$\Delta H_{298}^\circ \text{ kcal/mol}$	Drift eu	$\Delta H_f^\circ \text{ kcal/mol}$
1	Calorimeter	(a) $\text{TiN(c)} + \text{O}_2(\text{g}) \rightarrow \text{TiO}_2(\text{rutile}) + 1/2\text{N}_2(\text{g})$	298	-145.05±.14		-80.75
1	Calorimeter	(a) $\text{TiN(c)} + \text{O}_2(\text{g}) \rightarrow \text{TiO}_2(\text{rutile}) + 1/2\text{N}_2(\text{g})$	298	-145.05±.14		-80.61*
2	Calorimeter	(a) $\text{TiN(c)} + \text{O}_2(\text{g}) \rightarrow \text{TiO}_2(\text{rutile}) + 1/2\text{N}_2(\text{g})$	298	-145.0		-80.80
3	Equilibrium	(b) $\text{TiN(c)} \rightarrow \text{Ti(g)} + 1/2\text{N}_2(\text{g})$	1987-2241	212±9	192.5	-79.5
4	Equilibrium	(c) $\text{TiN(c)} \rightarrow \text{Ti(g)} + 1/2\text{N}_2(\text{g})$	2088-2141	230±17	194.2	-81.2

*Assumes that the product TiO_2 is 95 per cent rutile and 5 per cent anatase.

References

- G. L. Humphrey, J. Am. Chem. Soc. **73**, 2261 (1951).
- B. Neumann, C. Kroger and H. Kunz, Z. Anorg. Allgem. Chem. **218**, 379-401 (1934).
- M. Hoch, D. P. Dingley and H. L. Johnston, J. Am. Chem. Soc. **77**, 304-6 (1955).
- M. J. Linevsky, General Electric Co., AFML-TR-64-420, February 1965.
- C. H. Shomate, J. Am. Chem. Soc. **68**, 310 (1946).
- B. F. Naylor, J. Am. Chem. Soc. **68**, 370 (1946).

NTi

(Liquid) GFW = 61.9067

TITANIUM NITRIDE (TiN) (LIQUID)

GFW = 61.9067

 $S_{298.15}^{\circ} = [12.603] \text{ gibbs/mol}$ $\Delta H_{298.15}^{\circ} = [-63.531 \pm 1] \text{ kcal/mol}$ $\Delta H_m^{\circ} = [16] \text{ kcal/mol}$ $T_m = 3220 \pm 50^{\circ}\text{K}$

Heat of Formation

The heat of formation is obtained from $\Delta H_{298}^{\circ}(\text{c})$ by adding ΔH_m° and the difference between ${}^{\circ}T_m$ and ${}^{\circ}T_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2200°K . Below 2200°K the heat capacity is obtained from the heat capacity of the crystal. Above 2200°K it is assumed constant and estimated as 15 gibbs/mol or 7.5 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

T_m is taken from C. Agte and K. Moers, Z. Anorg. Allgem. Chem. 198, 233-43 (1931). ΔH_m° is derived from an estimated $\Delta S_m = 2.5 \text{ gibbs/g-atom}$ as suggested by O. Kubaschewski, E. L. Evans and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon Press, New York, 1967.

T, °K	C_p°	S°	$-(C_p^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
298	P. 462	12.603	12.603	.000	- 63.531	- 58.261	42.721
300	8.900	12.658	12.603	.016	- 63.532	- 58.249	42.434
400	15.471	15.456	12.974	.993	- 63.552	- 56.465	36.662
500	11.247	17.666	13.719	2.063	- 63.459	- 54.737	23.795
600	11.445	19.674	14.952	3.229	- 63.306	- 53.010	19.309
700	11.698	21.788	15.493	4.407	- 63.178	- 51.304	16.018
800	12.098	23.390	16.382	5.606	- 63.060	- 49.616	13.554
900	12.281	24.426	17.242	6.825	- 62.956	- 47.941	11.642
1000	12.463	25.129	18.067	8.063	- 62.870	- 46.279	10.114
1100	12.648	25.732	18.855	9.318	- 62.797	- 44.622	8.666
1200	12.839	26.434	19.607	10.592	- 63.676	- 42.935	7.819
1300	13.035	27.470	20.327	11.886	- 63.501	- 41.214	6.929
1400	13.237	30.443	21.015	13.200	- 63.327	- 39.507	6.167
1500	13.443	31.363	21.674	14.534	- 63.153	- 37.811	5.509
1600	13.654	32.238	22.307	15.886	- 62.979	- 36.126	4.935
1700	13.867	33.072	22.916	17.264	- 62.808	- 34.454	4.429
1800	14.084	33.871	23.503	18.662	- 62.640	- 32.791	3.981
1900	14.304	34.638	24.069	20.081	- 62.474	- 31.137	3.582
2000	14.526	35.377	24.616	21.523	- 62.309	- 29.493	3.206
2100	14.749	36.091	25.145	22.987	- 62.145	- 27.871	2.859
2200	15.000	36.783	25.659	24.473	- 62.373	- 25.614	2.545
2300	15.000	37.450	26.157	25.973	- 66.158	- 23.767	2.258
2400	15.000	38.088	26.641	27.493	- 65.943	- 21.927	1.997
2500	15.000	38.700	27.111	28.973	- 65.731	- 20.098	1.757
2600	15.000	39.289	27.568	30.473	- 65.519	- 18.277	1.536
2700	15.000	39.655	28.013	31.973	- 65.309	- 16.464	1.333
2800	15.000	40.000	28.446	33.473	- 65.099	- 14.659	1.144
2900	15.000	40.427	28.867	34.973	- 64.890	- 12.859	.969
3000	15.000	41.435	29.277	36.473	- 64.683	- 11.066	.806
3100	15.000	41.927	29.678	37.973	- 64.476	- 9.285	.655
3200	15.000	42.403	30.068	39.473	- 64.270	- 7.510	.513
3300	15.000	42.865	30.449	40.973	- 64.065	- 5.738	.380
3400	15.000	43.313	30.821	42.473	- 63.860	- 3.972	.255
3500	15.000	43.747	31.184	43.973	- 63.656	- 2.216	.138
3600	15.000	44.170	31.539	45.473	- 63.453	- .400	.012
3700	15.000	44.581	31.886	46.973	- 63.250	- 1.414	
3800	15.000	44.981	32.225	48.473	- 63.047	- 2.428	
3900	15.000	45.371	32.557	49.973	- 62.844	- 3.442	
4000	15.000	45.750	32.882	51.473	- 62.641	- 4.456	
4100	15.000	46.121	33.201	52.973	- 62.438	- 5.470	
4200	15.000	46.482	33.512	54.473	- 62.235	- 6.484	
4300	15.000	46.835	33.818	55.973	- 62.032	- 7.498	
4400	15.000	47.180	34.119	57.473	- 61.829	- 8.512	
4500	15.000	47.517	34.412	58.973	- 61.626	- 9.526	

Dec. 30, 1960; June 30, 1968

Monozirconium Mononitride (ZrN)
(Crystal) Mol. Wt. = 105.228

INTERIM TABLE

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	$-(F^\circ - H_{298}^\circ)/T$	H° - H ₂₉₈ [°] kcal. mole ⁻¹	ΔH _f [°]	ΔF _f [°]	Log K _p
0	.000	INFINITE	1.575	-	86.522	-	INFINITE
100	3.716	1.944	1.480	-	86.522	-	105.526
200	9.470	9.288	1.000	-	86.522	-	185.526
298	9.470	9.288	1.000	-	86.522	-	50.583
300	9.493	9.348	1.018	-	87.300	-	58.589
400	10.697	12.265	1.041	-	87.260	-	42.693
500	11.259	14.740	1.055	-	87.161	-	33.162
600	11.630	16.826	1.137	-	87.096	-	26.913
700	11.925	18.642	1.262	-	87.007	-	22.284
800	12.175	20.251	1.362	-	86.911	-	18.690
900	12.400	21.698	1.432	-	86.807	-	16.254
1000	12.604	23.015	1.485	-	86.697	-	14.147
1100	12.806	24.226	1.526	-	86.590	-	12.426
1200	12.997	25.349	1.563	-	86.439	-	10.984
1300	13.182	26.396	1.596	-	87.309	-	9.760
1400	13.364	27.360	1.626	-	87.174	-	8.713
1500	13.544	28.308	1.653	-	87.032	-	7.806
1600	13.721	29.188	1.673	-	86.881	-	7.014
1700	13.896	30.025	1.688	-	86.725	-	6.317
1800	14.071	30.824	1.698	-	86.560	-	5.698
1900	14.244	31.590	1.703	-	86.387	-	5.145
2000	14.417	32.325	1.703	-	86.207	-	4.649
2100	14.573	33.032	1.703	-	86.018	-	4.201
2200	14.760	33.714	1.703	-	85.724	-	3.778
2300	14.931	34.374	1.703	-	85.424	-	3.367
2400	15.102	35.013	1.703	-	85.119	-	2.969
2500	15.272	35.633	1.703	-	84.809	-	2.584
2600	15.443	36.236	1.703	-	84.494	-	2.212
2700	15.612	36.822	1.703	-	84.174	-	1.851
2800	15.782	37.392	1.703	-	83.849	-	1.500
2900	15.952	37.949	1.703	-	83.519	-	1.158
3000	16.121	38.493	1.703	-	83.184	-	0.825
3100	16.290	39.024	1.703	-	82.844	-	0.498
3200	16.459	39.544	1.703	-	82.499	-	0.171
3300	16.628	40.053	1.703	-	82.149	-	-0.156
3400	16.797	40.552	1.703	-	81.794	-	-0.483
3500	16.966	41.041	1.703	-	81.434	-	-0.810
3600	17.135	41.522	1.703	-	81.069	-	-1.137
3700	17.303	41.993	1.703	-	80.699	-	-1.464
3800	17.472	42.457	1.703	-	80.324	-	-1.791
3900	17.641	42.913	1.703	-	79.944	-	-2.118
4000	17.809	43.362	1.703	-	79.559	-	-2.445
4100	17.978	43.804	1.703	-	79.169	-	-2.772
4200	18.146	44.239	1.703	-	78.774	-	-3.099
4300	18.315	44.668	1.703	-	78.374	-	-3.426
4400	18.483	45.091	1.703	-	77.969	-	-3.753
4500	18.652	45.508	1.703	-	77.559	-	-4.080
4600	18.820	45.920	1.703	-	77.144	-	-4.407
4700	18.988	46.326	1.703	-	76.724	-	-4.734
4800	19.157	46.724	1.703	-	76.299	-	-5.061
4900	19.325	47.110	1.703	-	75.869	-	-5.388
5000	19.493	47.517	1.703	-	75.434	-	-5.715

June 30, 1961

NZr

MONOZIRCONIUM MONONITRIDE (ZrN) (Crystal)

Mol. Wt. = 105.228

$\Delta H_f^\circ = -86.5 \pm 2$ kcal. mole⁻¹

ΔH_f° 298.15 = -87.3 ± 2 kcal. mole⁻¹

$\eta_m = [3225^\circ K]$

$S_{298.15}^\circ = 9.29 \pm 0.05$ cal. deg.⁻¹ mole⁻¹

$\Delta H_m^\circ = [16.1]$ kcal. mole⁻¹

Heat of Formation. The heat of reaction I, -174.25 ± 0.30 kcal. mole⁻¹, was measured by A. D. Mah and N. L. Gelbert. The ΔH_f° 298.15 of ZrN was obtained using -261.5 ± 0.2 kcal. mole⁻¹ for ΔH_f° 298.15 of ZrO₂. For the same reaction B. Neumann, C. Kroger and H. Kunz, Z. anorg. Chem. 218, 379 (1934) obtain -176.0 kcal. mole⁻¹ on a sample of unspecified purity. Vapor pressure measurements of M. Hoch, D. P. Dingley and H. L. Johnston, J. Am. Chem. Soc. 77, 304 (1955) lead to -81 kcal. mole⁻¹ for the ΔH_f° 298.15 of ZrN. However, this value is uncertain by 10% as evidenced by the work on ZrO₂ by W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 26, 1207 (1957).

(I) $ZrN(c) + O_2(g) = ZrO_2(c) + 1/2 N_2(g)$

Heat Capacity and Entropy. Low temperature measurements, 53-297°K, of S. S. Todd, J. Am. Chem. Soc. 72, 2914 (1950), were smoothly joined to those of J. P. Coughlin and E. G. King, J. Am. Chem. Soc. 72, 2262 (1950), 298-1073°K.

Melting. Estimated by C. B. Henderson and R. S. Scheffer, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

NZr

Monozirconium Mononitride (ZrN)
(Liquid) Mol. Wt. = 105.228

INTERIM TABLE

T, °K.	C _p	S°	$\int_{T_0}^T C_p \frac{dT}{T}$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _f
0							
100	9.666	14.899	14.899	-0.000	-69.489	-64.332	47.155
200	9.693	14.959	14.959	-0.016	-69.489	-64.300	46.880
300	10.697	17.906	17.906	-1.045	-69.445	-62.576	34.188
400	11.252	20.356	20.356	-2.144	-69.369	-60.867	26.604
500	11.630	22.888	22.888	-3.289	-69.293	-59.174	21.550
600	11.925	25.259	25.259	-4.487	-69.194	-57.484	17.950
700	12.175	27.468	27.468	-5.732	-69.098	-55.832	15.252
800	12.400	29.544	29.544	-7.022	-68.994	-54.179	13.156
900	12.608	31.500	31.500	-8.353	-68.884	-52.539	11.482
1000	12.804	33.344	33.344	-9.722	-68.777	-50.910	10.116
1100	12.987	35.086	35.086	-11.133	-68.666	-49.243	9.048
1200	13.162	36.734	36.734	-12.582	-68.550	-47.550	7.993
1300	13.334	38.298	38.298	-14.069	-68.431	-45.868	7.160
1400	13.504	39.786	39.786	-15.592	-68.304	-44.194	6.439
1500	13.671	41.200	41.200	-17.150	-68.168	-42.528	5.809
1600	13.834	42.544	42.544	-18.742	-68.027	-40.870	5.263
1700	14.000	43.822	43.822	-20.368	-67.884	-39.231	4.763
1800	14.171	45.034	45.034	-22.028	-67.740	-37.595	4.324
1900	14.344	46.186	46.186	-23.722	-67.594	-35.970	3.930
2000	14.517	47.286	47.286	-25.450	-67.446	-34.354	3.575
2100	14.683	48.334	48.334	-27.212	-67.296	-32.742	3.252
2200	14.850	49.334	49.334	-29.008	-67.144	-31.134	2.952
2300	15.016	50.286	50.286	-30.838	-66.990	-29.530	2.675
2400	15.181	51.194	51.194	-32.702	-66.834	-27.921	2.433
2500	15.344	52.054	52.054	-34.600	-66.676	-26.309	2.236
2600	15.506	52.866	52.866	-36.532	-66.516	-24.691	2.075
2700	15.666	53.634	53.634	-38.500	-66.354	-23.068	1.946
2800	15.825	54.354	54.354	-40.504	-66.190	-21.442	1.841
2900	15.981	55.022	55.022	-42.544	-66.024	-19.812	1.755
3000	16.136	55.644	55.644	-44.620	-65.856	-18.178	1.688
3100	16.289	56.216	56.216	-46.732	-65.686	-16.540	1.633
3200	16.440	56.744	56.744	-48.880	-65.514	-14.898	1.588
3300	16.589	57.222	57.222	-51.064	-65.340	-13.252	1.553
3400	16.736	57.654	57.654	-53.284	-65.164	-11.602	1.527
3500	16.881	58.044	58.044	-55.540	-64.986	-9.946	1.500
3600	17.024	58.394	58.394	-57.832	-64.806	-8.284	1.473
3700	17.166	58.704	58.704	-60.160	-64.624	-6.616	1.444
3800	17.306	59.000	59.000	-62.524	-64.440	-4.944	1.414
3900	17.444	59.286	59.286	-64.924	-64.254	-3.268	1.383
4000	17.581	59.566	59.566	-67.360	-64.066	-1.588	1.351
4100	17.716	59.844	59.844	-69.832	-63.876	0.096	1.318
4200	17.850	60.116	60.116	-72.340	-63.684	1.772	1.283
4300	17.981	60.386	60.386	-74.884	-63.490	3.444	1.247
4400	18.111	60.654	60.654	-77.464	-63.294	5.111	1.210
4500	18.240	60.916	60.916	-80.080	-63.096	6.772	1.172
4600	18.366	61.174	61.174	-82.732	-62.896	8.428	1.133
4700	18.491	61.426	61.426	-85.420	-62.694	10.078	1.093
4800	18.614	61.674	61.674	-88.144	-62.490	11.722	1.053
4900	18.736	61.916	61.916	-90.904	-62.284	13.360	1.012
5000	18.856	62.154	62.154	-93.700	-62.076	14.992	0.970
5100	18.974	62.386	62.386	-96.532	-61.866	16.618	0.927
5200	19.091	62.614	62.614	-99.400	-61.654	18.238	0.883
5300	19.206	62.836	62.836	-102.304	-61.440	19.852	0.838
5400	19.319	63.054	63.054	-105.244	-61.224	21.460	0.792
5500	19.431	63.266	63.266	-108.220	-61.006	23.062	0.745
5600	19.541	63.474	63.474	-111.232	-60.790	24.658	0.697
5700	19.649	63.676	63.676	-114.280	-60.572	26.248	0.648
5800	19.756	63.874	63.874	-117.364	-60.354	27.832	0.598
5900	19.861	64.066	64.066	-120.484	-60.134	29.410	0.547
6000	19.964	64.254	64.254	-123.640	-59.912	30.982	0.495

June 30, 1961

Monozirconium Mononitride (ZrN)

(Ideal Gas) Mol. Wt. = 105.228

T, °K.	C _p ^o	S ^o - (R°-H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	4.000	INFINITE	-	2.118	169.418	169.418	INFINITE
100	6.959	47.924	-	1.423	169.770	166.877	- 364.691
200	7.141	52.851	-	0.721	170.121	165.849	- 179.037
298	7.567	55.780	-	0.000	170.500	165.468	- 119.820
300	7.575	55.827	-	0.014	170.497	163.425	- 119.049
400	7.965	58.062	-	0.792	170.291	161.098	- 88.016
500	8.243	59.871	-	1.603	170.080	158.824	- 69.419
600	8.434	61.392	-	2.438	169.854	156.594	- 57.037
700	8.564	62.635	-	3.299	169.624	154.403	- 46.464
800	8.664	63.653	-	4.150	169.368	152.246	- 41.590
900	8.736	64.478	-	5.020	169.114	150.122	- 36.453
1000	8.791	65.002	-	5.897	168.849	148.026	- 32.350
1100	8.835	66.642	-	6.778	168.566	145.956	- 28.997
1200	8.868	68.123	-	7.662	168.262	143.922	- 26.242
1300	8.901	69.123	-	8.552	167.922	141.927	- 23.876
1400	8.926	69.784	-	9.443	167.551	140.115	- 21.872
1500	8.948	69.400	-	10.337	167.152	138.226	- 20.138
1600	8.968	69.978	-	11.233	166.729	136.259	- 18.625
1700	8.985	70.519	-	12.130	166.280	134.210	- 17.305
1800	9.001	71.027	-	13.030	165.804	132.080	- 16.109
1900	9.016	71.524	-	13.931	165.300	129.870	- 15.053
2000	9.029	71.986	-	14.833	164.774	127.587	- 14.104
2100	9.042	72.427	-	15.736	164.234	125.232	- 13.248
2200	9.054	72.849	-	16.640	163.679	122.800	- 12.479
2300	9.065	73.251	-	17.547	163.109	120.300	- 11.801
2400	9.076	73.637	-	18.454	162.524	117.733	- 11.173
2500	9.087	74.008	-	19.362	161.924	115.100	- 10.597
2600	9.097	74.364	-	20.271	161.309	112.416	- 10.067
2700	9.107	74.705	-	21.180	160.679	109.672	- 9.579
2800	9.116	75.039	-	22.093	160.034	106.878	- 9.123
2900	9.125	75.359	-	23.003	159.374	104.034	- 8.701
3000	9.135	75.669	-	23.918	158.698	101.148	- 8.309
3100	9.143	75.968	-	24.832	158.004	98.218	- 7.942
3200	9.151	76.259	-	25.745	157.294	95.242	- 7.600
3300	9.159	76.541	-	26.658	156.569	92.220	- 7.279
3400	9.170	76.814	-	27.579	155.829	89.152	- 6.977
3500	9.178	77.080	-	28.496	155.074	86.048	- 6.694
3600	9.186	77.339	-	29.414	154.304	82.908	- 6.427
3700	9.193	77.591	-	30.333	153.519	79.732	- 6.175
3800	9.200	77.836	-	31.252	152.719	76.522	- 5.936
3900	9.211	78.075	-	32.174	151.904	73.278	- 5.711
4000	9.219	78.308	-	33.094	151.074	70.008	- 5.497
4100	9.227	78.536	-	34.018	150.229	66.722	- 5.295
4200	9.234	78.759	-	34.943	149.369	63.422	- 5.105
4300	9.243	78.976	-	35.868	148.494	60.108	- 4.926
4400	9.251	79.188	-	36.789	147.604	56.782	- 4.744
4500	9.259	79.396	-	37.715	146.699	53.446	- 4.578
4600	9.266	79.600	-	38.641	145.780	50.100	- 4.420
4700	9.274	79.799	-	39.568	144.846	46.744	- 4.268
4800	9.282	79.994	-	40.494	143.898	43.378	- 4.130
4900	9.290	80.186	-	41.426	142.936	40.002	- 4.000
5000	9.297	80.374	-	42.354	141.959	36.616	- 3.878
5100	9.305	80.558	-	43.284	140.968	33.220	- 3.764
5200	9.313	80.739	-	44.215	140.000	29.814	- 3.656
5300	9.320	80.919	-	45.146	139.054	26.398	- 3.552
5400	9.328	81.091	-	46.079	138.130	22.972	- 3.454
5500	9.335	81.262	-	47.012	137.224	19.536	- 3.362
5600	9.343	81.430	-	47.946	136.334	16.090	- 3.274
5700	9.350	81.596	-	48.880	135.459	12.634	- 3.190
5800	9.358	81.758	-	49.810	134.598	9.168	- 3.114
5900	9.365	81.918	-	50.752	133.750	5.692	- 3.044
6000	9.373	82.076	-	51.689	132.914	2.206	- 2.978

June 30, 1963

NZr

MOL. WT. = 105.228

(IDEAL GAS)

MONOZIRCONIUM MONONITRIDE (ZrN)

Ground State Configuration [Σ]
 $\Delta H_f^o = [169.4] \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = [55.78] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o \text{ 298.15} = [170.5] \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$\frac{E_e}{\text{cm.}^{-1}}$	$\frac{g_e}{[2]}$
0	[2]
$\omega_e^x = [5] \text{ cm.}^{-1}$	
$\omega_e = [640] \text{ cm.}^{-1}$	
$\nu_e = [0.4146] \text{ cm.}^{-1}$	
$\sigma_e = [0.0025] \text{ cm.}^{-1}$	
$r_e = [1.83] \text{ \AA}$	

Heat of Formation

ΔH_f^o was estimated as 170.7 kcal. mole⁻¹ by J. S. Gordon, AstroSystems International, Livingston, New Jersey, private communication, January 10, 1963. $\Delta H_f^o \text{ 298.15}$ was then calculated.

Heat Capacity and Entropy

Molecular constants were estimated by J. S. Gordon, loc. cit. r_e was calculated from the relationship $r_e = (16.858778 / \mu^{1/2} B_e)^{1/2} \text{ \AA}$.

NZr

Nitrogen, Diatomic (N₂)
(Reference State - Ideal Gas) Mol. Wt. = 28.0134

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	38.170	51.957	2.072	∞.000	∞.000	∞.000	∞.000
200	6.956	42.992	1.379	∞.000	∞.000	∞.000	∞.000
298	6.957	46.407	.683	∞.000	∞.000	∞.000	∞.000
300	6.961	45.776	.013	∞.000	∞.000	∞.000	∞.000
400	6.961	45.813	∞.000	∞.000	∞.000	∞.000	∞.000
500	6.990	47.818	46.043	.710	∞.000	∞.000	∞.000
600	7.069	49.386	46.561	1.413	∞.000	∞.000	∞.000
700	7.196	50.685	47.163	2.125	∞.000	∞.000	∞.000
800	7.350	51.806	47.731	2.853	∞.000	∞.000	∞.000
900	7.512	52.798	48.303	3.596	∞.000	∞.000	∞.000
1000	7.670	53.692	48.853	4.355	∞.000	∞.000	∞.000
1100	7.815	54.507	49.378	5.129	∞.000	∞.000	∞.000
1200	7.945	55.258	49.870	5.917	∞.000	∞.000	∞.000
1300	8.061	55.955	50.337	6.718	∞.000	∞.000	∞.000
1400	8.162	56.604	50.813	7.529	∞.000	∞.000	∞.000
1500	8.252	57.212	51.248	8.350	∞.000	∞.000	∞.000
1600	8.330	57.784	51.665	9.179	∞.000	∞.000	∞.000
1700	8.398	58.324	52.065	10.015	∞.000	∞.000	∞.000
1800	8.458	58.835	52.448	10.858	∞.000	∞.000	∞.000
1900	8.512	59.320	52.816	11.707	∞.000	∞.000	∞.000
2000	8.559	59.782	53.171	12.560	∞.000	∞.000	∞.000
2100	8.601	60.222	53.513	13.418	∞.000	∞.000	∞.000
2200	8.638	60.642	53.842	14.280	∞.000	∞.000	∞.000
2300	8.672	61.045	54.160	15.144	∞.000	∞.000	∞.000
2400	8.703	61.431	54.468	16.015	∞.000	∞.000	∞.000
2500	8.731	61.802	54.766	16.886	∞.000	∞.000	∞.000
2600	8.756	62.159	55.055	17.761	∞.000	∞.000	∞.000
2700	8.778	62.503	55.335	18.638	∞.000	∞.000	∞.000
2800	8.800	62.835	55.606	19.517	∞.000	∞.000	∞.000
2900	8.820	63.155	55.870	20.398	∞.000	∞.000	∞.000
3000	8.838	63.465	56.127	21.280	∞.000	∞.000	∞.000
3100	8.855	63.765	56.376	22.165	∞.000	∞.000	∞.000
3200	8.871	64.055	56.610	23.051	∞.000	∞.000	∞.000
3300	8.886	64.337	56.836	23.930	∞.000	∞.000	∞.000
3400	8.900	64.611	57.087	24.820	∞.000	∞.000	∞.000
3500	8.914	64.877	57.312	25.719	∞.000	∞.000	∞.000
3600	8.927	65.135	57.532	26.611	∞.000	∞.000	∞.000
3700	8.939	65.387	57.747	27.505	∞.000	∞.000	∞.000
3800	8.950	65.632	57.957	28.395	∞.000	∞.000	∞.000
3900	8.962	65.871	58.162	29.295	∞.000	∞.000	∞.000
4000	8.972	66.104	58.362	30.191	∞.000	∞.000	∞.000
4100	8.983	66.331	58.559	31.089	∞.000	∞.000	∞.000
4200	8.993	66.553	58.751	31.988	∞.000	∞.000	∞.000
4300	9.002	66.770	58.940	32.888	∞.000	∞.000	∞.000
4400	9.012	66.982	59.124	33.788	∞.000	∞.000	∞.000
4500	9.021	67.189	59.305	34.690	∞.000	∞.000	∞.000
4600	9.030	67.392	59.482	35.593	∞.000	∞.000	∞.000
4700	9.039	67.591	59.657	36.496	∞.000	∞.000	∞.000
4800	9.048	67.785	59.827	37.400	∞.000	∞.000	∞.000
4900	9.057	67.976	59.995	38.306	∞.000	∞.000	∞.000
5000	9.066	68.162	60.160	39.212	∞.000	∞.000	∞.000
5100	9.074	68.346	60.322	40.119	∞.000	∞.000	∞.000
5200	9.083	68.525	60.481	41.027	∞.000	∞.000	∞.000
5300	9.091	68.702	60.637	41.935	∞.000	∞.000	∞.000
5400	9.100	68.875	60.791	42.845	∞.000	∞.000	∞.000
5500	9.109	69.045	60.942	43.755	∞.000	∞.000	∞.000
5600	9.118	69.213	61.091	44.667	∞.000	∞.000	∞.000
5700	9.127	69.377	61.238	45.579	∞.000	∞.000	∞.000
5800	9.136	69.539	61.382	46.492	∞.000	∞.000	∞.000
5900	9.145	69.698	61.524	47.406	∞.000	∞.000	∞.000
6000	9.155	69.854	61.664	48.321	∞.000	∞.000	∞.000
6100	9.165	70.008	61.802	49.237	∞.000	∞.000	∞.000

Dec. 31, 1950; Mar. 31, 1951; Sept. 30, 1965

NITROGEN, DIATOMIC (N₂) (IDEAL GAS - REFERENCE STATE) MOL. WT. = 28.0134

Ground State Configuration $1 \Sigma^+ g$
 $S_{298.15}^o = 45.77 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = 0$
 $\Delta H_f^o_{298.15} = 0$

$\omega_e x_e = 2557.55 \text{ cm.}^{-1}$
 $\omega_e = 1.9825 \text{ cm.}^{-1}$
 $B_e = 0.01791 \pm 0.0001 \text{ cm.}^{-1}$
 $\sigma^- = 2$
 $r_e = 1.08758 \pm 0.0001 \text{ \AA}$

Heat of Formation.
 The heat of formation (ΔH_f^o) for N_{2(g)} is zero at all temperatures by definition.

Heat Capacity and Entropy.

The functions adopted here are based on the direct summation calculations of L. Glatte, J. Belzer and H. L. Johnston, Ohio State Univ. Res. Found. Proj. 316, Report No. 9, 1953. They calculated the functions for N₂ by a direct summation using spectroscopic data given by O. Herzberg, "Diatomic Molecules", D. Van Nostrand Co., New York, 1950. The entropies were changed by -R ln 9 to remove the effects of nuclear spin included by Glatte, Belzer, and Johnston, and by 0.012 for the difference in spectroscopic constants. J. A. Goff and S. Oretch, Trans. Am. Soc. Mech. Engrs., 72, 741 (1950), calculated a set of functions by a direct summation over the ground state levels only. Agreement with the functions of Glatte, Belzer, and Johnston is within 0.1%.

B. P. Stoicheff, Can. J. Phys. 32, 630 (1954), determined the spectroscopic constants of N₂ by combining his measured rotational spectra with the results of band spectra given in the literature. The constants listed above have been corrected to apply to the naturally occurring isotopic composition listed by D. Strominger, J. M. Hollander and O. T. Seaborg, Rev. Mod. Phys., 30, 565 (1956).

Dinitrogen Monoxide (N₂O)

(Ideal Gas) Mol. Wt. = 44.016

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	20.430	20.430	INFINITE
100	7.015	43.988	2.260	20.430	21.573	- 47.145
200	7.230	50.924	1.504	20.084	21.815	- 47.353
298	7.290	52.546	0.000	19.610	22.058	- 47.561
300	9.250	52.603	0.017	19.608	22.058	- 47.561
400	10.201	55.400	2.892	19.530	22.716	- 48.159
500	10.953	57.761	5.659	19.520	28.514	- 48.463
600	11.565	59.813	8.360	19.458	30.311	- 48.597
700	12.070	61.635	10.821	19.423	32.097	- 48.681
800	12.486	63.275	13.089	19.410	33.873	- 48.723
900	12.830	64.766	15.149	19.410	35.638	- 48.735
1000	13.113	66.133	17.000	19.420	37.391	- 48.717
1100	13.348	67.394	18.676	20.036	39.132	- 48.664
1200	13.544	68.565	20.187	20.156	40.863	- 48.580
1300	13.707	69.655	21.564	20.279	42.583	- 48.466
1400	13.845	70.676	22.820	20.404	44.293	- 48.323
1500	13.961	71.635	23.958	20.530	45.996	- 48.160
1600	14.060	72.540	24.987	20.657	47.691	- 47.977
1700	14.145	73.395	25.904	20.783	49.377	- 47.773
1800	14.218	74.205	26.714	20.908	51.054	- 47.550
1900	14.282	74.976	27.413	21.032	52.728	- 47.308
2000	14.337	75.710	28.098	21.155	54.392	- 47.047
2100	14.385	76.411	28.764	21.277	56.049	- 46.767
2200	14.428	77.081	29.415	21.396	57.703	- 46.468
2300	14.466	77.723	30.050	21.513	59.350	- 46.151
2400	14.499	78.339	30.672	21.630	60.993	- 45.818
2500	14.529	78.932	31.282	21.742	62.630	- 45.470
2600	14.556	79.502	31.877	21.853	64.262	- 45.108
2700	14.580	80.052	32.457	21.963	65.889	- 44.733
2800	14.602	80.583	33.023	22.069	67.517	- 44.346
2900	14.621	81.095	33.576	22.174	69.140	- 43.947
3000	14.639	81.591	34.116	22.275	70.757	- 43.535
3100	14.655	82.072	34.646	22.376	72.371	- 43.110
3200	14.670	82.537	35.166	22.475	73.981	- 42.673
3300	14.684	82.989	35.676	22.568	75.591	- 42.225
3400	14.696	83.427	36.176	22.661	77.197	- 41.767
3500	14.707	83.853	36.666	22.752	78.797	- 41.300
3600	14.718	84.268	37.146	22.841	80.390	- 40.823
3700	14.727	84.671	37.616	22.928	81.979	- 40.336
3800	14.736	85.064	38.076	23.013	83.561	- 39.839
3900	14.745	85.447	38.526	23.097	85.143	- 39.332
4000	14.752	85.820	38.966	23.177	86.724	- 38.816
4100	14.760	86.185	39.396	23.253	88.300	- 38.291
4200	14.766	86.541	39.816	23.324	89.871	- 37.757
4300	14.772	86.888	40.226	23.394	91.437	- 37.213
4400	14.778	87.228	40.626	23.461	92.997	- 36.660
4500	14.784	87.560	41.016	23.528	94.550	- 36.100
4600	14.789	87.885	41.396	23.594	96.097	- 35.533
4700	14.794	88.203	41.766	23.660	97.639	- 34.958
4800	14.798	88.515	42.126	23.726	99.176	- 34.373
4900	14.802	88.820	42.481	23.791	100.709	- 33.779
5000	14.806	89.119	42.830	23.856	102.237	- 33.176
5100	14.810	89.412	43.172	23.920	103.760	- 32.564
5200	14.814	89.700	43.506	23.984	105.279	- 31.943
5300	14.817	89.982	43.833	24.047	106.793	- 31.314
5400	14.820	90.259	44.154	24.110	108.303	- 30.677
5500	14.823	90.531	44.470	24.173	109.808	- 30.032
5600	14.826	90.798	44.781	24.236	111.308	- 29.379
5700	14.829	91.060	45.087	24.299	112.803	- 28.717
5800	14.831	91.318	45.388	24.362	114.293	- 28.047
5900	14.834	91.577	45.684	24.425	115.778	- 27.369
6000	14.836	91.821	45.976	24.488	117.258	- 26.683

Dec. 31, 1960; Dec. 31, 1964

DINITROGEN MONOXIDE (N₂O)

(IDEAL GAS)

MOL. WT. = 44.016

Point Group C_{∞v}

S_{298.15}^o = 52.55 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH_f^o 0 = 20.43 ± 0.1 kcal. mole⁻¹
ΔH_f^o 298.15 = 19.61 ± 0.1 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

W₂, cm.⁻¹

1276.5 (1)

589.2 (2)

2223.7 (1)

N-O = 1.1842 Å

Bond Angle: N-N-O = 180°

P_e = 0.42109 cm.⁻¹

Heat of Formation

An analysis of the heat of reaction data is summarized below. Carlton-Sutton, et al., studied the direct decomposition at pressures of 40 to 50 atmospheres and made P-V-T measurements in order to reduce the data. They obtained a similar but less certain heat of formation by combustion of N₂O in CO. Flame calorimetric measurements of the combustion by Ambler and Griffiths are in good agreement, but the bomb calorimetry of Penning and Cotton gives a heat of formation about 0.2 kcal. larger. The selected heat of formation is a weighted average of these values.

Source	Method	Reaction	ΔH _f ^o (kcal. mole ⁻¹)
1	Bomb Calorimetry	N ₂ O(g) → N ₂ (g) + 0.5 O ₂ (g)	-19.52 ± 0.10
1	Bomb Calorimetry	N ₂ O(g) + CO(g) → CO ₂ (g) + N ₂ (g)	-87.10 ± 0.30
2	Flame Calorimetry	N ₂ O(g) + CO(g) → CO ₂ (g) + N ₂ (g)	-87.09 ± 0.22
3	Bomb Calorimetry	N ₂ O(g) + CO(g) → CO ₂ (g) + N ₂ (g)	-87.37 ± 0.12
3	Bomb Calorimetry	N ₂ O(g) + H ₂ (g) → H ₂ O(l) + N ₂ (g)	-88.03 ± 0.12

*Based on ΔH_f^o 298.15 = -68.32 (H₂O, l), -94.054 (CO₂, g), -26.417 (CO, g)

- 1) T. Carlton-Sutton, H. R. Ambler, G. W. Williams, Proc. Phys. Soc. (London) **48**, 189 (1936).
- 2) J. H. Ambler, E. Griffiths, Proc. Roy. Soc. (London) **A141**, 17 (1933).
- 3) R. W. Penning, F. T. Cotton, *ibid.*, **1** (1933).

Heat Capacity and Entropy

The functions are based on the rotational constants of Pilve, J. Mol. Spect. **12**, 360 (1964), and the frequencies determined by Tidwell, Plyler and Benedict, J. Opt. Soc. Am. **50**, 1243 (1960). The bond distances reported by Pilve were obtained from measurements of isotopic shifts in the infrared. They include higher-order corrections for vibration-rotation interaction and are in satisfactory agreement with the infrared and microwave studies of Douglas and Moller, J. Chem. Phys. **22**, 275 (1954) and the electron diffraction data of Schomaker and Spurr, J. Am. Chem. Soc. **61**, 1184 (1942).

N₂O

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	10.347	50.000	2.639	24.641	-	53.850
100	10.403	50.000	1.639	24.617	-	53.850
200	10.468	50.000	1.000	24.615	-	53.850
300	10.518	50.012	0.299	24.608	-	53.837
400	10.553	50.012	1.687	24.601	-	53.837
500	10.581	50.012	3.496	24.594	-	53.837
600	10.621	50.012	5.425	24.585	-	53.837
700	10.693	50.012	7.453	24.575	-	53.837
800	10.749	50.012	9.558	24.565	-	53.837
900	10.801	50.012	11.725	24.554	-	53.837
1000	10.851	50.012	13.961	24.542	-	53.837
1100	10.897	50.012	16.267	24.529	-	53.837
1200	10.940	50.012	18.645	24.515	-	53.837
1300	10.979	50.012	21.096	24.500	-	53.837
1400	11.015	50.012	23.621	24.484	-	53.837
1500	11.048	50.012	26.221	24.467	-	53.837
1600	11.078	50.012	28.896	24.449	-	53.837
1700	11.105	50.012	31.645	24.430	-	53.837
1800	11.129	50.012	34.468	24.410	-	53.837
1900	11.150	50.012	37.365	24.389	-	53.837
2000	11.168	50.012	40.336	24.367	-	53.837
2100	11.183	50.012	43.381	24.344	-	53.837
2200	11.195	50.012	46.499	24.320	-	53.837
2300	11.205	50.012	49.690	24.295	-	53.837
2400	11.212	50.012	52.953	24.269	-	53.837
2500	11.217	50.012	56.288	24.242	-	53.837
2600	11.220	50.012	59.693	24.214	-	53.837
2700	11.221	50.012	63.168	24.185	-	53.837
2800	11.221	50.012	66.713	24.155	-	53.837
2900	11.220	50.012	70.328	24.124	-	53.837
3000	11.218	50.012	74.013	24.092	-	53.837
3100	11.215	50.012	77.768	24.059	-	53.837
3200	11.211	50.012	81.593	24.025	-	53.837
3300	11.206	50.012	85.488	23.990	-	53.837
3400	11.200	50.012	89.453	23.954	-	53.837
3500	11.193	50.012	93.488	23.917	-	53.837
3600	11.185	50.012	97.593	23.879	-	53.837
3700	11.176	50.012	101.768	23.840	-	53.837
3800	11.166	50.012	106.013	23.799	-	53.837
3900	11.155	50.012	110.328	23.757	-	53.837
4000	11.143	50.012	114.713	23.714	-	53.837
4100	11.130	50.012	119.168	23.670	-	53.837
4200	11.116	50.012	123.693	23.625	-	53.837
4300	11.101	50.012	128.288	23.579	-	53.837
4400	11.085	50.012	132.953	23.532	-	53.837
4500	11.068	50.012	137.688	23.484	-	53.837
4600	11.050	50.012	142.493	23.435	-	53.837
4700	11.031	50.012	147.268	23.385	-	53.837
4800	11.011	50.012	152.013	23.334	-	53.837
4900	10.990	50.012	156.728	23.282	-	53.837
5000	10.968	50.012	161.413	23.229	-	53.837
5100	10.945	50.012	166.068	23.175	-	53.837
5200	10.921	50.012	170.693	23.120	-	53.837
5300	10.896	50.012	175.288	23.064	-	53.837
5400	10.870	50.012	179.853	23.007	-	53.837
5500	10.843	50.012	184.388	22.949	-	53.837
5600	10.815	50.012	188.893	22.890	-	53.837
5700	10.786	50.012	193.368	22.830	-	53.837
5800	10.756	50.012	197.813	22.769	-	53.837
5900	10.725	50.012	202.228	22.707	-	53.837
6000	10.693	50.012	206.613	22.644	-	53.837

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1964

Point Group C_{2v}

S°_{298,15} = 73.91 ± 0.5 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies	ω _v , cm. ⁻¹	ω _v , cm. ⁻¹	ω _v , cm. ⁻¹
1863 (1)	783 (1)	313 (1)	
1589 (1)	827 (1)	253 (1)	
1297 (1)	407 (1)		

Bond Distance: N-N = 2.08 Å N-O (nitroso) = 1.12 Å N-O (nitro) = 1.18 Å

Bond Angle: O-N-N (nitroso) = 110° O-N-O = 134°

Product of Moments of Inertia: I_AI_BI_C = 4.6201 X 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation.

Equilibria for the reaction N₂O₃(g) → NO(g) + NO₂(g) have been studied by Beattie and Bell, J. Chem. Soc. 1957, 1681 (1957), Verhoek and Daniels, J. Am. Chem. Soc. 53, 1250 (1931) and Abel and Proiel, Z. Elektrochem. 35, 712 (1939). The results of Beattie and Bell are the most extensive, but they depend on the early analysis of Glaue and Kemp, J. Chem. Phys. 2, 40 (1938), for the simultaneous equilibrium N₂O₄(g) → 2NO₂(g). The JANAF analysis of the tetroxide dissociation has been used to recalculate the data of Beattie and Bell. Non-ideality of N₂O₄ and NO₂ was allowed for by use of the equations of state of Glaue and Kemp, while non-ideality of NO and N₂O₃ was removed by extrapolation of the equilibrium constants to zero pressure in a manner similar to that of Beattie and Bell. The data of Verhoek and Daniels and of Abel and Proiel have not been recalculated. Second and third law analyses of the results are summarized below. The heat of formation was obtained from ΔH°_f 298 = 9.70 kcal. mole⁻¹.

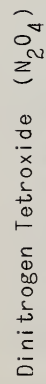
Source	Temp. Range °K	T °K	Third Law ΔS° (cal. deg. ⁻¹ mole ⁻¹)	Second Law ΔH° _f (kcal. mole ⁻¹)	Third Law ΔH° _f 298 (kcal. mole ⁻¹)
Beattie - Bell ^a	278 - 318	298	—	33.25 ± 0.35	9.527 ± 0.096
Beattie - Bell ^b	278 - 318	298	33.77	33.04 ± 0.31	9.476 ± 0.093
Beattie - Bell ^c	278 - 318	298	33.77	33.56 ± 0.52	9.642 ± 0.155
Verhoek - Daniels	298 - 318	308	33.78	—	38.8 ± 11.1
Abel - Proiel	281 - 308	294	33.77	—	32.9 ± 0.6

c) From author's K_p values

Heat Capacity and Entropy.

The functions are similar to those calculated by I. C. Hisatsune, J. Phys. Chem. 65, 2249 (1961), based on the analysis of Devlin and Hisatsune, Spectrochim. Acta 17, 218 (1961), of the Raman and infrared spectra in terms of Urey - Bradley force constants. Devlin and Hisatsune used observed isotopic shifts in the spectra along with force constants transferred from nitrogen oxides and oxyhalides in order to select the N-N bond distance and the O-N bond angle.

The unobserved mode was assumed to be free internal rotation around the N-N bond, leading to S°₂₉₈ = 73.91 cal. deg.⁻¹ mole⁻¹ which is in good agreement with 74.13 ± 0.52 cal. deg.⁻¹ mole⁻¹ obtained from the recalculated second law of Beattie and Bell. The principal moments of inertia are I_A = 22.694 X 10⁻³⁹, I_B = 29.577 X 10⁻³⁹, and I_C = 6.883 X 10⁻³⁹ g. cm.², while the reduced moment for internal rotation was calculated as I_r = 0.990 X 10⁻³⁹ g. cm.².



(Crystal) Mol. Wt. = 92.016

MOL. WT. = 92.016

(CRYSTAL)

DINITROGEN TETROXIDE (N₂O₄)

T, °K.	C _p	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$S^0 - (T^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$ kcal. mole ⁻¹	ΔH_f^0	ΔF_f^0	Log K _p
0	0.000	0.000	INFINITE	5.112	7.263	7.263	INFINITE
100	14.508	13.415	56.802	4.339	8.601	2.174	4.750
200	21.917	25.613	38.353	2.508	8.893	1.306	14.300
298	29.185	35.920	35.920	0.000	8.893	2.174	17.474
300	29.320	36.101	35.021	0.054	8.358	23.984	17.471
400	36.720	45.648	37.172	3.390	7.141	34.600	18.904
500	40.000	54.271	39.749	7.261	5.435	44.844	19.600

$\Delta H_f^0 = -7.263 \pm 0.4$ kcal. mole⁻¹
 $\Delta H_f^{298.15} = -8.373 \pm 0.4$ kcal. mole⁻¹
 $\Delta H_m^0 = 3.502 \pm 0.003$ kcal. mole⁻¹

$S_{298.15}^0 = 35.92$ cal. deg.⁻¹ mole⁻¹
 $T_m = 261.95 \pm 0.05^\circ K.$

Heat of Formation.

The heat of formation was back calculated from that of the liquid using the measured heat of melting and the enthalpy of the crystal and liquid.

Heat Capacity and Entropy.

W. F. Giauque and J. D. Kemp, J. Chem. Phys. 5, 40 (1939) measured the low temperature heat capacity from 15-295°K. The entropy was obtained by integration of this data using $S_{15}^0 = 0.34$ cal. deg.⁻¹ mole⁻¹.

Melting Data.

The temperature and heat of melting were also measured by Giauque and Kemp, loc. cit.



Dinitrogen Tetroxide (N_2O_4)
(Liquid) Mol. Wt. = 92.016

N_2O_4
MOL. WT. = 92.016

DINITROGEN TETROXIDE (N_2O_4) (LIQUID)

T, °K.	C_p°	$\int_0^T C_p^\circ dT - (F^\circ - H_{298}^\circ)/T$	$\int_0^T C_p^\circ dT - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _f
0	0.000	INFINITE	6.034	4.488	-	INFINITE
100	26.980	17.417	6.034	4.488	3.775	8.249
200	30.060	24.592	6.034	4.488	3.250	8.449
298	34.060	30.007	6.034	4.488	2.825	8.649
300	34.140	50.218	6.034	4.488	23.455	17.086
400	38.440	60.828	6.034	4.488	3.692	17.615
500	42.740	69.668	6.034	4.488	3.142	18.066

$S_{298.15}^\circ = 50.007$ cal. deg.⁻¹ mole⁻¹
 $T_m = 261.95 \pm 0.05^\circ K.$
 $T_b = 294.25^\circ K. (to N_2O_4 + NO_2)$
 $T_b = [301.4^\circ K.] (to N_2O_4)$

$\Delta H_f^\circ = -4.488 \pm 0.4$ kcal. mole⁻¹
 $\Delta H_f^\circ 298.15 = -4.676 \pm 0.4$ kcal. mole⁻¹
 $\Delta H_m^\circ = 3.502 \pm 0.003$ kcal. mole⁻¹
 $\Delta H_v^\circ = 9.11 \pm 0.1$ kcal. mole⁻¹ (to $N_2O_4 + NO_2$)
 $\Delta H_v^\circ = [6.79]$ kcal. mole⁻¹ (to N_2O_4)

Heat of Formation.

The heat of formation was back calculated from that of the gas using the calorimetrically measured heat of vaporization to the equilibrium mixture, in conjunction with a dissociation constant $\alpha_c = 0.161$.

Heat Capacity and Entropy.

W. F. Giauque and J. D. Kemp, J. Chem. Phys. 5, 40 (1938) measured the low temperature heat capacity from 15°-295°K., above 295°K. the heat capacity was smoothly extrapolated.

Melting and Vaporization Data.

Giauque and Kemp, loc. cit. measured the temperature and heat of melting and also the boiling point and the calorimetric value of the heat of vaporization to the equilibrium mixture. The heat of vaporization to a hypothetical pure N_2O_4 gas at 294.25°K. was calculated to be 6.91 kcal. mole⁻¹.

N_2O_4

Dinitrogen Tetroxide (N₂O₄)
(Ideal Gas) Mol. Wt. = 92.016

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ cal. mole ⁻¹	ΔH° _f kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞
100	11.107	57.759	3.919	4.473	4.473
200	11.107	57.759	2.962	3.319	9.721
298	18.465	72.724	0.000	2.170	23.955
300	18.520	72.838	0.034	2.165	23.966
400	21.157	75.484	2.023	2.035	30.619
500	23.233	83.496	4.247	2.094	37.761
600	24.860	87.881	6.655	2.280	44.880
700	26.127	91.813	9.207	2.548	51.959
800	27.113	95.369	11.871	2.873	58.994
900	27.884	98.609	14.623	3.238	65.988
1000	28.492	101.579	17.443	3.630	72.942
1100	28.977	104.318	20.317	4.038	79.852
1200	29.367	106.857	23.235	4.459	86.726
1300	29.684	109.221	26.188	4.887	93.564
1400	29.946	111.430	29.170	5.320	100.369
1500	30.163	113.504	32.176	5.755	107.143
1600	30.345	115.457	35.201	6.190	113.888
1700	30.499	117.301	38.244	6.626	120.607
1800	30.630	119.048	41.300	7.055	127.299
1900	30.743	120.707	44.369	7.481	133.970
2000	30.840	122.287	47.448	7.902	140.612
2100	30.925	123.794	50.537	8.319	147.238
2200	30.999	125.234	53.633	8.725	153.843
2300	31.064	126.613	56.736	9.127	160.430
2400	31.121	127.937	59.845	9.521	167.002
2500	31.172	129.208	62.960	9.905	173.553
2600	31.218	130.432	66.080	10.284	180.092
2700	31.259	131.611	69.204	10.653	186.617
2800	31.295	132.748	72.331	11.013	193.128
2900	31.329	133.847	75.463	11.367	199.629
3000	31.358	134.908	78.597	11.710	206.116
3100	31.386	135.938	81.734	12.047	212.589
3200	31.410	136.935	84.874	12.375	219.050
3300	31.433	137.902	88.016	12.695	225.502
3400	31.454	138.841	91.161	13.008	231.947
3500	31.473	139.753	94.307	13.314	238.378
3600	31.490	140.639	97.455	13.612	244.811
3700	31.506	141.502	100.605	13.904	251.229
3800	31.521	142.343	103.756	14.189	257.640
3900	31.535	143.162	106.909	14.470	264.039
4000	31.549	143.960	110.063	14.742	270.434
4100	31.559	144.739	113.218	15.008	276.826
4200	31.570	145.500	116.375	15.271	283.206
4300	31.580	146.243	119.532	15.528	289.589
4400	31.590	146.969	122.691	15.779	295.953
4500	31.597	147.679	125.850	16.025	302.320
4600	31.607	148.374	129.011	16.269	308.686
4700	31.615	149.054	132.172	16.506	315.036
4800	31.623	149.719	135.334	16.740	321.391
4900	31.630	150.371	138.496	16.970	327.723
5000	31.636	151.011	141.660	17.197	334.062
5100	31.642	151.637	144.824	17.419	340.402
5200	31.648	152.252	147.988	17.639	346.726
5300	31.654	152.854	151.153	17.856	353.065
5400	31.659	153.446	154.319	18.070	359.377
5500	31.664	154.027	157.485	18.282	365.706
5600	31.668	154.598	160.652	18.489	372.011
5700	31.673	155.158	163.819	18.695	378.325
5800	31.677	155.709	166.986	18.898	384.640
5900	31.681	156.251	170.154	19.099	390.935
6000	31.685	156.783	173.322	19.297	397.243

Dec. 31, 1960; June 30, 1961; Sept. 30, 1964

DINITROGEN TETROXIDE (N₂O₄)

(IDEAL GAS)

MOL. WT. = 92.016

Point Group V_hΔH°_f 0 = 4.47 ± 0.4 kcal. mole⁻¹S°_{298.15} = 72.72 cal. deg.⁻¹ mole⁻¹ΔH°_f 298.15 = 2.17 ± 0.4 kcal. mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e , cm. ⁻¹	ω_e , cm. ⁻¹	ω_e , cm. ⁻¹
1373 (1)	1710 (1)	1748 (1)
823 (1)	480 (1)	385 (1)
260 (1)	430 (1)	1261 (1)
[50](1)	675 (1)	750 (1)

Bond Distance: N-N = 1.750 Å N-O = 1.180 Å

Bond Angle: O-N-O = 133.7°

Product of the Moments of Inertia: I_AI_BI_C = 9.9304 X 10⁻¹¹⁴ g.³ cm.⁶

σ = 4

Heat of Formation.

W. P. Olsauke and J. D. Kemp, J. Chem. Phys. 5, 40 (1938) calculated idealized equilibrium constants for the reaction N₂O₄(g) = 2NO₂(g) from the work of Bodenstein and Bode (1), Zeits. für physik. Chem. 100, 75 (1922), Verhoek and Daniels (2), J. Am. Chem. Soc. 53, 1250 (1931) and Moutzel (3), Compt. Rend. 169, 1397 (1919). The second and third law analysis of these equilibrium constants has been repeated using more recent functions. The results are shown below.

Ref.	Third Law ΔH° ₂₉₈	Second Law ΔH° ₂₉₈
1.	13.644	13.634 ± 0.015*
2.	13.672	14.429 ± 0.126
3.	13.657	13.599 ± 0.019**

* Ten points rejected because of statistically significant scatter.

** One point rejected.

The second law value of Verhoek and Daniels was not considered significant due to the extremely small temperature range and the use of only three temperatures. The adopted value was 13.65 ± 0.03 kcal. which leads to 2.17 kcal. mole⁻¹ for the heat of formation of N₂O₄(g).

Heat Capacity and Entropy.

The structural parameters were taken from the electron diffraction measurements of D. W. Smith and K. Hedberg, J. Chem. Phys. 25, 1282 (1956). The vibrational frequencies are those chosen by I. C. Hitaatane, J. P. Devlin and Y. Wada, J. Chem. Phys. 33, 714 (1960). The torsional frequency of 50 cm.⁻¹ was estimated in order to bring the entropy of the gas into agreement with that determined by Glaue and Kemp loc. cit. From low temperature heat capacities and heats of fusion and vaporization. The individual moments of inertia were I_A = 12.508 X 10⁻³⁹ g. cm.², I_B = 22.609 X 10⁻³⁹ g. cm.², and I_C = 35.117 X 10⁻³⁹ g. cm.²

MOL. WT. = 108.016

(IDEAL GAS)

DINITROGEN PENTOXIDE (N₂O₅)Point Group C_{2v} $\Delta H_f^\circ = 0$ Unknown $S_{298.15}^\circ = 82.8 \pm 1.0$ cal. deg. mole⁻¹ $\Delta H_f^\circ = 298.15 = 2.7 \pm 0.3$ kcal. mole⁻¹

Ground State Quantum Weight = 1

Dinitrogen Pentoxide (N₂O₅)
(Ideal Gas) Mol. Wt. = 108.016

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	cal. mole ⁻¹	ΔH _f °	Log K _p
0							
100	18.691	74.506	84.772	-2.053	3.036	19.848	-21.688
200	23.017	82.801	82.801	.000	2.700	28.186	-20.660
298							
300	23.089	82.984	82.901	.043	2.697	28.343	-20.647
400	26.494	90.077	83.751	2.530	2.710	30.698	-20.159
500	28.965	96.270	85.669	5.311	2.960	45.421	-16.852
600	30.684	101.713	87.882	8.268	3.348	53.879	-19.624
700	32.274	106.856	90.210	11.431	4.805	62.576	-17.430
800	33.794	111.856	92.794	14.856	6.480	71.480	-15.450
900	35.365	116.750	94.782	17.971	8.416	78.834	-13.613
1000	36.806	121.527	96.658	21.331	5.334	87.032	-11.920
1100	38.137	126.197	99.047	24.728	5.846	95.176	-10.400
1200	39.412	130.788	101.098	28.077	6.835	103.355	-9.008
1300	40.642	135.312	102.868	31.407	7.818	111.650	-7.831
1400	41.832	139.788	104.387	34.677	7.340	119.950	-6.831
1500	42.993	144.216	106.538	38.562	7.818	127.435	-6.052
1600	44.127	148.503	108.216	42.000	8.287	135.249	-5.476
1700	45.237	152.658	109.595	45.000	8.866	143.350	-5.010
1800	46.327	156.698	110.732	47.600	9.186	150.803	-4.640
1900	47.400	160.638	111.657	50.000	9.610	158.683	-4.340
2000	48.457	164.483	112.427	52.000	10.038	166.983	-4.090
2100	49.500	168.243	113.064	53.600	10.445	174.661	-3.876
2200	50.530	171.928	113.575	55.000	10.815	182.670	-3.686
2300	51.547	175.548	114.000	56.200	11.150	190.043	-3.510
2400	52.552	179.113	114.343	57.200	11.450	196.740	-3.340
2500	53.545	182.628	114.600	58.000	11.720	202.799	-3.180
2600	54.527	186.098	114.780	58.600	11.960	208.250	-3.030
2700	55.498	189.528	114.890	59.000	12.180	213.100	-2.890
2800	56.458	192.918	114.930	59.200	12.380	217.380	-2.760
2900	57.407	196.270	114.900	59.300	12.560	221.080	-2.640
3000	58.345	199.585	114.800	59.300	12.720	224.220	-2.530
3100	59.272	202.865	114.630	59.100	12.870	226.810	-2.430
3200	60.188	206.110	114.400	58.800	13.000	228.850	-2.340
3300	61.093	209.325	114.110	58.400	13.110	230.350	-2.260
3400	61.987	212.510	113.760	57.900	13.200	231.320	-2.190
3500	62.870	215.670	113.360	57.300	13.270	231.770	-2.130
3600	63.742	218.810	112.910	56.600	13.320	231.700	-2.080
3700	64.603	221.930	112.420	55.800	13.350	231.100	-2.040
3800	65.454	225.040	111.890	54.900	13.360	230.000	-2.000
3900	66.295	228.140	111.320	53.900	13.350	228.400	-1.970
4000	67.126	231.230	110.710	52.800	13.320	226.300	-1.940
4100	67.947	234.310	110.060	51.600	13.270	223.700	-1.910
4200	68.758	237.380	109.380	50.300	13.200	220.600	-1.880
4300	69.559	240.440	108.670	48.900	13.110	217.000	-1.840
4400	70.350	243.490	107.930	47.400	13.000	212.900	-1.800
4500	71.131	246.530	107.160	45.800	12.870	208.300	-1.750
4600	71.902	249.560	106.370	44.100	12.720	203.200	-1.700
4700	72.663	252.580	105.560	42.300	12.550	197.600	-1.640
4800	73.414	255.590	104.730	40.400	12.360	191.500	-1.580
4900	74.155	258.590	103.880	38.400	12.150	184.900	-1.510
5000	74.886	261.580	103.010	36.300	11.920	177.800	-1.440
5100	75.607	264.560	102.120	34.100	11.670	170.200	-1.360
5200	76.318	267.530	101.210	31.800	11.400	162.100	-1.280
5300	77.019	270.490	100.280	29.400	11.110	153.500	-1.190
5400	77.710	273.440	99.330	26.900	10.800	144.400	-1.100
5500	78.391	276.380	98.360	24.300	10.470	134.800	-1.000
5600	79.062	279.310	97.370	21.600	10.120	124.700	-0.900
5700	79.723	282.230	96.360	18.800	9.750	114.100	-0.800
5800	80.374	285.140	95.330	15.900	9.360	103.000	-0.700
5900	81.015	288.040	94.280	12.900	8.950	91.400	-0.600
6000	81.646	290.930	93.210	9.800	8.520	79.300	-0.500

Dec. 31, 1960; Dec. 31, 1964

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
1728 (1)	614 (1)	[614] (1)	[Rotation]
1338 (1)	353 (1)	[Rotation]	1728 (1)
743 (1)	[85] (1)	577 (1)	1247 (1)
			353 (1)

Bond Distance: O-N = 1.21 Å

Bond Angle: O-N-O = 134°

O-N-O planes perpendicular to N-O-N plane

Product of the Moments of Inertia: $I_A I_B I_C = 2.066 \times 10^{-113}$ g.³ cm.⁶

Heat of Formation.

The heat of formation was obtained by recalculation of the calorimetric data of Ray and Ogg for the reaction of N₂O₅(g) with NO.The stoichiometry of the reaction products, originally based on the results for N₂O₄ → 2 NO₂ from Oiaque and Kemp, J. Chem. Phys. 5, 40 (1938), was based on the JANAF analysis of this simultaneous equilibrium. A correction of 0.23 kcal. was made in the heat of reaction because of the additional formation of N₂O₃ from NO and NO₂.Confirmation of the heat of formation was obtained by combination of the heats of hydrolysis and sublimation of N₂O₅(c). The results are summarized below. Second law values are given for the heats of sublimation, but third law analyses suggest that the value from Russ and Pokorny is more reliable. Most of the uncertainty in this path, however, arises from the heat of hydrolysis.

Reaction

N₂O₅(g) + NO(g) →N₂O₄(g) + NO₂(g)N₂O₅(c) + H₂O(l) → 2 HNO₃(aq)N₂O₅(c) → N₂O₃(g)

Silicon Nitride, Alpha (α -Si₃N₄)
(Crystal) GFW = 140.2848

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	23.789	27.000	27.000	.000	-178.000	-154.734	113.423
300	23.850	27.147	27.000	.044	-178.009	-154.590	112.619
400	26.450	34.367	27.967	2.560	-178.408	-146.721	101.165
500	29.850	40.531	29.477	5.327	-179.079	-139.753	90.693
600	31.000	45.989	32.116	8.324	-179.810	-130.766	87.631
700	33.000	50.920	34.456	11.525	-178.820	-122.756	78.326
800	34.850	55.450	36.800	15.920	-178.711	-114.755	71.350
900	36.400	59.688	39.109	19.485	-178.500	-106.769	65.927
1000	37.800	63.536	41.360	22.176	-178.209	-98.815	61.576
1100	39.120	67.222	43.546	26.044	-177.842	-90.893	58.059
1200	40.270	70.677	45.665	30.014	-177.409	-83.008	55.118
1300	41.236	73.939	47.715	34.091	-176.919	-75.161	52.636
1400	42.046	77.026	49.700	38.256	-176.371	-67.354	50.514
1500	42.700	79.950	51.620	42.495	-175.785	-59.583	48.661
1600	43.152	82.720	53.478	46.789	-175.269	-51.850	47.092
1700	43.540	85.348	55.276	51.123	-174.684	-44.337	45.636
1800	43.846	87.846	57.017	55.493	-174.062	-36.843	44.133
1900	44.106	90.284	58.702	59.891	-173.420	-29.389	42.794
2000	44.320	92.492	60.355	64.313	-172.664	-21.972	41.592
2100	44.492	94.456	61.919	68.749	-171.792	-14.599	40.510
2200	44.622	96.724	63.434	73.193	-170.860	-7.271	39.541
2300	44.758	98.703	64.944	77.645	-169.876	1.341	38.683
2400	44.850	100.601	66.390	82.104	-168.840	9.916	37.924
2500	44.700	102.424	67.795	86.571	-167.762	18.453	37.264
2600	44.766	104.178	69.161	91.044	-166.643	27.064	36.611
2700	44.830	105.859	70.490	95.524	-165.481	35.741	36.065
2800	44.890	107.500	71.783	100.010	-164.287	44.485	35.631
2900	44.946	109.077	73.042	104.502	-163.062	53.295	35.305
3000	45.000	110.601	74.268	108.999	-161.807	62.168	35.080

SILICON NITRIDE, ALPHA (α -Si₃N₄)

(CRYSTAL)

GFW = 140.2848

ΔHf° = Unknown

ΔHf°_{298.15} = -176 ± 7 kcal/mol

S°_{298.15} = [27 ± 4] gibbs/mol

T₀ = [2151]°K

Heat of Formation.

The equilibria (A) Si₃N₄(c) = 3 Si(l) + 2 N₂(g) and (B) Si₃N₄(c) = 3 Si(c) + 2 N₂(g) have been investigated by three groups. R. D. Fehlke and J. P. Elliott, Trans. Met. Soc. AIME 215, 781 (1959), made four series of measurements which mainly concerned reaction (A). W. B. Hinke and L. R. Brantley, J. Amer. Chem. Soc. 52, 48 (1930), made a single series of measurements which covered reactions (A) and (B). C. Matignon, Bull. Soc. Chim. France 13, 791 (1913), also gave a single equilibrium point for reaction (C) 3 SiO₂(c) + 6 C + 2 N₂ = Si₃N₄(c) + 6 CO(g). Below are shown 2nd and 3rd law analyses of the data. It should be noted that these analyses are based on the estimated heat capacities above 900°K, and on an estimated entropy. The uncertainty due to these estimates is estimated as ± 7 kcal in ΔHf°₂₉₈.

Reference	Points	Range °K	Reaction	ΔHf° ₂₉₈ kcal/mol	2nd law	3rd law	Drift	*ΔHf° ₂₉₈ kcal/mol
Fehlke - 1	9	1699-1934	A		190.1±7.6	211.79	11.6±4.3	-177.04
Fehlke - 2	9	1691-1959	A		210.7±8.6	213.29	1.8±4.9	-178.53
Fehlke - 3	10	1692-1966	A		212.3±3.3	212.61	0.1±1.9	-177.85
Fehlke - 4	6	1690-1872	A		207.0±7.5	212.47	2.6±4.3	-177.71
Fehlke	30**	1690-1966	A		212.6±3.2	212.67	-0.2±1.8	-177.91
Hinke	4	1709-1802	A		196.0±18.5	213.43	10.3±10.4	-178.67
Fehlke	4	1653-1666	B			177.41		-177.41
Hinke	3	1606-1675	B			177.82	22.6±11.8	-177.82
Matignon	1	1700	C			318.9		-175.1

*Calculated from the third law ΔHf°₂₉₈ values.

**Four points rejected due to failure of a statistical test; this set is a combination of the first four sets.

The adopted ΔHf°₂₉₈(α -Si₃N₄) = -178±7 kcal/mol.

L. A. McClaine and C. F. Coppel, A. D. Little, Inc., "Equilibrium Studies of Refractory Nitrides," Tech. Rept. AFML-TR-65-99, Part 11, Dec. 1966, have investigated the decomposition reaction (B). They conclude that at 1618°K the equilibrium pressure is roughly 0.15 mm. This corresponds to ΔHf°₂₉₈ = -182.3 kcal, and was not given any weight in the adopted value.

Heat Capacity and Entropy.

The enthalpy of α -Si₃N₄ has been measured at three temperatures, in the range 373° - 858°K, by S. Sato, Bull. Chem. Soc. Japan 13, 41 (1938). The heat capacity is calculated from the data assuming that a limit of 45 gibbs/mol is attained by 3000°K. The entropy is obtained from the equilibrium data of Fehlke and Elliott, loc. cit.

Decomposition Data.

The temperature of decomposition is calculated as the point at which the decomposition pressure of nitrogen reaches 1 atm.

Triphosphorus Pentanitride (P_3N_5)

(Crystal) GFW = 162.9549

T, °K	C_p^0	$\frac{gibbs/mol}{S^0}$	$-(G^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	$\frac{kcal/mol}{\Delta H^0}$	ΔG^0	Log Kp
0							
100							
200							
298	35.600	44.000	44.000	.000	- 64.000	- 36.129	27.949
300	35.900	44.221	44.001	.066	- 63.993	- 37.967	27.659
400	46.000	56.017	45.540	4.191	- 63.210	- 29.386	16.056
500	52.000	66.963	48.748	9.108	- 61.764	- 21.088	9.218
600	56.000	74.813	52.620	18.514	- 59.038	- 13.420	4.779
700	59.000	85.684	56.720	20.374	- 57.499	- 12.079	3.710
800	61.000	91.698	60.850	24.574	- 57.007	- 11.063	3.583
900	62.500	100.975	64.910	32.459	- 114.027	- 1.375	.334
1000	63.400	107.609	68.853	38.755	- 110.082	- 10.976	2.399
1100	64.027	113.482	72.657	45.128	- 107.002	- 23.023	4.574
1200	64.500	118.275	76.312	50.355	- 104.401	- 31.486	6.085
1300	64.920	124.451	79.818	58.023	- 101.699	- 46.296	7.783
1400	64.987	129.262	83.180	64.515	- 98.594	- 57.563	8.986
1500	65.000	133.787	86.403	71.015	- 95.504	- 66.611	9.997

Dec. 31, 1960; Sept. 30, 1962; Mar. 31, 1967

TRIPHOSPHORUS PENTANITRIDE (P_3N_5)

(CRYSTAL)

GFW = 162.9549

$S_{298.15}^0 = [44 \pm 6] \text{ gibbs/mol}$
 $T_d = [730]^\circ K$
 $\Delta H_f^0 = \text{Unknown}$
 $\Delta H_f^0_{298.15} = -64 \pm 5 \text{ kcal/mol}$

Heat of Formation.

The heat of formation is based on the work of A. Stock and F. Wrede, Chem. Ber. 40, 2923 (1907), who burned P_3N_5 in oxygen. They report a $\Delta H_f^0_{298} = -949.4 \text{ kcal}$ for the reaction $2 P_3N_5(c) + 7.5 O_2(g) = 1.5 P_4O_{10}(\text{amorph}) + 5 N_2(g)$. In NBS Technical Note 270-1, "Selected Values of Chemical Thermodynamic Properties," Washington, D.C. (1965), a value of -947.7 kcal is used for the above reaction and we adopt this value. Using the JANAP value for $P_4O_{10}(c)$ and correcting this to $P_4O_{10}(\text{amorph})$ by adding -13.8 kcal/mol , from Technical Note 270-1, we obtain $\Delta H_f^0_{298} P_4O_{10}(\text{amorph}) = -716.5 \text{ kcal/mol}$. Thus, we derive $\Delta H_f^0_{298} P_3N_5(c) = -63.525 \text{ kcal/mol}$; however, because of the uncertainties in the heat of reaction and correction for amorphous P_4O_{10} we round the value to $-64 \pm 5 \text{ kcal/mol}$.

Heat Capacity and Entropy.

S. Sato, Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 34, 594 (1958), gave an equation for the heat capacity in the range $273^\circ - 578^\circ K$. Judging from his results for $Be_3N_2(c)$ in the same paper, we believe his values will be slightly high at the upper end of the range. Thus, taking 6.2 gibbs/g-atom as the limiting value, a curve was drawn through Sato's values at the low end and approaching the limit asymptotically. The entropy was estimated from that of $Si_3N_4(c)$ by assuming that the ratio Op_{298}/S_{298} on a gram atom basis would be the same for $P_3N_5(c)$.

Temperature of Decomposition.

T_d is calculated as the point at which the total pressure reaches 1 atm. This corresponds to $\log K_p = -0.76$ for the reaction $P_3N_5(c) = 0.75 P_4(g) + 2.5 N_2(g)$. The temperature of decomposition has been reported by V. P. Postnikov and L. L. Kuzmin, J. Appl. Chem. (USSR) 2, 429 (1935) as $1075^\circ K$. This has been confirmed by H. Moreau and P. Rocquet, Compt. Rend. 199, 1691 (1934) and Bull. Chim. France, 3, 1801 (1936); and E. O. Huffman, G. Tarbuton, G. V. Elmore, A. J. Smith and M. G. Rountree, J. Am. Chem. Soc. 79, 1765 (1957). However, it was also noted that $P_3N_5(c)$ is not reformed on cooling the decomposition products; thus the decomposition is non-equilibrium. It is known that the decomposition of AlN , BN and Be_3N_2 is kinetically limited and the equilibrium pressure is not attained until the average energy is greater than the activation energy. It appears that this is also the case for P_3N_5 and a high activation energy is expected.

Sodium (Na)

(Reference State) At. Wt. = 22.991

Na

AT. WT. = 22.991

(REFERENCE STATE)

SODIUM (Na)

0° to 370.98°K Crystal
370.98° to 1176.9°K Liquid
1176.9° to 6000°K Ideal Monatomic Gas

See crystal, liquid, and ideal monatomic gas for details.

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T cal. mole ⁻¹	H°-H° ₂₉₈ ΔH° _f kcal. mole ⁻¹	ΔF° kcal. mole ⁻¹	Log K _p
0	0.000	0.000	INFINITE	1.541	0.000	0.000
100	5.366	5.690	17.697	1.221	0.000	0.000
200	6.211	9.725	12.694	0.634	0.000	0.000
298	6.730	12.298	12.298	0.000	0.000	0.000
300	6.741	12.340	12.298	-0.12	0.000	0.000
400	7.531	16.086	12.695	1.356	0.000	0.000
500	7.302	17.741	13.546	2.097	0.000	0.000
600	7.124	19.056	14.358	2.818	0.000	0.000
700	6.916	20.173	15.129	3.520	0.000	0.000
800	6.690	21.073	15.798	4.219	0.000	0.000
900	6.492	21.865	16.430	4.909	0.000	0.000
1000	6.318	22.512	17.012	5.599	0.000	0.000
1100	6.169	23.074	17.552	6.295	0.000	0.000
1200	6.043	23.571	18.055	6.995	0.000	0.000
1300	5.936	24.022	18.535	7.698	0.000	0.000
1400	5.848	24.437	18.991	8.399	0.000	0.000
1500	5.774	24.820	19.429	9.095	0.000	0.000
1600	5.712	25.183	19.852	9.785	0.000	0.000
1700	5.660	25.529	20.262	10.468	0.000	0.000
1800	5.616	25.860	20.658	11.145	0.000	0.000
1900	5.579	26.178	21.033	11.815	0.000	0.000
2000	5.548	26.484	21.390	12.478	0.000	0.000
2100	5.522	26.779	21.730	13.135	0.000	0.000
2200	5.500	27.065	22.055	13.785	0.000	0.000
2300	5.481	27.343	22.367	14.428	0.000	0.000
2400	5.464	27.614	22.666	15.064	0.000	0.000
2500	5.449	27.879	22.953	15.693	0.000	0.000
2600	5.435	28.138	23.229	16.315	0.000	0.000
2700	5.422	28.392	23.494	16.931	0.000	0.000
2800	5.410	28.641	23.748	17.541	0.000	0.000
2900	5.399	28.885	24.000	18.145	0.000	0.000
3000	5.389	29.125	24.250	18.743	0.000	0.000
3100	5.380	29.361	24.498	19.335	0.000	0.000
3200	5.372	29.593	24.744	19.921	0.000	0.000
3300	5.364	29.822	24.988	20.502	0.000	0.000
3400	5.357	30.048	25.230	21.078	0.000	0.000
3500	5.350	30.271	25.470	21.649	0.000	0.000
3600	5.344	30.491	25.708	22.215	0.000	0.000
3700	5.338	30.708	25.944	22.776	0.000	0.000
3800	5.333	30.922	26.178	23.332	0.000	0.000
3900	5.328	31.133	26.410	23.883	0.000	0.000
4000	5.323	31.341	26.640	24.429	0.000	0.000
4100	5.318	31.547	26.868	24.970	0.000	0.000
4200	5.313	31.751	27.094	25.506	0.000	0.000
4300	5.308	31.953	27.318	26.037	0.000	0.000
4400	5.303	32.154	27.540	26.563	0.000	0.000
4500	5.298	32.353	27.760	27.085	0.000	0.000
4600	5.293	32.550	27.978	27.602	0.000	0.000
4700	5.288	32.745	28.194	28.115	0.000	0.000
4800	5.283	32.938	28.408	28.623	0.000	0.000
4900	5.278	33.130	28.620	29.127	0.000	0.000
5000	5.273	33.320	28.830	29.627	0.000	0.000
5100	5.268	33.508	29.038	30.122	0.000	0.000
5200	5.263	33.694	29.244	30.613	0.000	0.000
5300	5.258	33.878	29.448	31.100	0.000	0.000
5400	5.253	34.060	29.650	31.583	0.000	0.000
5500	5.248	34.241	29.850	32.062	0.000	0.000
5600	5.243	34.420	30.048	32.537	0.000	0.000
5700	5.238	34.597	30.244	33.008	0.000	0.000
5800	5.233	34.772	30.438	33.475	0.000	0.000
5900	5.228	34.945	30.630	33.938	0.000	0.000
6000	5.223	35.116	30.820	34.397	0.000	0.000

June 30, 1962

Na

T. °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	0.000	0.000	INFINITE	-	0.000	0.000	INFINITE
100	5.394	5.690	17.867	1.221	0.000	0.000	0.000
200	6.211	9.725	12.854	0.634	0.000	0.000	0.000
298	6.740	12.296	12.296	0.000	0.000	0.000	0.000
300	6.741	12.338	12.296	0.042	0.000	0.000	0.000
400	7.400	14.234	12.572	0.278	0.000	0.000	0.000
500	8.000	16.194	13.124	1.535	0.562	0.211	0.092
600	8.000	17.653	13.761	2.335	0.883	0.359	0.131
700	8.000	18.868	14.408	3.135	0.389	0.491	0.152
800	8.000	19.954	15.036	3.935	0.174	0.715	0.174
900	8.000	20.954	15.646	4.735	0.064	0.808	0.177
1000	8.000	21.740	16.205	5.535	-	-	-

SODIUM (Na)

(CRYSTAL)

AT. WT. = 22.991

$$\Delta H^\circ_f 298.15 = 0$$

$$\Delta H^\circ_g 298.15 = 25.755 \text{ kcal. mole}^{-1} \text{ (Monatomic gas)}$$

$$\Delta H^\circ_g 298.15 = 32.87 \text{ kcal. mole}^{-1} \text{ (Diatomic gas)}$$

$$S^\circ_{298.15} = 12.296 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H^\circ_m = 0.622 \text{ kcal. mole}^{-1}$$

$$T_m = 370.98 \pm 0.02^\circ\text{K.}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

D. L. Martin, Proc. Roy. Soc. A254, 433 (1960) reports that the low temperature heat capacity of sodium depends on the thermal history of the sample and ascribes this to a martensitic transformation. The effect is most pronounced in the range 40-80°K., where the graph of C_p against T increases continually for some samples and rises to a peak at 55°K. for others. Martin lists heat capacities obtained in several runs on "high purity" sodium at 21° to 300°K. and the higher values, those defining the peak at 55°K., have been selected here. The heat capacities reported by T. M. Dauphinee, D. L. Martin, and H. Preston-Thomas, Proc. Roy. Soc. A233, 214 (1955), have not been used, since one of the authors in a later publication (Martin, loc. cit.) questions the accuracy of the measurements above 100°K. and at lower temperatures there is no rise to a peak at 55°K. In the range 1.5° to 20°K., L. M. Roberts, Proc. Phys. Soc. B70, 744 (1957) and D. H. Parkinson and J. E. Quarrington Proc. Phys. Soc. A62, 782 (1955) have measured the heat capacity of very high purity sodium. The values of Parkinson and Quarrington are somewhat higher than those of Roberts and have been given greater weight, since they show better continuity with Martin's results. The results of O. L. Picard and F. E. Simon, Proc. Phys. Soc. 61, 1 (1948) have been rejected below 10°K., since they show a peak between 5° and 8°, a feature not verified by other workers; between 10° and 25°K they agree exactly with the results of Parkinson and Quarrington. J. Rayne, Phys. Rev. 95, 1428 (1954) states that the graph of C_p against T has a small peak at about 0.9°K. This peak has not been observed in the work of W. H. Liden and N. E. Phillips, Phys. Rev. 119, 959 (1960) from 0.15° to 1°K. R. E. Osamer and C. V. Heer, Phys. Rev. 119, 955 (1960) from 0.4° to 2°K and D. L. Martin, Phys. Rev. 124, 438 (1961) from 0.4 to 1.5°K.

T. B. Douglas, A. P. Ball, D. C. Olinings, and W. D. Davis, J. Am. Chem. Soc. 74, 2472 (1952) report heat capacities in the range 273° to 1173°K on a sample of not less than 99.9% purity. These values agree to within 1% with those of Martin in the range 273° to 300°K, and the two sets of data have been smoothly joined.

Melting.

Douglas et al. (loc. cit.) have determined the triple point to be $97.82 \pm 0.02^\circ\text{C.}$, from which the melting point is calculated to be $97.83 \pm 0.02^\circ\text{C.}$, and have measured the heat of fusion.

Heat of Sublimation.

At the boiling point and higher temperatures sodium vapor contains an appreciable proportion of diatomic molecules. O. W. Thompson and E. Oerelia "Sodium - its Manufacture, Properties and Uses," Ed. M. Sittig, Chapter 3, Reinhold Publishing Corporation, Inc., New York (1956), have made a careful analysis of the available vapor pressure data. Their results are consistent with the free energy functions calculated in the present work and have been adopted.

Sodium (Na)

(Liquid) At. Wt. = 22.991

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _f
0						
100	7.617	13.827	13.827	.000	.119	.087
200				.575		
300	7.812	13.875	13.827	.014	.117	.085
400	7.937	13.883	13.130	.000	.000	.000
500	7.992	13.883	1.522	.000	.000	.000
600	7.992	13.883	2.243	.000	.000	.000
700	7.992	13.883	2.814	.000	.000	.000
800	7.992	13.883	3.284	.000	.000	.000
900	7.992	13.883	3.684	.000	.000	.000
1000	7.992	13.883	4.024	.000	.000	.000
1100	7.992	13.883	4.314	.000	.000	.000
1200	7.992	13.883	4.554	.000	.000	.000
1300	7.992	13.883	4.744	.000	.000	.000
1400	7.992	13.883	4.884	.000	.000	.000
1500	7.992	13.883	4.984	.000	.000	.000
1600	7.992	13.883	5.044	.000	.000	.000
1700	7.992	13.883	5.074	.000	.000	.000
1800	7.992	13.883	5.084	.000	.000	.000
1900	7.992	13.883	5.084	.000	.000	.000
2000	7.992	13.883	5.074	.000	.000	.000

Na

SODIUM (Na)

(LIQUID)

AT. WT. = 22.991

$\Delta H_f^o 298.15 = 0.575 \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = 13.827 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_m^o = 0.622 \text{ kcal. mole}^{-1}$
 $T_m = 370.99 \pm 0.02^\circ \text{K}$
 $T_b = 1156^\circ \text{K (Equilibrium mixture)}$
 $\Delta H_v 1176.9 = 23.285 \text{ kcal. mole}^{-1}$
 $T_b \text{ (Monatomic Gas)} = 1176.9^\circ \text{K}$

Heat of Formation.

Obtained from the heat of fusion by adding $H_{370.99}^o - H_{298.15}^o$ for the solid and subtracting $H_{370.99}^o - H_{298.15}^o$ for the liquid.

Heat Capacity.

The heat capacity data of T. B. Douglas, A. F. Ball, D. C. Ginnings and W. D. Davis, J. Am. Chem. Soc. **74**, 2472 (1952) were used and were extrapolated below T_m and above 1173°K in a reasonable manner.

Entropy.

Back calculated from the entropy of the liquid at the melting point and the extrapolated heat capacity from the melting point to 298°K .

Vaporization.

Sodium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1156°K . The vapor pressure of the monatomic gas reaches 1 atm. at 1176.9°K and the heat of vaporization to monatomic gas is $23.285 \text{ kcal. mole}^{-1}$ [See Na(cryatal)].

Na

Sodium, Monatomic (Na)

(Ideal Gas) At. Wt. = 22.991

Na

AT. WT. = 22.991

(IDEAL GAS)

SODIUM, MONATOMIC (Na)

T, °K.	C_p°	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	INFINITE	-1.481	25.815	25.815	INFINITE
100	4.966	31.266	41.131	25.992	23.432	51.208
200	4.966	34.730	37.168	25.991	20.900	72.838
298	4.966	36.714	36.714	25.755	18.475	13.542
300	4.966	36.745	36.714	25.752	18.431	13.426
400	4.966	38.174	36.909	24.905	16.070	6.780
500	4.966	39.282	37.277	24.661	13.890	6.071
600	4.966	40.188	37.689	24.637	11.757	5.282
700	4.966	40.958	38.102	24.227	9.660	4.462
800	4.966	41.617	38.501	24.029	7.593	3.608
900	4.966	42.203	38.880	23.990	5.550	2.078
1000	4.966	42.726	39.239	23.643	3.529	1.348
1100	4.966	43.200	39.578	23.688	1.524	0.771
1200	4.966	43.632	40.000	23.688	0.000	0.303
1300	4.966	44.030	40.201	0.000	0.000	0.000
1400	4.966	44.398	40.688	5.977	0.000	0.000
1500	4.966	44.740	40.760	0.000	0.000	0.000
1600	4.966	45.061	41.019	0.000	0.000	0.000
1700	4.966	45.362	41.501	0.000	0.000	0.000
1800	4.970	45.646	41.726	0.000	0.000	0.000
1900	4.971	45.915	41.726	0.000	0.000	0.000
2000	4.973	46.170	41.942	0.000	0.000	0.000
2100	4.975	46.413	42.169	0.000	0.000	0.000
2200	4.979	46.642	42.388	0.000	0.000	0.000
2300	4.984	46.866	42.580	0.000	0.000	0.000
2400	4.990	47.078	42.725	0.000	0.000	0.000
2500	5.001	47.282	42.903	0.000	0.000	0.000
2600	5.013	47.478	43.075	0.000	0.000	0.000
2700	5.027	47.668	43.242	0.000	0.000	0.000
2800	5.044	47.851	43.403	0.000	0.000	0.000
2900	5.065	48.028	43.560	0.000	0.000	0.000
3000	5.089	48.200	43.711	0.000	0.000	0.000
3100	5.118	48.369	43.859	0.000	0.000	0.000
3200	5.148	48.531	44.002	0.000	0.000	0.000
3300	5.184	48.690	44.142	0.000	0.000	0.000
3400	5.225	48.845	44.278	0.000	0.000	0.000
3500	5.272	48.997	44.411	0.000	0.000	0.000
3600	5.324	49.146	44.540	0.000	0.000	0.000
3700	5.381	49.293	44.665	0.000	0.000	0.000
3800	5.440	49.437	44.780	0.000	0.000	0.000
3900	5.522	49.580	44.911	0.000	0.000	0.000
4000	5.614	49.721	45.030	0.000	0.000	0.000
4100	5.696	49.860	45.146	0.000	0.000	0.000
4200	5.794	49.999	45.259	0.000	0.000	0.000
4300	5.913	50.136	45.372	0.000	0.000	0.000
4400	6.041	50.274	45.482	0.000	0.000	0.000
4500	6.182	50.411	45.590	0.000	0.000	0.000
4600	6.339	50.549	45.694	0.000	0.000	0.000
4700	6.513	50.687	45.801	0.000	0.000	0.000
4800	6.705	50.826	45.904	0.000	0.000	0.000
4900	6.915	50.966	46.006	0.000	0.000	0.000
5000	7.147	51.104	46.106	0.000	0.000	0.000
5100	7.399	51.252	46.206	0.000	0.000	0.000
5200	7.674	51.399	46.306	0.000	0.000	0.000
5300	7.972	51.548	46.402	0.000	0.000	0.000
5400	8.294	51.700	46.498	0.000	0.000	0.000
5500	8.639	51.855	46.594	0.000	0.000	0.000
5600	9.006	52.018	46.690	0.000	0.000	0.000
5700	9.402	52.184	46.785	0.000	0.000	0.000
5800	9.816	52.344	46.879	0.000	0.000	0.000
5900	10.256	52.515	46.973	0.000	0.000	0.000
6000	10.716	52.692	47.067	0.000	0.000	0.000

June 30, 1962

$\Delta H_{f,0}^\circ = 25.815$ kcal. mole⁻¹ $\Delta H_{f,298.15}^\circ = 25.755$ kcal. mole⁻¹
 $\Delta F_{f,0}^\circ = 25.815$ kcal. mole⁻¹ $\Delta F_{f,298.15}^\circ = 25.755$ kcal. mole⁻¹
 Ground State Configuration $2s_{1/2}^2$ $S_{298.15}^\circ = 36.714$ cal. deg.⁻¹ mole⁻¹

Electronic Levels and Multiplicities

ϵ_1	ϵ_1 cm. ⁻¹	ϵ_1	ϵ_1 cm. ⁻¹	ϵ_1	ϵ_1 cm. ⁻¹
0	0	2	34,549	10	39,012
2	16,956	2	34,589	14	39,399
4	16,973	4	35,042	6	38,541
25,740	25,740	2	36,373	2	39,230
29,173	29,173	10	37,037	10	40,700
30,267	30,267	2	37,058	14	40,736
30,273	30,273	4	37,060	18	41,330
33,201	33,201	2	37,237	6	

Heat of Formation.

Same as the heat of sublimation to the monatomic species; see notes on Na(crystal)

Heat Capacity and Entropy.

The energy levels have been taken from C. E. Moore, "National Bureau of Standards Circular 487," U. S. Government Printing Office, Washington (1949) p. 83-91. Closely spaced levels have been averaged and the appropriate multiplicities assigned to the averages.

Na

Na⁺

Sodium Unipositive Ion (Na⁺)
(Ideal Gas) At. Wt. = 22.991

SODIUM UNIPOSITIVE ION (Na⁺) (IDEAL GAS)

AT. WT. = 22.991

Ground State Configuration 1S₀
S_{298.15} = 35.336 cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ = 144.334 kcal. mole⁻¹
ΔH_f⁰ 298.15 = 145.755 kcal. mole⁻¹

Electronic Levels and Multiplicities

E, cm. ⁻¹	g _i
0	1
266192	12
298614	36
331860	72
358298	27

Heat of Formation.

The heat of formation at 0°K. was obtained from that of the ideal monatomic sodium gas by adding the enthalpy of ionization, calculated from the ionization limit given by C. E. Moore "Atomic Energy Levels" Natl. Bur. Standards Circ. 467 (1949). This was converted to 298°K. by using the formation equation Na(ref. state) - e⁻(ref. state) = Na⁺(monatomic gas), thus Na⁺ involves the difference in enthalpies of the two reference states as well as its own enthalpy.

Heat Capacity and Entropy.

These were calculated using the electronic energy levels tabulated above, taken from C. E. Moore loc. cit.

T.°K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈)/T kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0					
100	4.968	35.336	145.755	137.399	-100.711
200	4.968	35.336	145.755	137.347	-100.083
298	4.968	35.336	145.755	137.347	-100.083
300	4.968	35.336	145.755	137.347	-100.083
400	4.968	35.336	145.755	131.803	-57.608
500	4.968	35.336	145.755	129.006	-46.988
600	4.968	35.336	145.755	126.159	-39.387
700	4.968	35.336	145.755	123.281	-33.625
800	4.968	35.336	145.755	120.374	-29.272
900	4.968	35.336	145.755	117.439	-25.655
1000	4.968	35.336	145.755	114.404	-22.729
1100	4.968	35.336	145.755	111.369	-20.369
1200	4.968	35.336	145.755	108.334	-18.622
1300	4.968	35.336	145.755	105.299	-17.478
1400	4.968	35.336	145.755	102.264	-16.810
1500	4.968	35.336	145.755	99.229	-16.600
1600	4.968	35.336	145.755	96.194	-16.600
1700	4.968	35.336	145.755	93.159	-16.600
1800	4.968	35.336	145.755	90.124	-16.600
1900	4.968	35.336	145.755	87.089	-16.600
2000	4.968	35.336	145.755	84.054	-16.600
2100	4.968	35.336	145.755	81.019	-16.600
2200	4.968	35.336	145.755	77.984	-16.600
2300	4.968	35.336	145.755	74.949	-16.600
2400	4.968	35.336	145.755	71.914	-16.600
2500	4.968	35.336	145.755	68.879	-16.600
2600	4.968	35.336	145.755	65.844	-16.600
2700	4.968	35.336	145.755	62.809	-16.600
2800	4.968	35.336	145.755	59.774	-16.600
2900	4.968	35.336	145.755	56.739	-16.600
3000	4.968	35.336	145.755	53.704	-16.600
3100	4.968	35.336	145.755	50.669	-16.600
3200	4.968	35.336	145.755	47.634	-16.600
3300	4.968	35.336	145.755	44.599	-16.600
3400	4.968	35.336	145.755	41.564	-16.600
3500	4.968	35.336	145.755	38.529	-16.600
3600	4.968	35.336	145.755	35.494	-16.600
3700	4.968	35.336	145.755	32.459	-16.600
3800	4.968	35.336	145.755	29.424	-16.600
3900	4.968	35.336	145.755	26.389	-16.600
4000	4.968	35.336	145.755	23.354	-16.600
4100	4.968	35.336	145.755	20.319	-16.600
4200	4.968	35.336	145.755	17.284	-16.600
4300	4.968	35.336	145.755	14.249	-16.600
4400	4.968	35.336	145.755	11.214	-16.600
4500	4.968	35.336	145.755	8.179	-16.600
4600	4.968	35.336	145.755	5.144	-16.600
4700	4.968	35.336	145.755	2.109	-16.600
4800	4.968	35.336	145.755	-0.926	-16.600
4900	4.968	35.336	145.755	-3.961	-16.600
5000	4.968	35.336	145.755	-6.996	-16.600
5100	4.968	35.336	145.755	-10.031	-16.600
5200	4.968	35.336	145.755	-13.066	-16.600
5300	4.968	35.336	145.755	-16.101	-16.600
5400	4.968	35.336	145.755	-19.136	-16.600
5500	4.968	35.336	145.755	-22.171	-16.600
5600	4.968	35.336	145.755	-25.206	-16.600
5700	4.968	35.336	145.755	-28.241	-16.600
5800	4.968	35.336	145.755	-31.276	-16.600
5900	4.968	35.336	145.755	-34.311	-16.600
6000	4.968	35.336	145.755	-37.346	-16.600

Na⁺

Mar. 31, 1965

Sodium Monoxide (NaO)
(Ideal Gas)

GFW = 38.9892

SODIUM MONOXIDE (NaO)

(IDEAL GAS)

NaO

GFN = 38.9892

Ground State Configuration [2P]
 $S_{298.15}^\circ = [54.7 \pm 0.5] \text{ gibbs/mol}$
 $\Delta H_f^\circ = [20.3 \pm 10] \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = [20.0 \pm 10] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\frac{E_i, \text{ cm}^{-1}}{0}$ $\frac{g_i}{[4]}$

$\omega_e = [440] \text{ cm}^{-1}$
 $\omega_e x_e = [3.0] \text{ cm}^{-1}$
 $\sigma = 1$
 $\alpha_e = [0.4467] \text{ cm}^{-1}$
 $r_e = [2.0] \text{ \AA}$

Heat of Formation

Bawn and Evans (2) have studied the reaction rate of sodium vapor with nitrous oxide, nitrogen peroxide, nitromethane, ethyl nitrate and amyl nitrite, using the diffusion flame method. On the avoidance of reaction rate measurements they estimated the value, $\Delta H_{298}^\circ < 0$, for the reaction $\text{Na(g)} + \text{NO}_2(\text{g}) = \text{NaO(g)} + \text{NO(g)}$. Based on this result, we calculate $\Delta H_{298}^\circ(\text{NaO, g}) > 12 \text{ kcal/mol}$, using $\Delta H_{298}^\circ = 25.8, 7.9$ and 21.6 kcal/mol for $\text{Na(g)}, \text{NO}_2(\text{g})$ and NO(g) , respectively.

Assuming that $D_0(\text{NaO}) = 1/2 D_0(\text{Na}_2) + D_0(\text{O}_2)$, or $\Delta H_0^\circ = 68.1 \text{ kcal/mol}$ for the reaction $\text{NaO(g)} = \text{Na(g)} + \text{O(g)}$, we derive $\Delta H_0^\circ = 16.7$ and $\Delta H_{298}^\circ = 16.4 \text{ kcal/mol}$, using $\Delta H_0^\circ = 25.8$ and 59.0 kcal/mol for Na(g) and O(g) , respectively.
Somayajulu (2) found that in a sequence of similar diatomic molecules the force constant (k_e), dissociation energy (D_0) and equilibrium bond distance (r_e) are related by the expression $k_e r_e^2/D_0 = \text{constant}$. Using $r_e = 1.62 \text{ \AA}$, $D_0 = 77.9 \text{ kcal/mol}$ for LiO(g) , $r_e = 2.0 \text{ \AA}$ for NaO(g) and $k_e(\text{NaO})/k_e(\text{LiO}) = 0.4827$, we evaluate $D_0 = 65.4 \text{ kcal/mol}$ for NaO(g) , yielding $\Delta H_{298}^\circ(\text{NaO, g}) = 19.4 \text{ kcal/mol}$. The value k_e is calculated from the relation $k_e = 4\pi^2 \nu^2 \mu$ where ν is the vibrational frequency of the diatomic molecule and μ is the reduced mass.

The value of $\Delta H_{298}^\circ(\text{NaO, g})$ is tentatively adopted as $20 \pm 10 \text{ kcal/mol}$. The corresponding $D_0^\circ(\text{NaO})$ is $65 \pm 10 \text{ kcal/mol}$.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that for OH(g) which has the same number of valence electrons as NaO(g) . The values of ω_e and $\omega_e x_e$ are estimated by comparison with those for LiO(g) , LiF(g) and NaF(g) . The value of r_e is estimated from those for OH(g) , HF(g) and NaF(g) . B_e and α_e are derived from r_e , ω_e and $\omega_e x_e$ by the method suggested by Herzberg (3).

References

1. C. E. H. Bawn and A. G. Evans, Trans. Faraday Soc. **33**, 1571 (1937).
2. G. R. Somayajulu, J. Chem. Phys. **33**, 1541 (1960).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

T, °K	Cp ^a	$\frac{g_i - g_0}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	H ^a - H ^a ₂₉₈	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	-2.253	20.326	20.126	INFINITE
100	7.113	46.297	61.889	-1.555	20.356	19.365	-40.137
200	7.315	51.475	55.492	-1.403	20.173	16.445	-17.970
298	4.400	54.737	-0.000	-0.000	20.000	14.632	-10.740
300	8.407	54.789	54.737	-0.014	19.097	14.619	-10.650
400	4.656	57.245	55.071	-0.870	19.152	12.906	-7.052
500	4.798	59.194	55.707	-1.743	18.919	11.373	-4.971
600	8.888	60.804	56.428	-2.628	18.705	9.884	-3.600
700	8.952	62.181	57.153	-3.520	18.502	8.428	-2.632
800	9.202	63.380	57.458	-4.418	18.306	7.004	-1.913
900	9.042	64.443	58.531	-5.320	18.111	5.603	-1.361
1000	9.077	65.397	59.171	-6.224	17.914	4.224	-0.923
1100	9.108	66.264	59.777	-7.135	17.707	2.844	-0.569
1200	9.135	67.056	60.350	-8.061	17.494	1.464	-0.311
1300	9.163	67.780	60.896	-8.983	17.275	0.084	-0.081
1400	9.188	68.470	61.413	-9.480	17.056	3.270	-0.510
1500	9.213	69.105	61.905	-10.400	16.837	3.916	-0.571
1600	9.236	69.700	62.373	-11.723	16.618	4.563	-0.623
1700	9.257	70.261	62.819	-13.042	16.398	5.212	-0.666
1800	9.276	70.793	63.245	-14.357	16.178	5.860	-0.701
1900	9.294	71.293	63.659	-15.658	15.958	6.509	-0.729
2000	9.325	71.771	64.053	-16.945	15.738	7.154	-0.782
2100	9.347	72.226	64.432	-18.219	15.518	7.803	-0.813
2200	9.369	72.658	64.795	-19.482	15.298	8.452	-0.840
2300	9.389	73.072	65.145	-20.735	15.078	9.101	-0.868
2400	9.410	73.478	65.483	-21.982	14.858	9.750	-0.889
2500	9.431	73.863	65.813	-23.214	14.638	10.401	-0.911
2600	9.452	74.233	66.130	-24.439	14.418	11.050	-0.931
2700	9.471	74.588	66.435	-25.658	14.198	11.700	-0.947
2800	9.489	74.935	66.732	-26.872	13.978	12.350	-0.961
2900	9.514	75.269	67.023	-28.083	13.758	13.000	-0.983
3000	9.538	75.592	67.303	-29.286	13.538	13.650	-0.998
3100	9.555	75.905	67.575	-30.482	13.318	14.300	-1.013
3200	9.569	76.208	67.840	-31.675	13.098	14.950	-1.026
3300	9.583	76.500	68.098	-32.865	12.878	15.600	-1.038
3400	9.596	76.790	68.350	-34.052	12.658	16.250	-1.051
3500	9.616	77.069	68.595	-35.238	12.438	16.900	-1.063
3600	9.655	77.341	68.834	-36.423	12.218	17.550	-1.074
3700	9.679	77.606	69.068	-37.608	11.998	18.200	-1.084
3800	9.699	77.865	69.298	-38.792	11.778	18.850	-1.094
3900	9.717	78.116	69.519	-39.975	11.558	19.500	-1.103
4000	9.737	78.362	69.737	-41.158	11.338	20.150	-1.113
4100	9.757	78.603	69.950	-42.342	11.118	20.800	-1.122
4200	9.774	78.839	70.159	-43.525	10.898	21.450	-1.130
4300	9.789	79.069	70.365	-44.708	10.678	22.100	-1.139
4400	9.804	79.294	70.564	-45.891	10.458	22.750	-1.147
4500	9.818	79.515	70.760	-47.075	10.238	23.400	-1.155
4600	9.854	79.711	70.953	-48.258	10.018	24.050	-1.162
4700	9.869	80.015	71.132	-49.442	9.798	24.700	-1.170
4800	9.884	80.152	71.322	-50.625	9.578	25.350	-1.177
4900	9.914	80.356	71.510	-51.808	9.358	26.000	-1.184
5000	9.938	80.557	71.649	-53.000	9.138	26.650	-1.191
5100	9.958	80.754	71.865	-54.183	8.918	27.300	-1.198
5200	9.979	80.948	72.071	-55.366	8.698	27.950	-1.205
5300	9.999	81.134	72.267	-56.549	8.478	28.600	-1.212
5400	10.019	81.325	72.459	-57.732	8.258	29.250	-1.219
5500	10.039	81.509	72.651	-58.915	8.038	29.900	-1.226
5600	10.059	81.690	72.841	-60.098	7.818	30.550	-1.233
5700	10.079	81.868	73.027	-61.281	7.598	31.200	-1.240
5800	10.099	82.043	73.211	-62.464	7.378	31.850	-1.247
5900	10.119	82.216	73.393	-63.647	7.158	32.500	-1.254
6000	10.139	82.386	73.573	-64.830	6.938	33.150	-1.261

Dec. 31, 1950; Dec. 31, 1957

NaO

Sodium Monoxide Uninegative Ion (NaO⁻)

(Ideal Gas)

GFW = 38.98975

NaO⁻

T, °K	C _p ^o	S ^o	-(G ^o -H ²⁹⁸)/T	H ^o -H ²⁹⁸	ΔH ^o	ΔG ^o	Log K _p
0							
100	9.390	51.954	51.954	0.000	29.000	32.031	23.479
200							
298	9.387	52.004	51.954	0.014	29.012	32.049	23.348
300	8.584	54.557	52.288	0.668	30.355	32.907	17.979
400	8.791	56.403	52.922	1.741	31.087	33.459	14.625
500							
600	9.955	58.015	53.640	2.625	31.799	33.955	12.336
700	8.952	59.390	54.366	3.517	32.497	34.155	10.644
800	9.083	60.552	55.076	4.431	33.182	34.448	9.365
900	9.083	61.552	55.740	5.317	33.882	34.448	8.365
1000	9.081	62.507	56.383	6.124	34.574	34.474	7.534
1100	9.114	63.474	56.999	7.133	35.279	34.432	6.841
1200	9.143	64.268	57.563	8.046	35.927	33.857	6.168
1300	9.171	65.001	58.107	8.862	36.723	33.171	5.514
1400	9.198	65.681	58.631	9.591	37.568	32.484	4.881
1500	9.222	66.317	59.114	10.801	60.749	27.7350	3.985
1600	9.247	66.913	59.595	11.725	61.258	25.106	3.429
1700	9.270	67.474	60.033	12.651	61.766	22.830	2.935
1800	9.294	68.005	60.461	13.579	62.275	20.525	2.492
1900	9.317	68.511	60.881	14.500	62.784	18.190	2.098
2000	9.339	68.988	61.265	15.442	63.298	15.833	1.730
2100	9.361	69.442	61.644	16.377	63.810	13.466	1.399
2200	9.383	69.878	62.008	17.314	64.324	11.035	1.096
2300	9.405	70.296	62.360	18.254	64.836	8.617	0.810
2400	9.427	70.697	62.699	19.197	65.345	6.210	0.544
2500	9.449	71.082	63.026	20.139	65.855	3.817	0.321
2600							
2700	9.470	71.453	63.343	21.085	66.365	1.170	0.098
2800	9.492	71.811	63.650	22.033	66.904	1.345	0.109
2900	9.513	72.156	63.948	22.983	67.429	3.093	0.303
3000	9.534	72.488	64.231	23.934	67.948	4.841	0.497
3100	9.554	72.811	64.517	24.890	68.473	6.515	0.657
3200							
3300	9.577	73.128	64.790	25.847	69.007	11.608	0.818
3400	9.598	73.432	65.055	26.806	69.539	14.214	0.971
3500	9.619	73.728	65.314	27.767	70.075	16.839	1.115
3600	9.640	74.013	65.566	28.730	70.610	19.450	1.258
3700	9.661	74.293	65.811	29.695	71.157	22.140	1.382
3800							
3900	9.682	74.568	66.050	30.662	71.706	24.813	1.506
4000	9.703	74.833	66.284	31.631	72.260	27.503	1.625
4100	9.724	75.092	66.513	32.602	72.819	30.209	1.737
4200	9.744	75.342	66.738	33.576	73.380	32.936	1.848
4300	9.764	75.592	66.958	34.551	73.958	35.658	1.948
4400							
4500	9.787	75.834	67.168	35.529	74.540	38.402	2.047
4600	9.808	76.070	67.377	36.509	75.131	41.165	2.142
4700	9.829	76.301	67.582	37.491	75.731	43.944	2.233
4800	9.849	76.526	67.783	38.474	76.331	46.730	2.321
4900	9.870	76.748	67.977	39.460	76.937	49.540	2.408
5000							
5100	9.891	76.966	68.172	40.449	77.605	52.356	2.497
5200	9.912	77.179	68.362	41.439	78.259	55.199	2.566
5300	9.933	77.397	68.548	42.431	78.931	58.036	2.642
5400	9.953	77.611	68.731	43.424	79.604	60.866	2.718
5500	9.975	77.796	68.909	44.422	80.331	63.768	2.789
5600							
5700	9.995	77.991	69.085	45.420	81.065	66.652	2.857
5800	10.016	78.186	69.259	46.421	81.823	69.561	2.924
5900	10.037	78.377	69.429	47.423	82.609	72.484	2.989
6000	10.057	78.566	69.596	48.426	83.424	75.415	3.052
6100	10.079	78.749	69.761	49.435	84.273	78.334	3.114
6200							
6300	10.099	78.931	69.923	50.444	85.154	81.331	3.174
6400	10.120	79.110	70.093	51.455	86.072	84.307	3.233
6500	10.141	79.286	70.240	52.468	87.028	87.309	3.290
6600	10.161	79.459	70.386	53.482	88.009	90.334	3.346
6700	10.182	79.631	70.547	54.500	89.069	93.354	3.400

Dec. 31, 1967

NaO⁻SODIUM MONOXIDE UNINEGATIVE ION (NaO⁻)

(IDEAL GAS)

GFW = 38.98975

Ground State Configuration {²S}ΔH_f^o = [-29 ± 20] kcal/molS_{298.15}^o = [52.0 ± 0.5] gibbys/molΔH_f^o_{298.15} = [-29 ± 20] kcal/mol

Electronic Levels and Quantum Weights

 $\frac{g_i}{0}$
 $\frac{g_i}{(1)}$ $\omega_{e'X} = [3.2] \text{ cm}^{-1}$
 $\omega_{e'e} = [0.00493] \text{ cm}^{-1}$
 $\sigma = 1$
 $r_e = [2.0] \text{ \AA}$

Heat of Formation

The electron affinity (E. A.) of NaO⁻(g) is unavailable, therefore the value of ΔH_f^o(NaO⁻, g) is estimated. We first assume that the enthalpy change (ΔH_f^o) of the reaction (1) NaO⁻(g) = Na(g) + O⁻(g) is close to the average of the ΔH_f^o values for the reactions (2) NaO(g) = Na(g) + O(g) and (3) NaF(g) = Na(g) + F(g). The atom F(g) is isoelectronic with O⁻(g). In other words, the ΔH_f^o for reaction (1) is approximately 1/2(64.8 + 113.4) = 89.3 kcal/mol. Then we compare the ΔH_f^o values for the reactions (4) HO(g) = H(g) + O(g), (5) HO⁻(g) = H(g) + O⁻(g), and (6) HF(g) = H(g) + F(g), and find that ΔH_f^o for reaction (5) is experimentally determined as 109.7 kcal/mol which is about 8 kcal/mol more negative than the average of ΔH_f^o values for reactions (4) and (6). Based on this fact we estimate ΔH_f^o = 80 kcal/mol for reaction (1), yielding ΔH_f^o₂₉₈(NaO⁻, g) = -29 kcal/mol which is tentatively adopted. The uncertainty of this value may be ±20 kcal/mol. Based on this ΔH_f^o₂₉₈ value we calculate E. A. = 2.1 ± 0.9 eV for NaO(g). The corresponding value for HO(g) is 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of NaF(g) which is isoelectronic with NaO⁻(g). The values of ω_e, ω_{e'X} and r_e are estimated by comparison with the observed data for NaF(g). The values of B_e and g_e are calculated from r_e, ω_e and ω_{e'X} using the method recommended by G. Herzberg, "Spectra of Diatomic Molecules." D. Van Nostrand Co., Inc., New York, 1950. The enthalpy at 0°K is -2.248 kcal/mol.

Sodium Dioxide (NaO₂)NaO₂

(Crystal) Mol. Wt. = 54.991

SODIUM DIOXIDE (NaO₂)

(CRYSTAL)

MOL. WT. = 54.991

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	0.000	INFINITE	4.384	63.070	63.070	INFINITE
100	10.850	7.310	3.527	63.549	63.549	6.0677
200	17.202	27.700	.000	62.100	52.282	38.332
300	17.240	27.807	.032	62.293	52.219	38.040
400	16.230	32.905	1.806	62.578	48.865	26.657
500	14.210	37.078	3.678	62.174	45.461	14.079
600	20.190	40.667	31.253	61.680	42.187	15.366
700	21.147	43.852	32.829	61.096	38.985	12.171
800	22.140	46.742	34.391	60.424	35.871	9.799
900	23.121	49.407	35.913	59.664	32.846	7.976
1000	24.100	51.894	37.388	58.820	29.710	6.536
1100	25.078	54.236	38.814	57.897	27.065	5.377
1200	26.055	56.460	40.193	56.921	23.948	4.343
1300	27.031	58.584	41.526	55.927	19.210	3.289
1400	28.004	60.623	42.818	54.927	14.076	2.291
1500	28.980	62.589	44.071	53.955	10.244	1.493
1600	29.957	64.490	45.288	53.022	7.432	.808
1700	30.935	66.336	46.472	52.116	5.214	.217
1800	31.913	68.132	47.626	51.241	3.443	-.297
1900	32.891	69.883	48.751	50.411	2.111	-.784
2000	33.870	71.595	49.851	49.629	1.156	-.1156

$S_{298.15}^0 = 27.7 \pm 0.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_{t_1} = 196.5^\circ \text{K.}$
 $T_{t_2} = 223.5^\circ \text{K.}$
 $T_m = 825^\circ \pm 10^\circ \text{K.}$

Heat of Formation.

ΔH_f^0 298.15 was obtained from National Bureau of Standards Report 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds," January 1, 1962. P. W. Olliea and J. L. Margrave, J. Phys. Chem. 60, 1333 (1956) measured the heat of decomposition of NaO₂(c) in H₂O, yielding ΔH_f^0 298.15 = -62.1 + 0.7 kcal. mole⁻¹. From the original experimental data by R. de Forcrand, Compt. rend., 127, 514 (1898); 158, 843, 931 (1914), the value of ΔH_f^0 298.15 was recalculated to be -65.0 kcal. mole⁻¹ by P. W. Olliea and J. L. Margrave, loc. cit.

Heat Capacity and Entropy.

The low temperature heat capacities, $52.13^\circ \sim 296.46^\circ \text{K.}$, were measured by S. S. Todd, J. Am. Chem. Soc., 75, 1229 (1953). The heat capacities above 298.15°K. were estimated by comparison with those for Na₂O(c). $S_{298.15}^0$ was given by S. S. Todd, loc. cit., using S_{51}^0 (extrap.) = 2.23 cal. deg.⁻¹ mole⁻¹.

Transition Data.

T_{t_1} , T_{t_2} , $\Delta H_{t_1}^0$, and $\Delta H_{t_2}^0$ were calculated from the data reported by S. S. Todd, loc. cit.

Temperature of Melting.

The melting temperature was obtained from J. L. Margrave, private communication, May 21, 1963.

June 30, 1963

~~Na₂O~~
 NaO₂

Sodium, Diatomic (Na₂)

(Ideal Gas) Mol. Wt. = 45.982

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° ₂₉₈	Log K _p
0	0.000	INF. NITE	2.485	33.467	INF. NITE
100	0.302	45.484	1.736	30.166	65.924
200	0.816	51.443	0.873	26.866	29.356
298	0.963	54.994	0.000	23.607	17.450
300	0.965	55.050	0.017	23.782	17.302
400	1.054	55.004	0.347	20.895	11.412
500	1.101	59.665	0.615	18.409	8.046
600	1.150	61.328	0.766	16.041	5.843
700	1.195	62.742	0.829	13.757	4.295
800	1.237	63.973	0.823	11.566	3.154
900	1.276	65.054	0.782	9.584	2.305
1000	1.319	66.043	0.611	7.865	1.592
1100	1.359	66.933	0.237	6.366	1.038
1200	1.399	67.749	0.029	5.129	0.619
1300	1.439	68.503	0.181	4.119	0.352
1400	1.475	69.205	0.321	3.307	0.181
1500	1.516	69.859	0.432	2.641	0.000
1600	1.555	70.474	0.515	2.100	-0.181
1700	1.594	71.055	0.579	1.682	-0.352
1800	1.633	71.605	0.623	1.362	-0.515
1900	1.672	72.126	0.643	1.108	-0.665
2000	1.711	72.623	0.649	0.908	-0.800
2100	1.749	73.098	0.640	0.752	-0.920
2200	1.786	73.552	0.617	0.632	-1.028
2300	1.823	73.987	0.583	0.546	-1.125
2400	1.865	74.407	0.531	0.493	-1.210
2500	1.904	74.811	0.470	0.469	-1.282
2600	1.942	75.200	0.400	0.469	-1.342
2700	1.981	75.576	0.317	0.484	-1.389
2800	2.019	75.940	0.225	0.514	-1.425
2900	2.056	76.290	0.125	0.556	-1.450
3000	2.097	76.634	0.016	0.606	-1.465
3100	2.135	76.965	0.000	0.663	-1.470
3200	2.174	77.288	0.076	0.729	-1.465
3300	2.213	77.601	0.144	0.806	-1.450
3400	2.251	77.901	0.204	0.894	-1.425
3500	2.290	78.204	0.256	0.994	-1.390
3600	2.328	78.495	0.302	1.106	-1.345
3700	2.367	78.778	0.356	1.230	-1.290
3800	2.406	79.054	0.406	1.366	-1.225
3900	2.444	79.324	0.452	1.514	-1.150
4000	2.482	79.591	0.500	1.674	-1.065
4100	2.521	79.850	0.540	1.846	-0.970
4200	2.559	80.104	0.598	2.030	-0.865
4300	2.596	80.357	0.656	2.226	-0.750
4400	2.634	80.607	0.713	2.434	-0.625
4500	2.675	80.837	0.770	2.654	-0.490
4600	2.713	81.072	0.825	2.886	-0.345
4700	2.752	81.303	0.878	3.130	-0.190
4800	2.790	81.529	0.929	3.386	-0.025
4900	2.829	81.751	0.978	3.654	0.140
5000	2.868	81.971	1.025	3.934	0.295
5100	2.906	82.187	1.070	4.226	0.440
5200	2.945	82.399	1.113	4.530	0.575
5300	2.984	82.606	1.156	4.846	0.700
5400	3.023	82.810	1.198	5.174	0.815
5500	3.062	83.016	1.239	5.514	0.920
5600	3.101	83.216	1.279	5.866	1.015
5700	3.140	83.413	1.318	6.230	1.100
5800	3.179	83.608	1.356	6.606	1.175
5900	3.218	83.800	1.394	6.994	1.240
6000	3.257	83.987	1.431	7.394	1.295

June 30, 1962

Na₂

MOL. WT. = 45.982

(IDEAL GAS)

SODIUM, DIATOMIC (Na₂)

ΔH°_f = 33.467 kcal. mole⁻¹
 ΔH°_f 298.15 = 32.87 kcal. mole⁻¹
 S°_{298.15} = 54.994 cal. deg.⁻¹ mole⁻¹

Ground State Configuration = 1Σ⁺

ω_e = 159.23 cm.⁻¹
 B_e = 0.15471 cm.⁻¹
 ω_ex_e = 0.726 cm.⁻¹
 α_e = 0.00079 cm.⁻¹
 σ = 2
 r_e = 3.076(6) Å

Heat of Formation.

Same as the heat of sublimation for the diatomic gas; see notes on Na(crystal)

Heat Capacity and Entropy.

Spectroscopic data from G. Herzberg, "Spectra of Diatomic Molecules," 2nd Edn., D. Van Nostrand Co., Inc., New York (1950).

Na₂

DISODIUM MONOXIDE (Na₂O)

(CRYSTAL)

GFW = 61.979

$$S_{298.15}^{\circ} = 17.935 \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} = -98.74 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_{298.15}^{\circ} = -99.90 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_f^{\circ}(\gamma + \beta) = 1023.2^{\circ}\text{K}$$

$$\Delta H_f^{\circ}(\beta + \alpha) = 1243.2^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 1405.2^{\circ}\text{K}$$

$$\Delta H_f^{\circ} = -98.74 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_{298.15}^{\circ} = -99.90 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_f^{\circ}(\gamma + \beta) = 1023.2^{\circ}\text{K}$$

$$\Delta H_f^{\circ}(\beta + \alpha) = 1243.2^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 1405.2^{\circ}\text{K}$$

Disodium Monoxide (Na₂O) GFW = 61.979

(Crystal)

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	7.428	3.479	30.857	2.665	98.744	98.744	INFINITE
200	14.213	11.761	19.367	1.585	96.642	96.642	71.1212
298	16.516	17.935	17.935	1.000	95.000	95.000	66.418
300	16.550	18.038	17.936	1.031	95.000	95.000	65.966
400	18.111	23.017	18.604	1.765	101.209	101.209	47.714
500	19.478	27.217	19.917	3.648	101.174	83.656	36.654
600	20.685	30.854	21.483	5.668	100.993	80.410	29.249
700	21.756	34.073	23.022	7.735	100.707	77.003	24.041
800	21.819	36.948	24.586	9.889	100.342	73.640	20.118
900	22.291	39.546	26.106	12.095	99.923	70.327	17.078
1000	22.666	41.915	27.570	14.345	99.467	67.062	14.656
1100	23.029	44.504	29.004	17.051	98.572	63.879	12.492
1200	23.534	47.521	30.390	19.369	97.558	59.832	10.697
1300	23.611	50.693	31.795	21.567	96.783	55.938	8.500
1400	23.667	52.452	33.205	24.591	95.635	46.217	7.215
1500	24.168	54.167	34.587	28.339	93.866	39.564	5.764
1600	24.336	55.470	35.818	31.743	92.474	32.975	4.504
1700	24.566	57.152	37.031	34.706	91.464	26.448	3.400
1800	24.765	58.561	38.168	36.472	90.837	19.983	2.476
1900	24.949	59.906	39.296	39.159	90.479	13.479	1.561
2000	25.169	61.192	40.355	41.666	90.331	7.224	.749

Heat of Formation

The enthalpy change of the reaction $\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(aq)$ has been determined by Matsui (1, 2), Roth (3, 4) and Rengade (5). Based on their reported ΔH_f° values, the corresponding ΔH_f° for $\text{Na}_2\text{O}(c)$ are calculated, using $\Delta H_f^{\circ}(\text{H}_2\text{O}, l) = -68.315 \text{ kcal/mol}$ obtained from U. S. Natl. Bur. Std. Tech. Note 270-1, 1955, and $\Delta H_f^{\circ}(\text{NaOH}, \text{aq})$ derived from JANAF $\Delta H_f^{\circ}(\text{NaOH}, c)$ and ΔH_{soln} and ΔH_{dil} reported by V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965. The sample employed by Matsui was prepared by the method of Rengade (2) and contains $\text{Na}_2\text{O}_2(c)$ and $\text{Na}(c)$ as impurities. The sample used by Roth also contains 3.96 per cent (by weight) $\text{Na}_2\text{O}_2(c)$. Corrections in the reported results for such impurities have been made by the authors. However, in order to obtain better results, more measurements using purer samples are necessary. The enthalpy change of the reaction $2\text{Na}(c) + \text{H}_2\text{O}(l) = \text{Na}_2\text{O}(c) + \text{H}_2(g)$ was calculated by Rengade (5) from his measurements (5) incorporating with $\Delta H_f^{\circ} = -85.2 \text{ kcal/mol}$ for the reaction $2\text{Na}(c) + 2\text{H}_2\text{O}(l) = 2\text{NaOH}(aq) + \text{H}_2(g)$ determined by Joannis (6). The value $\Delta H_f^{\circ} = -94.9 \text{ kcal/mol}$ is derived from the data of Forcand (6) using $\Delta H_f^{\circ}(\text{Na}_2\text{O}_2, c) = -122.6 \text{ kcal/mol}$. The results are presented in the table below.

Brewer (11) determined the equilibrium constants, 918-1467°K, for the vaporization of $\text{Na}_2\text{O}(c)$, using an effusion method. The Na_2O vapor consists predominantly of $\text{Na}(g)$ and $\text{O}_2(g)$ molecules with any oxide molecules being not important. The Na/O ratio was not measured and assumed to be 2/1 in all calculations on Na_2O . Based on the reported data, we derive the equilibrium constants for the reaction $\text{Na}_2\text{O}(c) = 2\text{Na}(g) + 1/2\text{O}_2(g)$ and evaluate the third law ΔH_f° as $117.1 \pm 10 \text{ kcal/mol}$. From this ΔH_f° value, we obtain $\Delta H_f^{\circ}(\text{Na}_2\text{O}, c) = -65.6 \pm 10 \text{ kcal/mol}$, employing $\Delta H_f^{\circ}(\text{Na}, g) = 25.76 \text{ kcal/mol}$ for $\text{Na}(g)$. The value -65.6 kcal/mol is not consistent with the other values described above. This may be caused by an invalid assumption used in the calculation.

The heat of formation at 298°K for $\text{Na}_2\text{O}(c)$ is tentatively selected as $-99.90 \pm 1.0 \text{ kcal/mol}$.

Investigator	Reaction	ΔH_f° , kcal/mol	ΔH_f° , kcal/mol
1. Matsui (1929)	$\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(7890 \text{ H}_2\text{O})$	-56.61 ± 0.16	-100.08
2. Matsui (1929)	$\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(4500 \text{ H}_2\text{O})$	-56.70 ± 0.07	-99.89
3. Roth (1947)	$\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(825 \text{ H}_2\text{O})$	-56.03 ± 0.13	-100.55
4. Roth (1948)	$\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(825 \text{ H}_2\text{O})$	-55.98 ± 0.13	-100.60
5. Rengade (1907)	$\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(aq)$	-56.50	-100.09
6. Forcand (1900)	$2\text{Na}(c) + \text{H}_2\text{O}(l) = \text{Na}_2\text{O}(c) + \text{H}_2(g)$	-28.70	-97.02
	$\text{Na}_2\text{O}(c) + 1/2\text{O}_2(g) = \text{Na}_2\text{O}_2(c)$	-27.76	-94.90

Heat Capacity and Entropy

The low temperature heat capacities, 15-380°K, were obtained from Furukawa (9). We make the corrections in the reported Cp values for impurity $\text{Na}_2\text{CO}_3(c)$ 2.33 per cent (by weight), analyzed by Grimley (10). The effect on heat capacity due to the presence of $\text{Na}_2\text{O}_2(0.91 \text{ per cent})$ impurity is insignificant. Using the smoothed low temperature Cp data the $S_{298.15}^{\circ}$ is calculated, based on $S_{15}^{\circ} = 0.0122 \text{ eu}$.

Grimley (10) measured the high temperature enthalpies, 380.1-1174.6°K, with a copper block drop-type calorimeter. The enthalpies for the γ phase, 380.1-980.4°K, are joined smoothly with the low temperature data and extrapolated to 1023.2°K (the $\gamma + \beta$ transition temperature). The enthalpies above 1023.2°K are obtained by extrapolation. The enthalpies measured at 1078.3 and 1174.6°K by Grimley are unreasonably large, and are not adopted.

Transition Data

The transition temperature and heats of transition were determined calorimetrically by Bouaziz (12) who used a very pure sample. The adopted $\Delta H^{\circ} = 0.42$ and 2.85 kcal/mol , are averages of the derived values, $0.36 - 0.48$ and $2.7 - 3.0 \text{ kcal/mol}$, respectively.

Melting Data

Tm and ΔH_m° were obtained from Bouaziz (12). The adopted ΔH_m° is an average of the reported 10.8-12.0 kcal/mol. Tm has been reported as 1193 and 1190 ± 10°K by Bunzel (13) and Brewer (11), respectively, which are not adopted.

References

1. W. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) 32, 79 (1929).
2. W. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) 32, 83 (1929).
3. W. A. Roth and H. L. Kaule, Z. Anorg. Chem. 253, 352 (1947).
4. W. A. Roth, Z. Anorg. Chem. 255, 324 (1948).
5. E. Rengade, Compt. Rend. 145, 236 (1907).
6. de Forcand, Compt. Rend. 130, 1465 (1900).
7. E. Rengade, Compt. Rend. 132, 172 (1901).
8. J. Furukawa, private communication, National Bureau of Standards, November 13, 1967.
9. G. T. Furukawa, private communication, National Bureau of Standards, November 13, 1967.
10. R. T. Grimley and J. L. Margrave, J. Phys. Chem. 54, 1763 (1950).
11. L. Brewer and J. Margrave, J. Phys. Chem. 59, 421 (1955).
12. R. Bouaziz, G. Papin and A. P. Rollet, Compt. Rend. Ser. C 262, 1051 (1966).
13. E. G. Bunzel and E. J. Kohlmeier, Z. Anorg. Chem. 234, 1 (1947).

June 30, 1962; June 30, 1968

Disodium Monoxide (Na₂O)

(Liquid)

GFw = 61.979

T, °K	C _p ^o	gibbs/mol S ^o - (C ^o - H ²⁹⁸)/T	H ^o - H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	Log Kp
100						
200						
298	25.000	21.895	21.895	.000	- 89.112	- 81.001
300	25.000	21.895	21.895	.000	- 89.112	- 81.001
400	25.000	21.895	21.895	.000	- 89.112	- 81.001
500	25.000	21.895	21.895	.000	- 89.112	- 81.001
600	25.000	21.895	21.895	.000	- 89.112	- 81.001
700	25.000	21.895	21.895	.000	- 89.112	- 81.001
800	25.000	21.895	21.895	.000	- 89.112	- 81.001
900	25.000	21.895	21.895	.000	- 89.112	- 81.001
1000	25.000	21.895	21.895	.000	- 89.112	- 81.001
1100	25.000	21.895	21.895	.000	- 89.112	- 81.001
1200	25.000	21.895	21.895	.000	- 89.112	- 81.001
1300	25.000	21.895	21.895	.000	- 89.112	- 81.001
1400	25.000	21.895	21.895	.000	- 89.112	- 81.001
1500	25.000	21.895	21.895	.000	- 89.112	- 81.001
1600	25.000	21.895	21.895	.000	- 89.112	- 81.001
1700	25.000	21.895	21.895	.000	- 89.112	- 81.001
1800	25.000	21.895	21.895	.000	- 89.112	- 81.001
1900	25.000	21.895	21.895	.000	- 89.112	- 81.001
2000	25.000	21.895	21.895	.000	- 89.112	- 81.001
2100	25.000	21.895	21.895	.000	- 89.112	- 81.001
2200	25.000	21.895	21.895	.000	- 89.112	- 81.001
2300	25.000	21.895	21.895	.000	- 89.112	- 81.001
2400	25.000	21.895	21.895	.000	- 89.112	- 81.001
2500	25.000	21.895	21.895	.000	- 89.112	- 81.001
2600	25.000	21.895	21.895	.000	- 89.112	- 81.001
2700	25.000	21.895	21.895	.000	- 89.112	- 81.001
2800	25.000	21.895	21.895	.000	- 89.112	- 81.001
2900	25.000	21.895	21.895	.000	- 89.112	- 81.001
3000	25.000	21.895	21.895	.000	- 89.112	- 81.001

DISODIUM MONOXIDE (Na₂O)

(LIQUID)

GFw = 61.979

S_{298.15} = [21.895] gibbs/molΔH_{298.15} = [-89.112] kcal/mol

Tm = 1405.2°K

ΔHm° = 11.4 kcal/mol

Td = 2223°K

Heat of Formation

The heat of formation is obtained from ΔH_{298.15}(c) by adding ΔHm° and the difference between H_{1405.2} - H₂₉₈ for Na₂O(c) and Na₂O(l).

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for Na₂SiO₃(l) and SiO₂(l). The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the Na₂O(c) table.

Decomposition Temperature

Td is the temperature at which the Gibbs energy change of the decomposition reaction Na₂O(l) = 2Na(g) + 1/2O₂(g) approaches zero.

Na₂O₂

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^c	Log K ^p
0	0.000	0.000	INFINITE	-	-121.257	-121.257	INFINITE
100	9.725	4.991	34.081	-	-122.246	-117.468	256.725
200	16.040	14.767	24.522	-	-122.658	-112.478	125.910
298	21.335	22.658	21.335	0.000	-122.660	-107.472	78.779
300	21.356	22.700	21.458	-0.040	-122.657	-107.376	78.224
400	21.356	25.223	23.522	2.280	-123.816	-102.200	55.839
500	24.401	34.598	25.214	4.691	-123.618	-96.814	42.317
600	25.919	39.219	27.172	7.228	-123.278	-91.483	33.323
700	26.848	43.286	28.185	9.869	-122.879	-86.220	25.919
800	27.150	46.682	29.135	13.527	-122.436	-81.000	19.919
900	27.150	50.062	30.133	17.387	-120.466	-76.038	16.478
1000	27.150	54.728	31.333	22.387	-119.898	-71.202	15.561
1100	27.150	57.308	32.215	22.102	-119.414	-66.359	13.184
1200	27.150	59.670	32.989	24.817	-165.627	-60.662	11.044
1300	27.150	61.853	40.665	30.537	-164.861	-55.000	9.743
1400	27.150	63.789	45.758	32.962	-162.856	-53.315	8.662
1500	27.150	65.729	47.758	35.677	-162.012	-50.231	7.583
1600	27.150	67.481	48.182	38.392	-161.171	-47.768	6.284
1700	27.150	69.127	48.543	41.107	-160.330	-45.305	5.136
1800	27.150	70.679	48.861	43.822	-159.489	-42.842	4.136
1900	27.150	72.139	49.139	46.537	-158.649	-40.379	3.288
2000	27.150	73.539	50.276	49.252	-157.878	-37.916	2.583
2100	27.150	74.664	51.410	51.967	-157.071	-35.453	1.624
2200	27.150	75.127	52.505	54.682	-156.230	-32.990	0.801
2300	27.150	75.334	53.559	57.397	-155.389	-30.527	0.146
2400	27.150	75.416	54.588	60.112	-154.548	-28.064	-0.466
2500	27.150	75.568	55.553	62.827	-153.707	-25.601	-1.124

June 30, 1963; June 30, 1968

DISODIUM DIOXIDE (Na₂O₂)

(CRYSTAL)



GFW = 77.9784

ΔH_f⁰ = -121.26 ± 1.2 kcal/mol
 ΔH_f^{298.15} = -122.66 ± 1.2 kcal/mol
 ΔH_f⁰ = 1.37 kcal/mol
 ΔH_m⁰ = Unknown

S_{298.15} = 22.66 ± 0.3 gibbs/molT_m = 785 ± 1°KT_m = 948°K

Heat of Formation

The enthalpy change of the reaction Na₂O₂(c) + H₂O(l) = 2NaOH(1200 H₂O) + 1/2O₂(g) was measured at 10.5°C by Roth (1). He employed a sample with composition 96.81 per cent Na₂O₂ and 3.43 per cent Na₂O by weight. Using ΔH_f⁰soln(Na₂O₂, c) = -56.02 kcal/mol, Roth derived the value ΔH_f⁰soln(Na₂O₂, c) = -34.55 kcal/mol. This value was later corrected to be -35.75 kcal/mol (2).

From this data we calculate the heat of formation (298°K) of Na₂O₂(c) as -121.0 kcal/mol. Forcand obtained ΔH_{soln} = -36.55 kcal/mol for the same reaction, quoted by Roth (1), yielding ΔH_f²⁹⁸(Na₂O₂, c) = -120.0 kcal/mol. The auxiliary data ΔH_f²⁹⁸(H₂O, l) = -68.315 kcal/mol is taken from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965; and ΔH_f²⁹⁸(NaOH·1200 H₂O) = -112.488 kcal/mol is derived based on ΔH_f²⁹⁸(NaOH, c) = -101.90 kcal/mol from JANAF Table and ΔH_f⁰ = -10.637 kcal/mol and ΔH_{soln}(1200 H₂O + aq.O) = -0.079 kcal/mol from V. B. Parker, U. S. Natl. Bur. Std. NBS-2, 1965.

Gilles (3) determined the enthalpy change of the reaction Na₂O₂(c) + H₂O(l) = 2NaOH(3800 H₂O) + 1/2O₂(g), using a purer sample (Na₂O₂ 99.2 per cent, Na₂O 0.8 per cent). Based on the reported value ΔH_f²⁹⁸ = -34.0 ± 0.3 kcal/mol and derived ΔH_f²⁹⁸(NaOH·3800 H₂O) = -112.487 kcal/mol, we calculate ΔH_f²⁹⁸ = -122.66 ± 1.2 kcal/mol for Na₂O₂(c).

Leffler (4) studied the oxygen pressure-melt composition for the liquid sodium-oxygen system between 760 and 960°C. These results, together with the thermodynamic data for Na₂O₂, were used to calculate the heats and free energies of formation of melt compositions between Na₂O and Na₂O₂. However, there are no numerical results reported. Therefore this data is not used for evaluation.

The heat of formation at 298°K is adopted as -122.66 ± 1.2 kcal/mol.

Heat Capacity and Entropy

The low temperature heat capacities, 52.31-256.22°K, were measured by Todd (5). His sample contains (per cent) 94 Na₂O₂(c), 3.6 Na₂O(c) and 2.4 Na₂CO₃. Corrections in the reported results have been made for Na₂CO₃ content, but not for Na₂O content which was estimated to be small. The Cp values below 52.31°K are calculated using the equation Cp = D(ΔH_f²⁹⁸) + 3E(ΔH_f²⁹⁸), reported by Todd. S₂₉₈⁰ is derived from the adopted Cp, based on S₂₉₈⁰ = 1.012 eu.

The high temperature enthalpies, 375.4-869.2°K, were determined by Chandrasekhariah (6), using drop calorimetry. Corrections were made for the contributions from impurities (Na₂O 1.5 and Na₂O 0.2 per cent). A discontinuity was observed in the enthalpies between 773 and 793°K, indicating some kind of transition (see Transition Data). The Cp for Na₂O₂(c) at temperatures 298-769.5°K are derived from the enthalpy measurements, 375.4-769.5°K, and joined smoothly with the low temperature data at 298°K, and extrapolated to 765°K(Tt). The Cp for Na₂O₂(p) is derived from the enthalpy data, 794-869.2°K, as constant, 27.15 gibbs/mol, and extrapolated to 2500°K.

Vedenev (7) measured the high temperature specific heat of Na₂O₂(c) in the temperature interval 292-373°K using adiabatic calorimetry. The reported average value, 21.46 gibbs/mol, is in fair agreement with the adopted ones.

Transition Data

It was reported by Tallman (8), who measured the X-ray powder diffraction pattern by a Geiger-counter diffractometer and found that at about 510°C the pattern changes entirely and a new set of peaks indicates a new phase. Separate thermal analysis measurements (9) confirm the transition temperature (α → β) is 512 ± 1°C or 785 ± 1°K, which is adopted here. Poppl (9) found a thermal anomaly at 485°C in both heating and cooling curves. ΔH⁰ is derived from the adopted enthalpy and Cp data on Na₂O₂(c) and Na₂O₂(p).

Melting Data

T_m is obtained from Benzel (10). T_m = 733 and 783°K were reported by Blumenthal (11) and Rode (12), respectively, which are not adopted.

References

1. W. A. Roth and H. L. Kaulke, Z. Anorg. Chem. **253**, 352 (1947).
2. W. A. Roth, Z. Anorg. Chem. **255**, 324 (1948).
3. P. W. Gilles and J. L. Margrave, J. Phys. Chem. **80**, 1333 (1956).
4. A. J. Leffler and N. M. Wiederhorn, J. Phys. Chem. **68**, 2882 (1964).
5. S. S. Todd, J. Am. Chem. Soc. **75**, 1229 (1953).
6. K. Chandrasekhariah, S. T. Grimley and J. L. Margrave, J. Phys. Chem. **63**, 1505 (1959).
7. H. Vedenev, Z. Anorg. Chem. **231**, 12 (1957).
8. R. L. Tallman and J. L. Margrave, J. Inorg. Nucl. Chem. **21**, 40 (1961).
9. H. Poppl, Z. Anorg. Chem. **231**, 12 (1957).
10. E. G. Bunzel and E. J. Kohlmeier, Z. Anorg. Chem. **254**, 1 (1947).
11. M. Blumenthal, Roczniki Chem. **11**, 865 (1931).
12. T. V. Rode and G. A. Gol'der, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk **3**, 299 (1956).





Sodium Metasilicate (Na_2SiO_3)

(Crystal) GFW = 122.0738

T, °K	C _p ^a	gkcal/mol S ^b	-(C _p ^a - H ^c ₂₉₈)/T	H ^c - H ^c ₂₉₈	kcal/mol ΔH ^f	ΔG ^f	Log K _p
0	11.000	4.000	INFINITE	-	-370.767	-370.767	INFINITE
100	11.466	4.111	37.623	-4.520	-370.767	-365.241	799.233
200	21.469	17.577	20.506	-7.384	-372.856	-358.059	391.268
298	26.740	27.210	27.210	.000	-373.190	-350.712	255.382
300	26.863	27.376	27.211	.050	-373.193	-350.572	255.382
400	30.540	35.640	28.312	2.111	-374.503	-348.288	164.328
500	33.154	42.750	30.506	4.122	-374.504	-338.598	119.154
600	35.161	48.079	33.076	9.542	-374.227	-327.121	99.691
700	34.794	54.525	35.751	13.142	-373.791	-319.304	85.114
800	34.181	59.531	38.416	16.492	-373.228	-311.558	73.184
900	39.398	64.100	41.019	20.772	-372.561	-303.596	64.755
1000	40.493	68.308	43.541	24.768	-371.810	-294.294	57.376
1100	41.499	72.215	45.972	28.468	-370.995	-288.785	51.074
1200	42.433	75.867	48.313	33.065	-369.955	-280.435	45.267
1300	43.315	79.288	50.565	37.952	-368.742	-269.182	39.696
1400	44.153	82.539	52.735	41.726	-367.383	-257.482	35.170
1500	44.957	85.613	54.825	44.182	-365.843	-246.875	32.222
1600	45.733	88.534	56.841	50.714	-364.005	-235.693	28.913
1700	46.785	91.345	58.789	55.345	-361.177	-224.903	25.911
1800	47.218	94.030	60.673	60.043	-357.457	-213.407	23.236
1900	47.934	96.602	62.426	64.401	-352.866	-201.105	20.639
2000	48.635	99.079	64.284	68.629	-347.453	-189.195	18.680
2100	49.325	101.468	65.979	74.527	-341.957	-179.494	16.727
2200	50.003	103.779	67.645	79.494	-335.004	-169.376	14.951
2300	50.673	106.016	69.265	84.528	-327.990	-157.348	13.322
2400	51.334	108.187	70.842	89.628	-320.921	-144.663	11.430
2500	51.986	110.296	72.376	94.794	-313.557	-135.357	

SODIUM METASILICATE (Na_2SiO_3) (CRYSTAL) GFW = 122.0738

ΔH^f₀ = -370.75 ± 1.0 kcal/mol

ΔH^f_{298.15} = -373.19 ± 1.0 kcal/mol

ΔH^m = 12.38 kcal/mol

S_{298.15} = 27.21 ± 0.3 gibbs/mol

T_m = 1362 ± 0.5°K

Heat of Formation

The heats of solution of NaCl(c), Na₂SO₄(c), SiO₂(quartz), Na₂SiO₃(c), HCl(aq) and H₂SO₄(aq) in 20 percent hydrofluoric acid at 74.7°C were measured by F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1933). The author derived two values of ΔH_{soln} of Na₂O(c) from those of NaCl(c), Na₂SO₄(c), HCl(aq) and H₂SO₄(aq) presumably employing auxiliary data from U. S. Natl. Bur. Std. Circ. 500, 1952. We recalculate ΔH_{soln} of Na₂O(c) in the calorimetric solution as -87.50 (chloride scheme, originally -87.66) and -86.74 kcal/mol (sulfate scheme, originally -89.19), using recent ΔH^f₂₉₈ values for NaCl(c), Na₂SO₄(c), HCl(aq), H₂SO₄(aq), and Na₂O(c). The corresponding enthalpy changes, ΔH^f₂₉₈, for the reaction Na₂O(c) + SiO₂(quartz) = Na₂SiO₃(c) are derived as -55.20 and -56.38 kcal/mol. Adopting the weighted average ΔH^f₂₉₈ = -55.59 kcal/mol with ΔH^f₂₉₈(Na₂O, c) = -99.9 kcal/mol and ΔH^f₂₉₈(SiO₂, quartz) = -217.7 kcal/mol, we obtain ΔH^f₂₉₈ = -373.19 kcal/mol for Na₂SiO₃(c). This ΔH^f₂₉₈(Na₂O, c) value is independent of future change in ΔH^f₂₉₈ of Na₂O(c) but the value of ΔH_{soln} and ΔH^f are not independent. The adopted value of ΔH^f₂₉₈(Na₂O, c) is the average of -100.1 and -99.7 kcal/mol reported by W. A. Roth and H. L. Kaule, Z. Anorg. Chem. 253, 352 (1947); ibid. 255, 324 (1948), and M. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) 32, 79 (1929), respectively.

W. A. Roth and H. Troitzsch, Z. Anorg. Chem. 260, 337 (1949), have measured the heats of solution of SiO₂(quartz), Na₂SiO₃(c) and Na₂O(c) in 10.3 percent HF at 22°C to be -32.85, -67.96 and -86.9 kcal/mol, respectively. Using these results, we calculate the enthalpy change of the reaction Na₂O(c) + SiO₂(quartz) = Na₂SiO₃(c) as -53.79 kcal/mol and ΔH^f₂₉₈(Na₂SiO₃, c) = -371.39 kcal/mol.

By use of high temperature reaction calorimetry D. C. Kroger and W. Janetzko, Z. Anorg. Allgem. Chem. 284, 83 (1956), have determined the enthalpy change of the reaction Na₂CO₃(c) + Na₂SiO₃(gl) = 2Na₂SiO₃(c) + CO₂(g) as 17.99 kcal/mol. Based on ΔH^f₂₉₈ = -270.26, -582.92 and -94.05 kcal/mol for Na₂CO₃(c), Na₂SiO₃(gl) and CO₂(g), respectively, we evaluate ΔH^f₂₉₈ = -370.57 kcal/mol for Na₂SiO₃(c).

The heats of solution of Na₂CO₃(c), SiO₂(quartz) and Na₂SiO₃(c) in 39 percent HF at 26.5°C were measured to be -244.1, -564.5 and -673.6 cal/g, by C. Hummel and H. E. Schwiete, Glasstech. Ber. 32, 327 (1959). From these results we calculate the enthalpy change to be 22.43 kcal/mol for the reaction Na₂CO₃(c) + SiO₂(quartz) = Na₂SiO₃(c) + CO₂(g), yielding ΔH^f₂₉₈(Na₂SiO₃, c) = -371.48 kcal/mol.

Many other older calorimetric measurements have been made in order to derive the heat of formation for Na₂SiO₃(c), but most of these are of questionable accuracy and in some cases the products of the reaction are uncertain. For further details the review by N. W. McCready, J. Phys. Colloid. Chem. 52, 1277 (1948).

Heat Capacity and Entropy

The low temperature heat capacities, 53.6 - 294.5°K, were measured by K. K. Kelley, J. Am. Chem. Soc. 61, 471 (1939), and high temperature enthalpies, 360.5 - 1747°K, were determined by B. F. Maylor, J. Am. Chem. Soc. 67, 466 (1945). The high temperature heat capacities are derived from the measured enthalpy data and joined smoothly with the low temperature Cp values. The entropy at 298°K is calculated using the adopted low temperature heat capacities, based on S₂₉₈ = 1.195 eu.

Melting Data

See Na₂SiO₃(l) table for details.



Sodium Metasilicate (Na₂SiO₃)

GFW = 122.0738

(Liquid)



GFW = 122.0738

(LIQUID)

SODIUM METASILICATE (Na₂SiO₃)

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^c	Log K _p
100							
200							
298	26.740	35.967	35.967	.000	- 361.107	- 341.240	250.136
300	26.863	36.132	35.967	.050	- 361.110	- 341.116	248.503
400	30.540	44.197	37.069	2.931	- 362.490	- 334.432	192.670
500	33.154	51.506	39.262	6.122	- 362.421	- 327.293	143.060
600	35.161	57.735	41.833	9.582	- 362.166	- 320.291	116.666
700	36.181	63.258	44.142	13.442	- 361.708	- 313.550	97.832
800	36.181	68.258	47.172	16.892	- 361.145	- 306.480	83.727
900	42.360	72.856	49.776	20.772	- 360.478	- 299.683	72.773
1000	42.360	77.322	52.311	25.010	- 359.484	- 292.982	64.031
1100	42.360	81.361	54.771	29.286	- 358.532	- 286.382	56.809
1200	42.360	85.081	57.062	33.728	- 357.592	- 279.948	50.803
1300	42.360	88.581	59.422	37.724	- 356.662	- 273.573	45.131
1400	42.360	91.858	61.808	41.562	- 355.732	- 267.257	40.322
1500	42.360	94.905	63.705	45.200	- 354.802	- 260.997	36.150
1600	42.360	97.240	65.716	50.436	- 353.968	- 254.800	32.511
1700	42.360	99.532	67.542	54.916	- 353.038	- 248.679	29.294
1800	42.360	101.532	69.502	59.614	- 352.116	- 242.622	26.374
1900	42.360	103.523	71.245	63.152	- 351.251	- 236.622	23.767
2000	42.360	105.497	73.002	67.390	- 350.400	- 230.679	21.428
2100	42.360	107.795	74.656	71.628	- 349.573	- 224.773	19.319
2200	42.360	110.250	76.522	76.004	- 348.748	- 218.923	17.407
2300	42.360	112.420	77.732	80.104	- 347.931	- 213.127	15.667
2400	42.360	114.424	79.261	84.342	- 347.124	- 207.574	14.076
2500	42.360	116.154	80.722	88.560	- 346.326	- 202.133	12.618

Dec. 31, 1960; June 30, 1965; Sept. 30, 1967

Heat of Formation

 $\Delta H_f^{298}(t)$ is obtained from $\Delta H_f^{298}(c)$ by adding ΔH_m^* and the difference between H_{1362}^* and H_{298}^* for crystal and liquid.

Heat Capacity and Entropy

The heat capacity above 900°K is derived as constant from the high temperature enthalpy data, 1414 - 1747°K, measured by B. F. Naylor, J. Am. Chem. Soc. **57**, 466 (1945). A glass transition temperature is assumed at 900°K; i.e. the heat capacities below 900°K are taken to be the same as those for Na₂SiO₃(c).

The entropy is obtained in a manner analogous to that of the heat of formation. The low temperature heat capacities, 63.74 - 162.48°K, have been measured by V. V. Tarasov and Y. S. Savitskaya, Dokl. Akad. Nauk SSSR, **88**, 1019 (1953); however, these are not adequate to be used to evaluate S_{298}^* .

Melting Data

The adopted $T_m = 1362^\circ\text{K}$, determined by F. C. Kracek, J. Phys. Chem. **24**, 1583 (1930), is in good agreement with the value 1261°K reported by F. M. Jaeger, J. Wash. Acad. Sci., **1**, 49 (1911), and later confirmed by G. W. Morey and N. L. Bowen, J. Phys. Chem. **28**, 1167 (1924).

Other reported T_m values are 1280, 1291 and 1329°K by N. V. Kultascheff, Z. Anorg. Chem. **35**, 186 (1903); R. C. Wallace, *ibid.*, **53**, 1 (1909); and H. S. van Klooster, *ibid.*, **53**, 135 (1910), respectively. These values are all lower than the adopted T_m value, probably because the sample compositions were not the exact composition of metasilicate.

The value of ΔH_m^* is evaluated from the adopted heat capacities for Na₂SiO₃(c) and Na₂SiO₃(l), and the enthalpy data reported by B. F. Naylor, *loc. cit.*, assuming the final state of the calorimetric sample to be Na₂SiO₃(c). From the phase diagrams of Na₂SiO₃ with other compounds, K. K. Kelley, U. S. Bur. Mines Bull. **393**, 1936, derived the values of ΔH_m of 9.8 - 10.5 kcal/mol.



Sodium Sulfate, V (Na_2SO_4)
(Crystal)

GFW = 142.0412



T, °K	C_p	S	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	- 5.550	- 328.815	- 328.815	INFINITE
100	15.991	10.329	9.049	- 4.872	- 330.329	- 321.648	702.962
200	25.232	24.622	38.407	- 2.757	- 331.173	- 312.596	341.589
298	30.549	35.764	35.764	0.000	- 331.550	- 303.383	222.386
300	30.633	35.953	37.765	0.957	- 331.553	- 303.308	220.884
400	37.999	43.725	37.061	3.331	- 333.688	- 293.615	160.424
500	47.820	53.450	39.511	6.969	- 333.732	- 283.610	123.966
600	40.670	60.622	42.443	10.607	- 333.603	- 273.592	99.656
700	42.780	67.056	45.508	15.084	- 333.194	- 263.596	82.259
800	44.490	72.865	48.571	20.829	- 332.546	- 253.690	69.176
900	45.830	78.033	51.533	26.610	- 331.400	- 243.541	50.822
1000	46.740	83.093	54.484	33.349	- 332.174	- 233.520	44.012
1100	47.820	87.610	57.293	38.166	- 337.377	- 209.691	36.190
1200	48.510	91.801	59.996	43.048	- 385.885	- 186.352	28.154
1300	49.100	95.708	62.594	47.985	- 382.092	- 165.878	24.168
1400	49.540	99.233	65.092	52.957			
1500	50.000	102.797	67.492				

SODIUM SULFATE, V (Na_2SO_4)

(CRYSTAL)

GFW = 142.0412

$\Delta H_f^\circ = -328.82 \pm 0.2$ kcal/mol
 $\Delta H_f^\circ(298.15) = -331.55 \pm 0.2$ kcal/mol
 $\Delta H_f^\circ(V-T) = 2.584$ kcal/mol

$S^\circ_{298.15} = 35.76 \pm 0.1$ gibbs/mol
 $\pi(V-T) = 521.7^\circ K$

Heat of Formation.

P. L. E. Shibata, S. Oda and S. Furukawa, J. Sci. Hiroshima Univ. (Japan) Ser. A, 3, 227 (1933), measured the ent of the cell: Na-amalg. (0.207%) $|Na_2SO_4$ (sat. soln.) $|Hg_2SO_4|Hg$ at 33-37°C. Extrapolating their results to 25°C, we obtain the $\Delta H_f^\circ(298.15) = -153.77$ kcal/mol for the reaction $2Na(c) + Hg_2SO_4(c) = 2Hg(l) + Na_2SO_4(c)$, which yields $\Delta H_f^\circ(298.15) = -303.36$ and $\Delta H_f^\circ(298.15) = -331.53$ kcal/mol for $Na_2SO_4(c)$. The auxiliary value, $\Delta H_f^\circ(298.15) = -149.59$ kcal/mol, for $Hg_2SO_4(c)$ is obtained from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Tech. Note 270-1, Natl. Bur. Std., Washington, D.C., 1965.

The heat of formation for $Na_2SO_4(\infty H_2O)$ is evaluated as -332.10 kcal/mol, using $\Delta H_f^\circ(298.15) = -57.39$ and -217.32 kcal/mol for $Na^+(\infty H_2O)$ and $SO_4^{2-}(\infty H_2O)$, respectively, from Tech. Note 270-1, loc. cit. J. F. Coughlin, J. Am. Chem. Soc. 77, 868 (1955), determined the enthalpy change, $\Delta H_f^\circ(298.15) = -0.301 \pm 0.035$ kcal/mol for the reaction $Na_2SO_4(c, V) = Na_2SO_4(1050 H_2O)$. Adopting $\Delta H_f^\circ(298.15) = 0.244$ kcal/mol for the reaction $Na_2SO_4(\infty H_2O) = Na_2SO_4(1050 H_2O)$ from Natl. Bur. Std. Circ. 500, Washington, D.C., 1952, we derive the value, $\Delta H_f^\circ(298.15) = 0.545$ kcal/mol for the reaction $Na_2SO_4(\infty H_2O) = Na_2SO_4(c, V)$, yielding $\Delta H_f^\circ(298.15) = -331.56$ kcal/mol for $Na_2SO_4(c, V)$.

The heat of formation for $Na_2SO_4(c, V)$ is adopted as -331.55 ± 0.2 kcal/mol.

Heat Capacity and Entropy.

The low temperature heat capacities, 13.74 - 313.44°K, have been measured by K. S. Pitzer and L. V. Coulter, J. Am. Chem. Soc. 60, 1310 (1938). The heat capacities in the temperature range 324.61 - 503.05°K were determined by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. 5, 1321 (1961), using an adiabatic calorimeter. These two sets of data are joined smoothly and extrapolated graphically to 1500°K. The enthalpy values derived from the adopted Cp data are in fair agreement with those determined by J. P. Coughlin, J. Am. Chem. Soc. 77, 868 (1955). The corresponding Cp values, reported by M. M. Popov and O. L. Galchenko, J. Gen. Chem. USSR, 21, 2489 (1951), seem too high at the high temperature end. $S^\circ_{298.15}$ is derived using the low temperature Cp data reported by K. S. Pitzer and L. V. Coulter, loc. cit., based on $S^\circ_{14} = 0.057$ eu.

Transition Data.

Polymorphism studies by P. C. Kracek, J. Phys. Chem. 33, 1281 (1929), and P. C. Kracek and R. E. Gibson, J. Phys. Chem. 33, 1304 (1929); ibid., 34, 188 (1930), indicate five distinct modifications, 1.e. V, IV, III, II, I, of which only V and I are stable forms. Calorimetric studies of Shmidt and Sokolov, loc. cit., suggest another form, stable at high temperatures, which is labeled as δ .

The transition temperature and heat of transition are from the calorimetric data for thenardite reported by Shmidt and Sokolov, loc. cit.



Sodium Sulfate, I (Na₂SO₄)
(Crystal)

GFW = 142.0412



T, °K	C _p	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
300	38.990	37.733	37.733	.000	- 330.096	- 302.517	221.751
400	39.000	37.975	37.734	.072	- 330.084	- 302.345	220.258
500	39.868	49.313	39.274	4.015	- 331.350	- 293.064	160.122
600	40.790	58.305	42.211	8.047	- 331.200	- 283.506	123.920
700	41.920	65.840	45.517	12.182	- 330.874	- 273.994	99.802
800	43.243	72.399	48.916	16.438	- 330.386	- 264.529	82.590
900	44.796	78.272	52.224	20.838	- 342.797	- 256.432	70.054
1000	46.581	83.649	55.421	25.405	- 341.676	- 245.700	59.664
	48.190	88.640	58.496	30.143	- 340.413	- 235.101	51.361
1100	49.570	93.299	61.451	35.033	- 339.036	- 224.641	44.632
1200	50.640	97.659	64.289	40.045	- 384.044	- 213.389	38.863
1300	51.570	101.750	67.014	45.157	- 382.085	- 199.244	33.466
1400	52.300	105.600	69.634	50.351	- 380.060	- 185.254	28.920
1500	52.917	109.230	72.154	55.613	- 377.982	- 171.417	24.975
1600	53.390	112.661	74.590	60.930	- 375.861	- 157.712	21.542
1700	53.696	115.907	76.916	66.285	- 373.711	- 144.141	18.531
1800	53.900	118.943	79.169	71.666	- 371.552	- 130.701	15.869
1900	54.001	121.900	81.341	77.062	- 369.390	- 117.376	13.501
2000	54.000	124.671	83.439	82.463	- 367.236	- 104.174	11.384

(CRYSTAL)

SODIUM SULFATE, I (Na₂SO₄)

GFW = 142.0412

$$\Delta H_f^{298.15} = -330.096 \text{ kcal/mol}$$

$$\Delta H_t^{\circ}(V \rightarrow I) = 2.584 \text{ kcal/mol}$$

$$\Delta H_t^{\circ}(I \rightarrow \delta) = 0.06 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 5.67 \text{ kcal/mol}$$

$$S_{298.15}^{\circ} = 37.733 \text{ gibbs/mol}$$

$$T_t(V \rightarrow I) = 521.7^{\circ}\text{K}$$

$$T_t(I \rightarrow \delta) = 980^{\circ}\text{K}$$

$$T_m = 1157^{\circ}\text{K}$$

Heat of Formation.

The ΔH_f° $\text{Na}_2\text{SO}_4(I)$ is obtained from $\Delta H_f^{298.15}(\text{Na}_2\text{SO}_4, V)$ by adding $\Delta H_t^{\circ}(V \rightarrow I)$ and the difference between $H_{521.7}^{\circ} - H_{298.15}^{\circ}$ for $\text{Na}_2\text{SO}_4(V)$ and $\text{Na}_2\text{SO}_4(I)$.

Heat Capacity and Entropy.

The heat capacities in the temperature range 538.65 - 917.65°K were measured with an adiabatic calorimeter by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. **6**, 1321 (1961). The Cp values below 538.65°K and above 917.65°K are obtained by graphical extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data.

The value $\Delta H_t^{\circ}(V \rightarrow I) = 2.584 \pm 0.015 \text{ kcal/mol}$ is the average of two determinations from the calorimetric studies of Shmidt and Sokolov, loc. cit. The transition temperature was derived from the heating curve obtained in measuring the heat of transition. It was taken to be the temperature at which the specimen began to show its lowest heating rate. The heat of transition was the difference between the quantity of heat actually dissipated and the sum of the heats calculated from the heat capacity curve of the apparatus and from the specific heat curves of (V) and (I) linearly extrapolated to the transition temperature.

The values of T_t and ΔH_t° for $\text{Na}_2\text{SO}_4(I) \rightarrow \text{Na}_2\text{SO}_4(\delta)$ transition were reported by Shmidt and Sokolov, loc. cit. See $\text{Na}_2\text{SO}_4(\delta)$ table for details.

Melting Data.

See $\text{Na}_2\text{SO}_4(I)$ table for details.



Sodium Sulfate, Delta (δ - Na₂SO₄)

GFW = 142.0412

(Crystal)

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S}$	$-(C^{\circ}-H^{\circ}_{298})/T$	$\frac{\text{kcal/mol}}{H^{\circ}-H^{\circ}_{298}}$	$\frac{\text{kcal/mol}}{\Delta H^{\circ}}$	ΔG°	Log Kp
100							
150							
200							
250							
300	38.990	37.741	37.741	.000	- 330.089	- 302.512	221.747
350							
400	39.000	37.982	37.741	.072	- 330.077	- 302.330	220.954
450	39.868	39.320	39.281	4.015	- 331.363	- 291.059	160.120
500	40.790	58.312	42.218	8.047	- 331.193	- 283.502	123.919
550							
600	41.920	65.847	45.545	12.182	- 330.847	- 273.991	99.801
650	43.243	72.496	48.923	16.438	- 330.379	- 264.527	82.569
700	44.581	78.556	52.458	20.805	- 329.769	- 255.099	69.043
750	45.824	84.156	56.055	25.224	- 328.931	- 245.699	57.644
800	46.984	89.333	59.565	30.224	- 327.822	- 235.102	51.382
850	48.060	94.118	63.018	35.140	- 326.492	- 224.453	44.434
900	49.060	98.540	66.417	40.228	- 324.954	- 213.416	38.868
950	50.000	102.615	69.700	45.417	- 323.161	- 201.944	33.624
1000	50.900	106.340	72.848	50.841	- 321.053	- 189.983	28.233
1050	51.710	109.774	75.800	56.290	- 318.679	- 177.560	22.995
1100	52.440	112.829	78.595	61.794	- 316.006	- 164.706	18.569
1150	53.110	115.493	81.277	67.344	- 313.094	- 151.407	14.565
1200	53.720	117.800	83.880	72.920	- 309.906	- 137.622	11.552
1250	54.290	120.000	86.418	78.500	- 306.494	- 123.322	9.144
1300	54.820	122.110	88.900	84.100	- 302.806	- 108.562	7.144
1350	55.310	124.140	91.340	89.700	- 298.894	- 93.282	5.444
1400	55.760	126.100	93.740	95.300	- 294.714	- 77.502	4.044
1450	56.180	127.990	96.100	100.900	- 290.314	- 61.162	2.944
1500	56.570	129.820	98.420	106.500	- 285.744	- 44.322	2.144
1550	56.940	131.600	100.700	112.100	- 281.054	- 26.982	1.544
1600	57.290	133.330	102.860	117.700	- 276.294	- 9.142	1.044
1650	57.620	135.010	104.990	123.300	- 271.414	9.142	0.644
1700	57.930	136.640	107.090	128.900	- 266.364	29.142	0.344
1750	58.220	138.220	109.160	134.500	- 261.104	49.142	0.144
1800	58.490	139.750	111.200	140.100	- 255.694	69.142	0.044
1850	58.740	141.240	113.210	145.700	- 250.094	89.142	0.004
1900	58.970	142.690	115.190	151.300	- 244.364	109.142	0.000
1950	59.190	144.100	117.140	156.900	- 238.494	129.142	0.000
2000	59.400	145.470	119.060	162.500	- 232.494	149.142	0.000

Dec. 31, 1966

(CRYSTAL)

SODIUM SULFATE, δ (Na₂SO₄)

OPW = 142.0412

 $\Delta H^{\circ}_{298.15} = -330.089$ kcal/mol $\Delta H^{\circ} (I \rightarrow \delta) = 0.08$ kcal/mol $\Delta H^{\circ} = 5.50$ kcal/mol $S^{\circ}_{298.15} = 37.741$ gibbs/mol $T_f (I \rightarrow \delta) = 980^{\circ}\text{K}$ $T_m = 1157^{\circ}\text{K}$

Heat of Formation

The heat of formation ($\Delta H^{\circ}_{298.15}$) is obtained from $\Delta H^{\circ}_{298.15}$ for Na₂SO₄ (I) by adding $\Delta H^{\circ} (I \rightarrow \delta)$ and the difference between $H_{980} - H^{\circ}_{298.15}$ for Na₂SO₄ (I) and Na₂SO₄ (δ).

Heat Capacity and Entropy

The heat capacities in the temperature range 930 - 1010°K were measured by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. **5**, 1321 (1961). The Cp values below 900°K are assumed to be the same as those for Na₂SO₄ (I). The heat capacities above 1010°K are obtained by graphical extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data

A small anomalous region between 690 - 720°C (963.15 - 993.15°K) on the Cp curve for Na₂SO₄ (c) was reported by N. E. Shmidt and V. A. Sokolov, loc. cit. By use of graphical integration of the area between the measured Cp curve and an arbitrary base line over the region 900 - 1100°K, a value of $\Delta H^{\circ} (I \rightarrow \delta) = 0.08$ kcal/mol was obtained. It is assumed to be 980°K. This anomalous region was first observed by G. W. Wyrouboff, Z. Krist. **21**, 284 (1933), and later confirmed by Y. P. Simanov and D. P. Kirikina, Zh. Neorg. Khim. **2**, 699 (1957), as a transition from a hexagonal to an orthorhombic structure. This transition was not observed by the earlier investigators because their measurements did not extend to that temperature range.

Melting Data

The temperature and heat of melting of Na₂SO₄ (I) $\rightarrow$ Na₂SO₄ (I) were reported to be 1157°K and 5.67 kcal/mol, respectively, by Coughlin, loc. cit. No mention was made of the δ phase and the enthalpy measurements were probably not sensitive enough to detect this phase. Based on our selected Cp values for δ and liquid Na₂SO₄, we derive $H_m^{\circ}(\delta \rightarrow I) = 5.50$ kcal/mol, using Coughlin's enthalpy data on Na₂SO₄ (I). The melting temperature is assumed to be the same as that reported by Coughlin.

T_m was reported to be 880°C (1153°K), 897°C (1170°K) and 888°C (1161°K) by Ruff and Plato, Ber. Deutsch. Chem. Ges. **35**, 2357 (1903); K. Hiltner and O. Temmeln, Z. Anorg. Chem. **43**, 215 (1905); and H. E. Boeke, Z. Anorg. Chem. **50**, 355 (1906), respectively.

Sodium Sulfate (Na_2SO_4)
(Liquid)

GFW = 142.0412



QFV = 142.0412

(LIQUID)

SODIUM SULFATE (Na_2SO_4)

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal/mol ΔH°	ΔG°	Log Kp
200							
250	34.920	42.777	42.777	.000	- 324.241	- 298.165	218.561
300	39.000	43.018	42.777	.072	- 324.229	- 298.003	217.095
400	39.868	54.356	44.317	4.015	- 325.495	- 289.226	198.026
500	40.790	63.346	47.234	8.047	- 325.345	- 280.172	122.453
600	41.920	70.894	50.581	12.182	- 325.019	- 271.165	98.772
700	43.243	77.442	53.959	16.438	- 324.531	- 262.204	81.664
800	47.180	83.315	57.268	20.838	- 336.942	- 254.211	69.556
900	47.180	88.872	60.477	25.554	- 335.670	- 244.395	59.347
1000	47.180	93.843	63.569	30.274	- 334.427	- 234.318	51.210
1100	47.180	98.340	66.529	34.992	- 333.222	- 224.372	44.579
1200	47.180	102.445	69.353	39.710	- 332.522	- 215.412	38.904
1300	47.180	106.221	72.046	44.428	- 376.959	- 199.930	33.611
1400	47.180	109.718	74.613	49.146	- 375.410	- 186.374	29.094
1500	47.180	112.973	77.064	53.864	- 373.876	- 172.926	25.195
1600	47.180	116.018	79.404	58.582	- 372.354	- 159.577	21.797
1700	47.180	118.878	81.643	63.300	- 370.841	- 146.322	18.811
1800	47.180	121.575	83.787	68.018	- 369.345	- 133.160	16.168
1900	47.180	124.126	85.844	72.736	- 367.861	- 120.076	13.812
2000	47.180	126.546	87.819	77.454	- 366.390	- 107.078	11.701
2100	47.180	128.848	89.718	82.172	- 364.928	- 94.150	9.798
2200	47.180	131.042	91.547	86.890	- 363.482	- 81.286	8.075
2300	47.180	133.140	93.310	91.608	- 362.045	- 68.496	6.509
2400	47.180	135.148	95.012	96.326	- 360.622	- 55.757	5.077
2500	47.180	137.074	96.656	101.044	- 359.211	- 43.091	3.767
2600	47.180	138.924	98.246	105.762	- 357.813	- 30.468	2.561
2700	47.180	140.705	99.786	110.480	- 356.429	- 17.909	1.450
2800	47.180	142.420	101.278	115.198	- 355.060	- 5.396	.421
2900	47.180	144.076	102.726	119.916	- 353.703	7.074	.533
3000	47.180	145.675	104.131	124.634	- 352.363	19.493	1.420

S_{298.15} = 42.777 gibbs/mol

Tm(δ = 1) = 1157°K

ΔH°_{298.15} = -324.241 kcal/mol

ΔHm°(δ = 1) = 5.50 kcal/mol

Heat of Formation.

The value of ΔH°_{298.15}(1) is obtained from ΔH°_{298.15}(I) by adding ΔHm° and the difference between H°₁₁₅₇ - H°_{298.15} for Na₂SO₄(δ) and Na₂SO₄(I).

Heat Capacity and Entropy.

The enthalpies for Na₂SO₄(l) were measured by drop calorimetry in the temperature range 1157 - 1828°K by J. P. Coughlin, J. Am. Chem. Soc. **77**, 868 (1955); and in the temperature range 1173 - 1250°K by M. M. Popov and D. M. Ginzburg, J. Gen. Chem. USSR **25**, 1107 (1956). The constant heat capacity adopted here is derived from the enthalpy measurements reported by J. P. Coughlin, loc. cit. Below 800°K, the heat capacities are assumed to be the same as those of the δ phase. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data.

The temperature and heat of melting of Na₂SO₄(I) → Na₂SO₄(l) were reported to be 1157°K and 5.67 kcal/mol, respectively, by Coughlin, loc. cit. No mention was made of the δ phase, and the enthalpy measurements were probably not sensitive enough to detect this phase. Based on our selected Cp values for δ liquid Na₂SO₄, we derive ΔHm°(δ = 1) = 5.50 kcal/mol, using Coughlin's enthalpy data on Na₂SO₄(l). The melting temperature is assumed to be the same as that reported by Coughlin.

Tm was reported to be 880°K(1153°K), 897°K(1170°K) and 889°K(1161°K) by Ruff and Plato, Ber. Deutsch. Chem. Ges. **36**, 2357 (1903); K. Hüttner and G. Tammann, Z. Anorg. Chem. **43**, 215 (1905); and H. E. Boeke, Z. Anorg. Chem. **50**, 355 (1906), respectively.

Sodium Tungstate (Na_2WO_4)
(Crystal) GFW = 293.8272



SODIUM TUNGSTATE (Na_2WO_4)

(CRYSTAL)

GFW = 293.8272

$\Delta H_f^\circ = -366.8 \pm 2 \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = -369.2 \pm 2 \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = 0.983 \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = 7.373 \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = 5.688 \text{ kcal/mol}$

$S_{298.15}^\circ = 38.32 \pm 0.5 \text{ gibbs/mol}$

$T_1 = 862.0^\circ\text{K}$

$T_2 = 860.8^\circ\text{K}$

$T_m = 968.7^\circ\text{K}$

Heat of Formation

The adopted heat of formation, $\Delta H_{298}^\circ(\text{Na}_2\text{WO}_4, \text{c}) = -369.2 \text{ kcal/mol}$, is calculated from $\Delta H_{298}^\circ(\text{H}_2\text{WO}_4, \text{c}) = -270.5 \text{ kcal/mol}$ for the reaction $\text{H}_2\text{WO}_4(\text{c}) + 2\text{HCl}(\text{l}) = \text{Na}_2\text{WO}_4(\text{c}) + 2\text{HCl}(\text{l})$ (12.731 H_2O), using the JANAF value of $\Delta H_{298}^\circ(\text{H}_2\text{WO}_4, \text{c}) = -270.5 \text{ kcal/mol}$ and $\Delta H_{298}^\circ(\text{NaCl}, \text{c}) = -98.26 \text{ kcal/mol}$, and auxiliary data for $\text{HCl}(\text{aq})$ (11). The value of $\Delta H_{298}^\circ(\text{Na}_2\text{WO}_4, \text{c})$ was determined by solution calorimetry by M. F. Koehler, L. B. Pankratz and R. Barany (1).

J. M. Sherfey and A. Brenner (2) measured by electrochemical calorimetry the heat of reaction $\Delta H_{298}^\circ = -7 \pm 1.5 \text{ kcal/mol}$ for $\text{W}(\text{c}) + \text{NaOH}(\text{ss}, 55\text{H}_2\text{O}) + 2\text{H}_2\text{O}(\text{l}) = \text{Na}_2\text{WO}_4(\text{c}) + \text{H}_2(\text{g})$. This value, combined with the heat of solution (3.33), $\Delta H_{\text{sol}}^\circ = -1.7 \pm 0.1 \text{ kcal/mol}$ for $\text{Na}_2\text{WO}_4(\text{c}) = \text{Na}_2\text{WO}_4(\text{aq})$, gives $\Delta H_{298}^\circ(\text{Na}_2\text{WO}_4, \text{c}) = -369.4 \text{ kcal/mol}$, which is in good agreement with the value adopted.

The previously accepted value (1,3), $\Delta H_{298}^\circ(\text{Na}_2\text{WO}_4, \text{c}) = -379 \pm 0.5 \text{ kcal/mol}$, was based on the unreliable $\Delta H_{298}^\circ(\text{H}_2\text{WO}_4, \text{c}) = -280.2 \pm 0.4 \text{ kcal/mol}$. (See JANAF $\text{H}_2\text{WO}_4(\text{c})$ table of March 31, 1967.) The other quoted value (4), $\Delta H_{298}^\circ(\text{Na}_2\text{WO}_4, \text{c}) = -395 \text{ kcal/mol}$, was obtained from W. G. Mixer's (5) measurement of the heat of reaction of tungsten powder with excess Na_2O_2 . This value was probably in error because the complex tungstate and peroxytungstates were formed in the reaction.

Heat Capacity and Entropy

Low temperature heat capacities (52-299.87°K) were measured calorimetrically by E. G. King and W. W. Weller (6). The heat capacities above 300°K are estimated by extrapolation of the low temperature heat capacity curve to $\text{Cp}_{860} = 49.0 \text{ gibbs/mol}$. The latter is obtained from an estimate of Cp equal to 7 gibbs/g-atom at the first transition temperature.

The entropy, $S_{298}^\circ = 38.32 \pm 0.5 \text{ eu}$, is calculated from low temperature heat capacity data of King and Weller (6), based on an extrapolation of $S_{298}^\circ = 2.77 \pm 0.5 \text{ eu}$.

Transition Data

Transition temperatures and heats were obtained from differential heating and cooling curves both at atmospheric and higher pressures by R. W. Goranson and F. C. Kracek (7). Existence of three phases is confirmed by the earlier birefringence studies of H. E. Boeke (8).

R. Riccardi and C. Sinistri (10) found only one transition at 864°K with $\Delta H^\circ = 8.23 \text{ kcal/mol}$ by differential thermal analysis. This heat is apparently the sum of the two adopted heats of transition.

Melting Data

The adopted melting data were measured by the differential heating and cooling curve method by Goranson and Kracek (7). R. Riccardi and C. Sinistri (10) found the melting point at 871°K with $\Delta H^\circ = 7.52 \text{ kcal/mol}$ by differential thermal analysis.

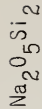
References

1. M. F. Koehler, L. B. Pankratz and R. Barany, U.S. Bur. Mines RI 5973 (1962).
2. J. M. Sherfey and A. Brenner, J. Electrochem. Soc. **105**, 565 (1958).
3. R. L. Graham and L. G. Hepler, J. Amer. Chem. Soc. **80**, 3538 (1958).
4. U. S. Natl. Bur. Std. Circ. **500**, 1952.
5. W. G. Mixer, Am. J. Sci. **26**, 125 (1908).
6. E. G. King and W. W. Weller, U.S. Bur. Mines RI 5791 (1961).
7. R. W. Goranson and F. C. Kracek, J. Chem. Phys. **3**, 87 (1935).
8. H. E. Boeke, Z. Anorg. Allgem. Chem. **50**, 359 (1906).
9. S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. **9**, 1309 (1964).
10. R. Riccardi and C. Sinistri, Ric. Sci. Rend. Sez. A **9**, 1026 (1965).
11. V. B. Parker, U.S. Natl. Bur. Std. NBS-RS-NBS 2, 1965, and U. S. Bur. Std. Tech. Note 270-1, 1965.

June 30, 1967



T, °K	Cp°	gibbs/mol $S^\circ - (G^\circ - H_{298}^\circ)/T$	kcal/mol ΔH°	$H^\circ - H_{298}^\circ$	ΔG°	Log Kp
0	0.000	INFINITE	-366.823	6.044	-366.823	INFINITE
100	16.627	61.976	-368.321	5.358	-350.714	786.154
200	28.522	63.540	-369.145	5.005	-330.763	1586.685
298	33.407	66.320	-369.200	0.000	-331.743	2507.505
300	33.490	66.527	-369.199	.062	-341.572	248.635
400	37.126	69.697	-370.354	3.406	-332.277	181.548
500	40.000	71.301	-370.038	7.467	-322.788	141.090
600	42.600	64.827	-369.469	11.599	-313.387	114.151
700	45.100	71.582	-368.673	15.284	-304.101	84.955
800	47.500	77.761	-367.662	20.614	-294.945	60.575
900	50.000	83.205	-356.081	33.845	-286.304	67.524
1000	52.400	88.597	-356.650	38.964	-278.402	60.645
1100	56.850	103.706	-355.021	44.327	-270.459	53.775
1200	57.300	108.584	-352.665	49.234	-262.153	47.705
1300	59.780	113.268	-350.791	55.788	-250.791	42.162
1400	62.250	117.789	-349.522	61.690	-239.631	37.408
1500	64.700	122.167	-391.619	68.237	-228.665	33.316



$\Delta H_f^\circ = -586.87 \pm 1.0$ kcal/mol
 $\Delta H_f^\circ(298.15) = -590.36 \pm 1.0$ kcal/mol
 $\Delta H^\circ = 0.1$ kcal/mol
 $\Delta H^\circ = 0.15$ kcal/mol
 $\Delta H_m^\circ = 8.5$ kcal/mol

$S_{298.15}^\circ = 39.21 \pm 1.0$ gibbs/mol
 $T(8 \rightarrow A\beta) = 951^\circ K$
 $T(A\beta \rightarrow A\alpha) = 980^\circ K$
 $T_m = 1147^\circ K$

Heat of Formation

The heats of solution of NaCl(c), Na₂SO₄(c), SiO₂(quartz), Na₂Si₂O₅(c), HCl(aq) and H₂SO₄(aq), in 20 percent hydrofluoric acid at 74.7°C were measured by Kracek (3). The author derived two values of ΔH_{soln} of Na₂O(c) from those of NaCl(c), Na₂SO₄(c), HCl(aq) and H₂SO₄(aq), presumably employing auxiliary data from (2). We recalculate ΔH_{soln} of Na₂O(c) in the calorimetric solution as -87.50 (chlorine scheme, originally -87.66) and -88.74 kcal/mol (sulfate scheme, originally -89.19), using recent ΔH_f° values (16, 17, 18) for NaCl(c), HCl(aq), H₂SO₄(aq), Na₂SO₄(c), and Na₂O(c). The corresponding enthalpy changes, $\Delta H_f^\circ(298)$ for the reaction Na₂O(c) + 2SiO₂(quartz) = Na₂Si₂O₅(c) are derived as -94.65 and -95.89 kcal/mol. Adopting the weighted average $\Delta H_f^\circ(298) = -95.06$ kcal/mol with $\Delta H_f^\circ(298)$ (Na₂O, c) = -99.9 kcal/mol and $\Delta H_f^\circ(298)$ (SiO₂, quartz) = -217.7 kcal/mol, we obtain $\Delta H_f^\circ(298) = -590.36$ kcal/mol for Na₂Si₂O₅(c). This $\Delta H_f^\circ(298)$ (Na₂Si₂O₅, c) value is independent of future changes in $\Delta H_f^\circ(298)$ of Na₂O(c), but the values of ΔH_{soln} and ΔH_m° are not independent.

Stevens et al. (3) measured the heats of solution of Na₂Si₂O₅(c), Na₂O(c) and SiO₂(quartz) in HF(aq) at 25°C. Based on the reported results, the enthalpy change for the reaction Na₂O(c) + 2SiO₂(quartz) = Na₂Si₂O₅(c) is calculated as -93.25 $\pm$ 0.32 kcal/mol, yielding $\Delta H_f^\circ(298)$ (Na₂Si₂O₅, c) = -588.55 kcal/mol.

Hummel (4) determined the heats of solution of Na₂Si₂O₅(c), SiO₂(quartz) and Na₂CO₃(c) in 39 percent HF at 26.5°C. From the data reported we derive the enthalpy change to be 70.68 kcal/mol for the reaction Na₂CO₃(c) + 2SiO₂(quartz) = Na₂Si₂O₅(c) + CO₂(g). Employing $\Delta H_f^\circ(298) = -270.26$, -217.7 and -94.05 kcal/mol for Na₂CO₃(c), SiO₂(quartz) and CO₂(g), respectively, we obtain $\Delta H_f^\circ(298) = -590.73$ kcal/mol for Na₂Si₂O₅(c) which is in good agreement with the adopted one.

Heat Capacity and Entropy

The low temperature heat capacities, 54.3 - 294.7 J K⁻¹ mol⁻¹, have been measured by Kelley (5) and the high temperature enthalpies, 376.8 - 1100.2 J K⁻¹ mol⁻¹, by Naylor (6). The derived high temperature heat capacities are joined smoothly with the low temperature ones at 298 K. An approximate Cp of 70 gibbs/mol is derived from the enthalpies above 980 K; this value is extrapolated to 2000 K. The value of S_{298}° is calculated from the adopted low temperature heat capacities based on $S_{298}^\circ = 2.945$ eu. The entropy extrapolation derives from the Debye-Einstein extrapolation of Kelley (5) which yields a Cp curve with an extra inflection in the region from 15 to 50 K. A more normal extrapolation would lead to a value of S_{298}° which is lower by 0.5 eu.

Transition Data

There are six slowly inverting polymorphous phases (1, 2-9), namely A, B, C, D, E and F, of which only the first two phases are stable. Two rapid transitions have been reported at 951 and 980 K (1, 10). Phase A, which has two subphases, A α and A β , is stable above 951 K. The stable phase below 951 K is known as phase B, previously called β -Na₂Si₂O₅. The two values of ΔH° are derived from the enthalpy data of Naylor (6) using the adopted Cp values. Three more rapid transitions have been reported at 822, 846 and 866 K (1, 10) in E, previously called γ -Na₂Si₂O₅. A recent examination of these transitions was reported by Willgallis and Range (10).

Melting Data

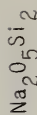
T_m is obtained from Morey (11). The selected value of ΔH_m° is based on the following ΔH_m° values derived from four different kinds of measurements.

Investigator	ΔH_m° , kcal/mol*		Method**	Reference
	at 298 K	at 1147 K		
Kelley (1936)	(7.51)	8.46	I	12
Kracek (1953)	5.25	(6.20)	II	1
Kröger-Janetzko (1956)	8.81	(9.76)	III	13
Kröger-Kreitlow (1956)	8.83	(9.78)	II	14
Schwiete-Ziegler (1958)	(7.50)	8.45	IV	15
Hummel-Schwiete (1959)	8.09	(9.04)	II	4

*The numbers in parentheses are derived from the measured ones at the other listed temperatures.
**I = phase diagram; II = solution calorimetry; III = high temperature reaction calorimetry; and
IV = dynamic-differential calorimetric method.

References

1. F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 58, 69 (1953).
2. U. S. Natl. Bur. Std. Circ. 500, 1952.
3. C. Stevens and E. J. Redmond, Trans. Faraday Soc. 51, 356 (1955).
4. C. Hummel and H. F. Schwiete, Z. Anorg. Allg. Chem. 287, 327 (1959).
5. K. Kelley, J. Am. Chem. Soc. 61, 471 (1939).
6. B. F. Naylor, J. Am. Chem. Soc. 61, 468 (1945).
7. G. W. Morey and N. L. Bowen, J. Soc. Glass Technol., 3, 226 (1925).
8. F. C. Kracek, J. Phys. Chem., 31, 1593 (1930).
9. A. Willgallis and J. Range, Z. Anorg. Allg. Chem. 287, 339 (1959).
10. G. W. Morey and N. L. Bowen, J. Phys. Chem., 28, 1167 (1924).
11. K. K. Kelley, U. S. Bur. Mines Bull. 393, 1936.
12. C. Kröger and W. Janetzko, Z. Anorg. Allg. Chem. 284, 84 (1956).
13. C. Kröger and G. Kreitlow, Glasstech. Ber. 29, 393 (1956).
14. H. F. Schwiete and G. Ziegler, Ber. Deut. Chem. Ges., 83, 193 (1958).
15. Soc. J. J. Natl. Bur. Std. Tech. Note 270-1, 1965, JANAF Na₂Si₂O₅ (c, v) table (Dec. 31, 1966).
16. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965, JANAF Na₂Si₂O₅ (c, v) table (Dec. 31, 1966).
17. The value of $\Delta H_f^\circ(298)$ (Na₂O, c) is selected based on the heat of solution data reported by W. A. Roth and H. L. Kaule, Z. Anorg. Chem. 253, 352 (1947), and M. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) 32, 79 (1929).
18. Z. Anorg. Chem. 253, 352 (1947), and M. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) 32, 79 (1929).



Sodium Disilicate (Na₂Si₂O₅)
(Liquid)
Na₂O₅Si₂

GFw = 182.1586

T, °K	Cp*	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0							
100	37.520	45.101	45.101	.000	- 582.811	- 549.716	4.02.953
200	37.642	45.134	45.102	-.070	- 582.816	- 549.510	400.318
300	43.834	57.040	46.556	4.154	- 584.211	- 538.281	294.103
400	48.577	67.358	48.785	8.786	- 583.976	- 538.815	230.270
500	52.002	76.527	53.493	13.820	- 583.408	- 515.432	187.765
600	54.750	84.572	57.390	19.368	- 582.487	- 504.172	157.409
700	65.050	93.296	61.360	25.548	- 580.792	- 493.098	134.708
800	66.020	101.053	64.347	32.135	- 578.844	- 482.249	117.106
900	64.000	107.827	66.269	38.658	- 577.017	- 471.616	103.071
1000	62.430	113.935	73.042	48.940	- 575.478	- 461.157	91.623
1100	62.430	118.387	77.696	51.703	- 570.551	- 430.713	81.860
1200	62.430	124.364	80.175	57.446	- 616.724	- 435.768	73.259
1300	62.430	128.991	83.498	61.689	- 616.965	- 421.762	65.840
1400	62.430	133.298	86.677	66.932	- 615.244	- 407.878	59.428
1500	62.430	137.327	89.718	74.175	- 613.587	- 394.108	53.833
1600	62.430	141.112	92.631	82.418	- 635.897	- 380.230	48.882
1700	62.430	144.680	95.424	86.661	- 634.161	- 365.740	44.346
1800	62.430	148.056	98.106	94.904	- 632.449	- 350.347	40.299
1900	62.430	151.258	100.684	101.147	- 630.752	- 335.546	36.667
2000	62.430	154.304	103.146	107.380	- 629.046	- 320.828	33.389
2100	62.430	157.208	105.557	113.633	- 627.389	- 306.180	30.417
2200	62.430	159.983	107.863	119.876	- 625.742	- 291.630	27.711
2300	62.430	162.640	110.091	126.119	- 624.102	- 277.130	25.236
2400	62.430	165.189	112.244	132.362	- 622.477	- 262.716	22.667
2500							

Dec. 31, 1960; June 30, 1965; Sept. 30, 1967

SODIUM DISILICATE (Na₂Si₂O₅)

(LIQUID)

S[°]_{298.15} = 45.101 gibbs/mol

T_m = 1147°K

ΔH_f° _{298.15} = -582.811 kcal/mol

ΔH_m° = 8.5 kcal/mol

GFw = 182.1586

Heat of Formation

The ΔH_f° ₂₉₈(*l*) is obtained from ΔH_f° ₂₉₈(*c*) by adding ΔH_m° and the difference between $H^\circ_{1147} - H^\circ_{298}$ for crystal and liquid. The heats of solution of NaCl(*c*), Na₂SO₄(*c*), HCl(aq), H₂SO₄(aq), SiO₂(quartz) and Na₂Si₂O₅(gl) in 20 percent hydrofluoric acid at 74.7°C were measured by Kracek (1). Following the same procedure as described in the Na₂Si₂O₅(*c*) table, we derive the enthalpy changes, ΔH_f° ₂₉₈, for the reaction Na₂O(*c*) + 2SiO₂(quartz) = Na₂Si₂O₅(gl) as -49.40 and -50.64 kcal/mol using the heats of solution of Na₂O(*c*) as -87.50 (chloride scheme) and -88.74 kcal/mol (sulfate scheme), respectively. Adopting the weighted average ΔH_f° ₂₉₈ = -49.81 kcal/mol with ΔH_f° ₂₉₈(Na₂O, *c*) = -99.9 kcal/mol and ΔH_f° ₂₉₈(SiO₂, quartz) = -217.7 kcal/mol, we obtain ΔH_f° ₂₉₈ = -585.113 kcal/mol for Na₂Si₂O₅(gl).

Using high temperature reaction calorimetry, Krögar (2) determined the enthalpy changes as 25.28 ± 0.22 and -18.58 ± 0.36 kcal/mol for the reactions Na₂CO₃(*c*) + 2SiO₂(quartz) = Na₂Si₂O₅(gl) + CO₂(g) and 2NaOH(*c*) + 2SiO₂(quartz) = Na₂Si₂O₅(gl) + H₂O(*l*), respectively. From the given results, we calculate the corresponding values of ΔH_f° ₂₉₈(Na₂Si₂O₅, gl) to be -586.32 and -589.46 kcal/mol, using ΔH_f° ₂₉₈ = -270.26, -217.70, -94.05, -101.90 and -68.32 kcal/mol for Na₂CO₃(*c*), SiO₂(quartz), CO₂(g), NaOH(*c*) and H₂O(*l*), respectively. These two ΔH_f° ₂₉₈(Na₂Si₂O₅, (*l*)) values, as well as the value -585.113 kcal/mol based on Kracek's data, are not adopted, because incorporating these ΔH_f° ₂₉₈(gl) values with the value of ΔH_f° ₂₉₈(*c*), gives values of the heat of melting at 298°K which are too low in comparison with the other values (see the Na₂Si₂O₅(*c*) table).

Hummel (3) measured the heats of solution of Na₂CO₃(*c*), SiO₂(quartz) and Na₂Si₂O₅(gl) in 39 percent hydrofluoric acid at 26.5°C, as -244.1, -584.5 and -673.7 cal/g, respectively. Based on these results, we derive the enthalpy change for the reaction Na₂CO₃(*c*) + 2SiO₂(quartz) = Na₂Si₂O₅(gl) + CO₂(g) to be 79.01 kcal/mol, yielding ΔH_f° ₂₉₈(Na₂Si₂O₅, gl) = -582.6 kcal/mol which is in good agreement with the adopted value.

Heat Capacity and Entropy

Using drop calorimetry, Naylor (4) has measured the enthalpies of Na₂Si₂O₅(gl), 445.5 - 1120.7°K, and Na₂Si₂O₅(*l*), 1173.2 - 1744°K. Based on the liquid enthalpy data, we evaluate the heat capacity of Na₂Si₂O₅(*l*) to be 62.43 gibbs/mol. The Cp values below 1147°K are derived from the enthalpies measured at 445.5 - 1120.7°K by Naylor (4). Below 600°K, Cp is identical with that of the crystal. The adopted curve rises rapidly to a maximum in the glass transition region, 650-950°K, then smoothly approaches the value of the real liquid near T_m. The heat capacity of Na₂Si₂O₅(*l*) is assumed to be constant in the temperature range 1147 to 2500°K.

S[°]₂₉₈ is obtained in a manner analogous to that of the heat of formation.

Melting Data

See Na₂Si₂O₅(*c*) table for details.

References

1. F. C. Kracek, Ann. Rpt. Director of the Geophysical Laboratory, No. 1215, 69 (1953).
2. C. Krögar and V. Janatko, Z. Anorg. Allgem. Chem. 284, 84 (1956).
3. C. Hummel and H. E. Schwiete, Glastsch. Ber. 32, 327 (1959).
4. B. F. Naylor, J. Am. Chem. Soc. 67, 466 (1945).

Na₂O₅Si₂

Disodium Sulfide (Na₂S)

INTERIM TABLE

(Solid) Mol. Wt. = 78.048

T. °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0									
100									
200									
298	18.990	23.400	23.400	4.000	-	89.000	-	86.368	63.307
300	19.000	23.517	23.400	4.035	-	88.999	-	86.351	62.903
400	19.300	29.025	24.469	11.871	-	80.871	-	85.342	46.427
500	19.600	33.353	29.573	31.893	-	91.366	-	83.903	36.672
600	19.900	36.964	27.180	54.870	-	91.670	-	82.381	30.006
700	20.200	40.054	28.803	74.875	-	91.877	-	80.793	25.523
800	20.500	42.771	30.383	94.910	-	103.070	-	77.508	18.796
900	20.800	45.202	31.897	114.870	-	104.536	-	74.377	16.254
1000	21.100	47.409	33.339	134.712	-	104.246	-	71.380	14.181
1100	21.400	49.435	34.712	154.350	-	104.013	-	68.589	12.270
1200	21.700	51.359	36.018	173.787	-	103.839	-	65.987	10.507
1300	22.000	53.088	37.262	193.025	-	103.725	-	63.565	8.896
1400	22.300	54.708	38.458	212.062	-	103.663	-	61.317	7.426
1500	22.600	56.228	39.605	230.999	-	103.653	-	59.222	6.081
1600	22.900	57.716	40.673	249.770	-	103.699	-	57.279	4.851
1700	23.200	59.114	41.717	268.375	-	103.795	-	55.489	3.726
1800	23.500	60.448	42.721	286.810	-	103.933	-	53.851	2.694
1900	23.800	61.727	43.687	305.083	-	104.113	-	52.366	1.756
2000	24.100	62.955	44.609	323.207	-	104.335	-	51.028	0.928

December 31, 1960.

Na₂SDISODIUM SULFIDE (Na₂S)

(Solid)

Mol. Wt. = 78.048

ΔH_f° 298.15 = -89 kcal. mole⁻¹S°_{298.15} = 23.4 cal. deg.⁻¹ mole⁻¹T_m = 1223°K.ΔH_m = 16 kcal. mole⁻¹

ΔH_f° 298.15', T_m' and ΔH_m' from National Bureau of Standards Circular 500 (1952). S°_{298.15} calculated from ΔH_f° 298.15' as reported by N. A. Landiya, Zhur. Fiz. Khim. 24, 257 (1950). C_p estimated.

Na₂S

Disodium Sulfide (Na₂S)Na₂S

INTERIM TABLE

(Liquid) Mol. Wt. = 78.048

T, °K.	C _p ^a	S ^b - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^c	ΔF _f ^c	Log K _p
100						
200	17.61*	24.136	.000	- 87.870	- 85.458	62.639
298						
300	17.666	24.245	1.033	- 87.871	- 85.441	62.291
400	19.445	24.853	3.893	- 87.876	- 85.447	60.445
500	20.341	24.936	5.955	- 87.876	- 85.447	58.329
600	20.848	24.986	7.681	- 87.876	- 85.447	56.747
700	21.142	24.995	8.956	- 87.876	- 85.447	55.031
800	21.346	24.995	10.183	- 87.876	- 85.447	53.183
900	21.511	24.995	12.273	- 87.876	- 85.447	51.183
1000	21.614	24.995	14.264	- 87.876	- 85.447	49.033
1100	21.690	24.995	16.160	- 87.876	- 85.447	46.747
1200	21.748	24.995	17.973	- 87.876	- 85.447	44.329
1300	21.794	24.995	19.708	- 87.876	- 85.447	41.783
1400	21.830	24.995	21.378	- 87.876	- 85.447	39.129
1500	21.860	24.995	22.995	- 87.876	- 85.447	36.379
1600	21.884	24.995	24.564	- 87.876	- 85.447	33.539
1700	21.904	24.995	26.089	- 87.876	- 85.447	30.619
1800	21.920	24.995	27.573	- 87.876	- 85.447	27.629
1900	21.934	24.995	29.019	- 87.876	- 85.447	24.579
2000	21.947	24.995	30.431	- 87.876	- 85.447	21.479
2100	21.956	24.995	31.815	- 87.876	- 85.447	18.329
2200	21.965	24.995	33.175	- 87.876	- 85.447	15.129
2300	21.973	24.995	34.515	- 87.876	- 85.447	11.879
2400	21.980	24.995	35.839	- 87.876	- 85.447	8.589
2500	21.987	24.995	37.151	- 87.876	- 85.447	5.259
2600	21.993	24.995	38.455	- 87.876	- 85.447	1.889
2700	21.998	24.995	39.755	- 87.876	- 85.447	- 1.511
2800	22.002	24.995	41.055	- 87.876	- 85.447	- 2.811
2900	22.006	24.995	42.355	- 87.876	- 85.447	- 4.061
3000	22.009	24.995	43.655	- 87.876	- 85.447	- 5.261

Mol. Wt. = 78.048

ΔH_f^{298.15} = [-87.870] kcal. mole⁻¹S_{298.15}^{298.15} = [24.136] cal. deg.⁻¹ mole⁻¹T_m = 1223°K.ΔH_m¹²²³ = 16 kcal. mole⁻¹

T_m and ΔH_m from National Bureau of Standards Circular 500 (1952).
Other data estimated.

DISODIUM SULFIDE (Na₂S) (Liquid)Na₂S

December 31, 1960.

Oxygen, Monatomic (0)

(Ideal Gas) At. Wt. = 16.000

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	58,989	58,989	INFINITE
100	5.666	32.466	1.008	58,989	58,989	126.730
200	5.434	36.340	1.523	58,989	58,989	61.902
298	5.237	38.468	2.000	58,989	58,989	40.604
300	5.235	38.501	2.010	58,989	58,989	40.334
400	5.135	39.991	3.672	58,989	58,989	29.473
500	5.041	41.131	5.055	58,989	58,989	22.940
600	4.959	42.054	6.138	58,989	58,989	18.574
700	4.892	42.831	7.005	58,989	58,989	15.449
800	4.835	43.501	7.698	58,989	58,989	13.101
900	4.786	44.092	8.252	58,989	58,989	11.272
1000	4.744	44.619	8.697	58,989	58,989	9.807
1100	4.708	45.095	9.051	58,989	58,989	8.604
1200	4.677	45.529	9.332	58,989	58,989	7.604
1300	4.649	45.928	9.568	58,989	58,989	6.755
1400	4.624	46.298	9.768	58,989	58,989	6.011
1500	4.602	46.642	9.940	58,989	58,989	5.395
1600	4.581	46.963	10.087	58,989	58,989	4.862
1700	4.561	47.269	10.213	58,989	58,989	4.398
1800	4.542	47.560	10.321	58,989	58,989	3.978
1900	4.524	47.838	10.413	58,989	58,989	3.599
2000	4.507	48.104	10.490	58,989	58,989	3.178
2100	4.491	48.359	10.554	58,989	58,989	2.840
2200	4.476	48.604	10.606	58,989	58,989	2.551
2300	4.461	48.840	10.649	58,989	58,989	2.307
2400	4.447	49.067	10.684	58,989	58,989	2.065
2500	4.434	49.286	10.711	58,989	58,989	1.842
2600	4.421	49.498	10.731	58,989	58,989	1.636
2700	4.409	49.703	10.745	58,989	58,989	1.446
2800	4.397	49.901	10.754	58,989	58,989	1.268
2900	4.386	49.999	10.759	58,989	58,989	1.103
3000	4.375	50.096	10.761	58,989	58,989	0.949
3100	4.364	50.191	10.761	58,989	58,989	0.805
3200	4.353	50.284	10.759	58,989	58,989	0.671
3300	4.343	50.374	10.754	58,989	58,989	0.546
3400	4.333	50.461	10.747	58,989	58,989	0.429
3500	4.323	50.546	10.737	58,989	58,989	0.310
3600	4.313	50.628	10.724	58,989	58,989	0.204
3700	4.303	50.707	10.708	58,989	58,989	0.107
3800	4.293	50.783	10.689	58,989	58,989	0.084
3900	4.283	50.856	10.667	58,989	58,989	0.061
4000	4.273	50.926	10.642	58,989	58,989	0.037
4100	4.263	50.993	10.615	58,989	58,989	0.013
4200	4.253	51.057	10.586	58,989	58,989	0.000
4300	4.243	51.118	10.554	58,989	58,989	0.000
4400	4.233	51.176	10.519	58,989	58,989	0.000
4500	4.223	51.231	10.482	58,989	58,989	0.000
4600	4.213	51.283	10.442	58,989	58,989	0.000
4700	4.203	51.332	10.399	58,989	58,989	0.000
4800	4.193	51.378	10.353	58,989	58,989	0.000
4900	4.183	51.421	10.304	58,989	58,989	0.000
5000	4.173	51.461	10.252	58,989	58,989	0.000
5100	4.163	51.498	10.197	58,989	58,989	0.000
5200	4.153	51.532	10.139	58,989	58,989	0.000
5300	4.143	51.563	10.078	58,989	58,989	0.000
5400	4.133	51.591	10.014	58,989	58,989	0.000
5500	4.123	51.616	9.947	58,989	58,989	0.000
5600	4.113	51.639	9.877	58,989	58,989	0.000
5700	4.103	51.659	9.804	58,989	58,989	0.000
5800	4.093	51.676	9.728	58,989	58,989	0.000
5900	4.083	51.691	9.649	58,989	58,989	0.000
6000	4.073	51.704	9.567	58,989	58,989	0.000

June 30, 1962

OXYGEN, MONATOMIC (0)

(IDEAL GAS)

At. Wt. = 16.000

ΔH_f⁰ = 58.989 kcal. mole⁻¹
 ΔH_f⁰ 298.15 = 59.559 ± 0.03 kcal. mole⁻¹
 S_{298.15} = 39.47 cal. deg.⁻¹ mole⁻¹

Electronic Levels and Multiplicities

E, cm. ⁻¹	E ₁	E ₂	E ₃	E ₄	E ₅
0.0	5	5	5	5	5
158.5	3	3	3	3	3
226.5	1	1	1	1	1
15,867.7	5	5	5	5	5
33,752.4	1	1	1	1	1

Heat of Formation

P. Brin and G. Herzberg, Can. J. Phys. 32, 110 (1954), observed 21 bands in the transition $X^3\Sigma^- \rightarrow B^3\Sigma^-$. The Birge-Sponer extrapolation to the dissociation products $^3P_2 + ^1D_2$ was corrected to the zero levels, $^3P_2 + ^3P_2$, to give the dissociation energy 41260 ± 15 cm.⁻¹. This is in agreement with the extrapolation of the band heads 3P_2 of the $X^3\Sigma^- \rightarrow A^3\Sigma^+$ transition which goes to the normal products. The extrapolation of the B level is very small, the lowest ΔG_{1/2} is 34 cm.⁻¹

Heat Capacity and Entropy

The electronic levels from C. E. Moore, Nat. Bur. Standards, Circ. 467, (1949), were averaged above 80,000 cm.⁻¹

Oxygen Uninegative Ion (O⁻)

(Ideal Gas) Mol. Wt. = 15.99995

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0								
100								
200								
298	5.149	37.712	37.712	0.000	24.300	21.849	16.015	
300	5.147	37.743	37.712	0.010	24.294	21.834	15.005	
400	5.081	39.214	37.613	0.521	23.953	21.064	11.508	
500	5.005	40.834	38.250	1.027	23.596	20.363	8.490	
600	5.024	41.261	38.711	1.530	23.225	19.776	7.203	
700	5.010	42.035	39.112	2.032	22.842	19.231	6.004	
800	5.001	42.703	39.538	2.532	22.446	18.742	5.120	
900	4.994	43.292	40.023	3.032	22.042	18.302	4.444	
1000	4.990	43.818	40.266	3.531	21.631	17.910	3.914	
1100	4.986	44.293	40.629	4.030	21.213	17.557	3.468	
1200	4.983	44.727	40.953	4.528	20.790	17.243	3.140	
1300	4.981	45.115	41.259	5.027	20.364	16.966	2.852	
1400	4.979	45.455	41.548	5.525	19.933	16.719	2.610	
1500	4.978	45.838	41.823	6.022	19.498	16.506	2.405	
1600	4.977	46.159	42.084	6.520	19.061	16.321	2.229	
1700	4.976	46.461	42.333	7.018	18.620	16.163	2.078	
1800	4.975	46.745	42.570	7.515	18.177	16.033	1.947	
1900	4.974	47.014	42.797	8.012	17.734	15.924	1.832	
2000	4.974	47.269	43.014	8.510	17.281	15.841	1.731	
2100	4.973	47.512	43.223	9.008	16.829	15.781	1.642	
2200	4.973	47.743	43.423	9.505	16.373	15.741	1.564	
2300	4.972	47.965	43.616	10.002	15.916	15.722	1.494	
2400	4.972	48.176	43.801	10.499	15.455	15.724	1.432	
2500	4.972	48.379	43.980	10.997	14.992	15.744	1.376	
2600	4.972	48.574	44.153	11.494	14.526	15.784	1.327	
2700	4.971	48.762	44.321	11.991	14.057	15.839	1.282	
2800	4.971	48.942	44.482	12.488	13.585	15.916	1.242	
2900	4.971	49.117	44.639	12.985	13.113	16.007	1.206	
3000	4.971	49.285	44.791	13.482	12.636	16.118	1.174	
3100	4.971	49.448	44.939	13.979	12.158	16.242	1.145	
3200	4.970	49.606	45.082	14.476	11.677	16.378	1.118	
3300	4.970	49.759	45.222	14.973	11.194	16.532	1.095	
3400	4.970	49.908	45.357	15.470	10.709	16.698	1.073	
3500	4.970	50.052	45.480	15.967	10.222	16.881	1.054	
3600	4.970	50.192	45.618	16.464	9.733	17.079	1.037	
3700	4.970	50.328	45.744	16.961	9.242	17.293	1.021	
3800	4.970	50.460	45.866	17.458	8.750	17.518	1.007	
3900	4.970	50.589	45.986	17.955	8.256	17.754	0.995	
4000	4.970	50.715	46.102	18.452	7.761	18.005	0.984	
4100	4.970	50.838	46.216	18.949	7.263	18.268	0.974	
4200	4.969	50.958	46.328	19.446	6.765	18.537	0.965	
4300	4.969	51.075	46.437	19.943	6.265	18.825	0.957	
4400	4.969	51.189	46.543	20.440	5.763	19.121	0.950	
4500	4.969	51.301	46.648	20.937	5.261	19.432	0.944	
4600	4.969	51.410	46.750	21.434	4.758	19.754	0.938	
4700	4.969	51.517	46.851	21.931	4.253	20.085	0.934	
4800	4.969	51.621	46.949	22.428	3.747	20.432	0.930	
4900	4.969	51.724	47.045	22.925	3.241	20.778	0.927	
5000	4.969	51.824	47.140	23.421	2.734	21.141	0.924	
5100	4.969	51.923	47.233	23.918	2.225	21.516	0.922	
5200	4.969	52.019	47.324	24.415	1.716	21.898	0.920	
5300	4.969	52.114	47.413	24.912	1.207	22.293	0.919	
5400	4.969	52.208	47.501	25.409	0.696	22.693	0.918	
5500	4.969	52.298	47.588	25.906	0.189	23.107	0.918	
5600	4.969	52.387	47.672	26.403	-0.326	23.533	0.918	
5700	4.969	52.475	47.756	26.900	-0.838	23.957	0.919	
5800	4.969	52.562	47.838	27.397	-1.350	24.399	0.919	
5900	4.969	52.648	47.919	27.894	-1.863	24.846	0.920	
6000	4.969	52.730	47.998	28.390	-2.377	25.304	0.922	

June 30, 1965

OXYGEN UNINEGATIVE ION (O⁻)

(IDEAL GAS)

MOL. WT. = 15.99995

Ground State Configuration $2p_{3/2}^2$

$\Delta F_f^0 = 25.2 \pm .5$ kcal/mole

$\Delta F_f^0 = 298.15 = 24.3 \pm .5$ kcal/mole

Electronic Levels and Quantum Weight

$\mathcal{E}_l$, cm. ⁻¹	$\frac{g_l}{4}$
0.0	2
[150.0]	2

Heat of Formation.

The heat of formation was calculated from the equation: $O(g) + e^- \rightarrow O^-(g)$ with the JANAF auxiliary value for $O(g)$; using the measured electron affinity = 1.465 e.v. (33.783 kcal/mole) obtained from L. M. Branscomb, D. S. Burch, S. J. Smith and S. Oulman, Phys. Rev. **111**, 504 (1958). Other calculated values for the electron affinity are: 1.22 e.v. E. Clementi and A. D. McLean, Phys. Rev. **133**, 4419 (1964); 1.16 e.v. E. Clementi, A. D. McLean, D. L. Rainondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964); and 1.47 e.v. B. Edlén, J. Chem. Phys. **33**, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were estimated by assuming that the extra electron would produce an electronic structure similar to the next higher atomic numbered element, in this case F(I). An analogy was then made between O^- and F(I) with $O(I)$ and F(II), and $O(II)$ and F(III) in order to estimate the height of the first level above the ground state. The data for F(I), O(I), F(II), O(II) and F(III) were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949. It is possible that the entropy below 3000°K. could be in error by 0.5 e.v. due to the estimation of the low lying electronic level. The electronic levels above 1×10^5 cm.⁻¹ were omitted because their contribution is negligible below 6000°K. The $H^\circ - H^\circ_{298}$ value at 0°K. is -1.567 kcal/mole.

Phosphorus Monoxide (P₀)

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 46.975

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.597	53.219	2.245	1.801	1.801	INFINITE
200	7.597	53.219	1.776	1.407	1.407	6.661
298	7.597	53.219	1.000	1.455	8.391	6.151
300	7.598	53.219	1.014	1.456	8.434	6.144
400	7.624	53.464	1.776	1.580	10.742	5.869
500	7.631	53.468	1.561	1.734	13.016	5.669
600	7.631	53.468	1.561	1.734	13.016	5.669
700	7.631	53.468	1.561	1.734	13.016	5.669
800	7.631	53.468	1.561	1.734	13.016	5.669
900	7.631	53.468	1.561	1.734	13.016	5.669
1000	7.631	53.468	1.561	1.734	13.016	5.669
1100	7.631	53.468	1.561	1.734	13.016	5.669
1200	7.631	53.468	1.561	1.734	13.016	5.669
1300	7.631	53.468	1.561	1.734	13.016	5.669
1400	7.631	53.468	1.561	1.734	13.016	5.669
1500	7.631	53.468	1.561	1.734	13.016	5.669
1600	7.631	53.468	1.561	1.734	13.016	5.669
1700	7.631	53.468	1.561	1.734	13.016	5.669
1800	7.631	53.468	1.561	1.734	13.016	5.669
1900	7.631	53.468	1.561	1.734	13.016	5.669
2000	7.631	53.468	1.561	1.734	13.016	5.669
2100	7.631	53.468	1.561	1.734	13.016	5.669
2200	7.631	53.468	1.561	1.734	13.016	5.669
2300	7.631	53.468	1.561	1.734	13.016	5.669
2400	7.631	53.468	1.561	1.734	13.016	5.669
2500	7.631	53.468	1.561	1.734	13.016	5.669
2600	7.631	53.468	1.561	1.734	13.016	5.669
2700	7.631	53.468	1.561	1.734	13.016	5.669
2800	7.631	53.468	1.561	1.734	13.016	5.669
2900	7.631	53.468	1.561	1.734	13.016	5.669
3000	7.631	53.468	1.561	1.734	13.016	5.669
3100	7.631	53.468	1.561	1.734	13.016	5.669
3200	7.631	53.468	1.561	1.734	13.016	5.669
3300	7.631	53.468	1.561	1.734	13.016	5.669
3400	7.631	53.468	1.561	1.734	13.016	5.669
3500	7.631	53.468	1.561	1.734	13.016	5.669
3600	7.631	53.468	1.561	1.734	13.016	5.669
3700	7.631	53.468	1.561	1.734	13.016	5.669
3800	7.631	53.468	1.561	1.734	13.016	5.669
3900	7.631	53.468	1.561	1.734	13.016	5.669
4000	7.631	53.468	1.561	1.734	13.016	5.669
4100	7.631	53.468	1.561	1.734	13.016	5.669
4200	7.631	53.468	1.561	1.734	13.016	5.669
4300	7.631	53.468	1.561	1.734	13.016	5.669
4400	7.631	53.468	1.561	1.734	13.016	5.669
4500	7.631	53.468	1.561	1.734	13.016	5.669
4600	7.631	53.468	1.561	1.734	13.016	5.669
4700	7.631	53.468	1.561	1.734	13.016	5.669
4800	7.631	53.468	1.561	1.734	13.016	5.669
4900	7.631	53.468	1.561	1.734	13.016	5.669
5000	7.631	53.468	1.561	1.734	13.016	5.669
5100	7.631	53.468	1.561	1.734	13.016	5.669
5200	7.631	53.468	1.561	1.734	13.016	5.669
5300	7.631	53.468	1.561	1.734	13.016	5.669
5400	7.631	53.468	1.561	1.734	13.016	5.669
5500	7.631	53.468	1.561	1.734	13.016	5.669
5600	7.631	53.468	1.561	1.734	13.016	5.669
5700	7.631	53.468	1.561	1.734	13.016	5.669
5800	7.631	53.468	1.561	1.734	13.016	5.669
5900	7.631	53.468	1.561	1.734	13.016	5.669
6000	7.631	53.468	1.561	1.734	13.016	5.669

December 31, 1950.

Phosphorus Monoxide (P₀)

(Ideal Gas)

Mol. Wt. = 46.975

ΔH_f^o 298.15 = -1.46 ± 2 kcal. mole⁻¹S_{298.15}^o = 53.22 cal. deg.⁻¹ mole⁻¹

Ground State Configuration 2Π

Electronic Levels and Multiplicities

E₁, cm.⁻¹ g₁

0 2

222.6 2

ω_e^x_e = 6.57 cm.⁻¹α_e = 0.0055 cm.⁻¹r_e = 1.473 Åω_e = 1233.42 cm.⁻¹B_e = 0.734 cm.⁻¹

σ = 1

Heat of formation based upon a dissociation energy of 49,000 cm.⁻¹,

which is the value of two predissociations observed by K. Dressler,

Helv. Phys. Acta 29, 563 (1955).

Heat Capacities and Entropies. Molecular and spectroscopic con-

stants based upon measurements of K. Dressler, loc. cit., K. S.

Hao, Can. J. Phys. 36, 1526 (1958), and those of M. L. Singh, Can.

J. Phys. 37, 136 (1959).

INTERIM TABLE

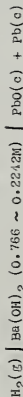
T, °K.	C _p ^o	$\int_0^T C_p^o dT$	$\int_0^T C_p^o dT / T$	$H^o - H_{298}^o$	ΔH_f^o	Log K _p
0	0.000	0.000	0.000	0.000	0.000	0.000
100	0.422	5.919	1.015	1.015	51.903	1.579
200	0.844	11.838	2.030	2.030	51.903	1.579
298	1.0943	15.592	2.592	2.592	51.903	1.579
300	1.0960	15.660	2.592	2.592	51.903	1.579
400	1.1760	18.928	3.268	3.268	51.903	1.579
500	12.420	21.676	3.639	3.639	51.903	1.579
600	12.970	23.940	3.876	3.876	51.903	1.579
700	13.400	25.974	4.090	4.090	51.903	1.579
800	13.800	27.789	4.281	4.281	51.903	1.579
900	14.200	29.438	4.451	4.451	51.903	1.579
1000	14.600	30.934	4.601	4.601	51.903	1.579
1100	15.000	32.365	4.734	4.734	51.903	1.579
1200	15.400	33.687	4.853	4.853	51.903	1.579
1300	15.800	34.935	4.959	4.959	51.903	1.579
1400	16.200	36.121	5.055	5.055	51.903	1.579
1500	16.600	37.252	5.142	5.142	51.903	1.579
1600	17.000	38.336	5.221	5.221	51.903	1.579
1700	17.400	39.374	5.293	5.293	51.903	1.579
1800	17.800	40.365	5.359	5.359	51.903	1.579
1900	18.200	41.308	5.420	5.420	51.903	1.579
2000	18.600	42.202	5.476	5.476	51.903	1.579
2100	19.000	43.048	5.528	5.528	51.903	1.579
2200	19.400	43.846	5.576	5.576	51.903	1.579
2300	19.800	44.594	5.620	5.620	51.903	1.579
2400	20.200	45.293	5.660	5.660	51.903	1.579
2500	20.600	45.943	5.697	5.697	51.903	1.579

March 31, 1952

Lead Monoxide, Red (PbO) (Crystal)

Mol. Wt. = 223.21
 $\Delta H_f^o 298.15 = -52.41 \pm 0.16 \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = 15.6 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o 298.15 = 63.88 \pm 0.22 \text{ kcal. mole}^{-1}$
 $T_f = 762^\circ \text{K}$
 $\Delta H_f^o = 0.18 \pm 0.23 \text{ kcal. mole}^{-1}$

Heat of Formation. Calculated from the cell reaction



reported by D. P. Smith and H. K. Woods, J. Am. Chem. Soc., 45, 2632 (1923), using $\Delta H_f^o 298.15$ for $\text{H}_2\text{O}(\text{l})$, $-68.317 \text{ kcal. mole}^{-1}$, given by Natl. Bur. Standards Circular 500 (1952). ΔH_f^o values reported by other investigators were discussed by R. W. Miller, J. Am. Chem. Soc., 51, 207 (1929).

Heat Capacity and Entropy. Heat capacity values (51° to 230.15°K) were obtained from E. O. King, J. Am. Chem. Soc., 80, 2400 (1958). For the higher temperature range, heat capacity given by K. K. Kelley, U. S. Bur. Mines Bull. 504 (1960) was used and joined smoothly to data of King at 230.15°K by graphical extrapolation. King obtained entropies below 51°K by empirical extrapolation of the heat capacity curve which fits the measured heat capacities within 1.3%.

Transition Data. Heat of transition recalculated from the data given by E. O. King, loc. cit.

Heat of Sublimation. Calculated from free-energy functions and vapor pressure reported by A. N. Neumayr, L. P. Pirova and E. P. Lukova, Zhur. Fiz. Khim. 33, 1699 (1960) and R. H6rbe and O. Knecko, Z. Erzhbergbau u. Metallurgie, 12, 321 (1959).

Lead Monoxide, Yellow (PbO)
(Crystal) Mol. Wt. = 223.21

INTERIM TABLE

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	0.000	INFINITE	-	51.598	-	INFINITE
100	9.591	6.352	24.842	-	52.013	-	40.492
200	9.720	11.980	17.040	-	52.125	-	47.305
298	10.958	16.114	16.114	0.000	52.066	-	44.949
300	10.970	16.182	16.182	0.020	52.068	-	44.905
400	11.631	19.433	16.553	1.552	51.940	-	42.535
500	12.084	22.080	17.402	2.339	51.791	-	40.202
600	12.489	24.319	18.373	3.568	51.630	-	37.898
700	12.853	26.257	19.362	5.242	51.452	-	35.622
800	13.185	27.907	20.357	7.453	51.265	-	33.387
900	13.415	29.557	21.276	9.453	51.069	-	31.197
1000	13.706	30.956	22.177	10.409	50.867	-	29.052
1100	13.992	32.306	23.038	10.194	50.652	-	26.953
1200	14.275	33.535	23.862	11.407	50.424	-	24.901
1300	14.553	34.681	24.658	12.516	50.184	-	22.893
1400	14.823	35.778	25.424	13.518	49.934	-	20.928
1500	15.110	36.811	26.134	14.015	49.677	-	18.998
1600	15.396	37.794	26.832	17.540	49.087	-	14.332
1700	15.660	38.735	27.505	19.092	48.565	-	12.116
1800	15.905	39.538	28.154	20.572	48.124	-	9.927
1900	16.135	40.207	28.784	21.993	47.663	-	8.133
2000	16.443	41.346	29.399	23.914	46.181	-	5.922
2100	16.756	42.156	29.977	25.576	45.129	-	4.203
2200	17.079	42.942	30.549	27.265	44.516	-	2.830
2300	17.397	43.507	31.118	28.982	43.846	-	1.722
2400	17.575	43.607	31.685	30.726	43.279	-	0.906
2500	17.647	45.170	32.172	32.497	42.655	-	0.366
2600	18.119	45.874	32.685	34.295	41.979	-	1.572
2700	18.391	46.564	33.187	36.120	41.253	-	1.042
2800	18.643	47.238	33.678	37.973	40.476	-	0.691
2900	18.885	47.991	34.155	39.855	39.649	-	0.481
3000	19.208	48.544	34.624	41.760	38.781	-	2.534

Lead Monoxide, Yellow (PbO) (Crystal)

Mol. Wt. = 223.21
 $\Delta H_f^{298.15} = -52.07 \pm 0.28$ kcal. mole⁻¹
 $S_{298.15}^{298.15} = 16.1 \pm 0.2$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_s^{298.15} = 63.54 \pm 0.32$ kcal. mole⁻¹
 $T_m = 1170 \pm 4^\circ K.$
 $\Delta H_m^{298.15} = 6.1 \pm 0.1$ kcal. mole⁻¹

Heat of Formation. Calculated from $\Delta H_f^{298.15}$ for PbO (c, red) and $\Delta H_c^{298.15}$ between PbO (c, red) and PbO (c, yellow).

Heat Capacity, Entropy, and Melting Data. C_p values (51° to 298.15°K.) obtained from E. G. King, J. Am. Chem. Soc., 80, 2400 (1958). For the higher temperature range, the heat capacity reported by E. N. Rodigina, K. Z. Gornel'skii and V. P. Luginina, Zhur. Fiz. Khim., 35, 1799 (1961) was used and joined smoothly to data of King at 298.15°K. by graphical extrapolation. T_m and $\Delta H_m^{298.15}$ given by E. N. Rodigina, K. Z. Gornel'skii and V. P. Luginina, loc. cit.

Heat of Sublimation. Calculated from $\Delta H_c^{298.15}$ and $\Delta H_s^{298.15}$ for PbO (c, red).

INTERIM TABLE

(Liquid) Mol. Wt. = 223.21

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0							
100	10.950	20.546	.000	- 46.712	- 40.916	- 29.991	
200	10.979	20.614	.002	- 46.710	- 40.880	- 29.740	
300	11.014	20.685	.003	- 46.586	- 36.924	- 21.283	
400	11.054	20.761	.004	- 46.437	- 37.064	- 16.200	
500	11.094	20.834	.005	- 46.276	- 35.204	- 12.822	
600	12.469	28.752	3.568	- 46.271	- 33.181	- 10.359	
700	12.462	30.700	4.832	- 46.271	- 33.181	- 10.359	
800	13.535	32.492	7.177	- 46.016	- 29.231	- 7.096	
900	13.535	34.295	8.674	- 46.180	- 27.314	- 5.969	
1000	13.535	36.100	10.337	- 45.745	- 25.449	- 5.056	
1100	13.535	37.911	12.165	- 45.306	- 23.622	- 4.302	
1200	13.535	40.034	14.268	- 44.867	- 21.939	- 3.674	
1300	13.535	42.257	16.650	- 43.997	- 18.353	- 2.674	
1400	13.535	44.680	19.332	- 43.569	- 16.656	- 2.275	
1500	13.535	47.307	22.434	- 43.145	- 14.989	- 1.927	
1600	13.535	50.202	25.957	- 42.730	- 13.345	- 1.620	
1700	13.535	53.330	29.865	- 42.322	- 11.725	- 1.350	
1800	13.535	56.728	34.137	- 41.922	- 10.124	- 1.106	
1900	13.535	60.402	38.826	- 41.529	- 8.551	- .886	
2000	13.535	64.407	43.913	- 41.142	- 7.002	- .686	
2100	13.535	68.780	49.450	- 40.760	- 5.476	- .506	
2200	13.535	73.553	55.583	- 40.383	- 3.973	- .332	
2300	13.535	78.780	62.350	- 40.010	- 2.492	- .166	
2400	13.535	84.407	69.800	- 39.642	- 1.036	- .016	
2500	13.535	90.480	77.983	- 39.279	- .606	- .006	
2600	13.535	97.053	86.850	- 38.920	- .206	- .002	
2700	13.535	104.180	96.450	- 38.565	- .830	- .002	
2800	13.535	111.807	106.850	- 38.215	- 1.472	- .002	
2900	13.535	120.000	118.000	- 37.870	- 2.136	- .002	
3000	13.535	128.750	130.000	- 37.530	- 2.820	- .002	

March 31, 1962

Lead Monoxide (PbO) (Liquid)

Mol. Wt. = 223.21

 ΔH_f^0 298.15 = [-46.712] kcal. mole⁻¹ $S_{298.15}^0$ = [20.546] cal. deg.⁻¹ mole⁻¹ T_m = 1170 ± 4°K. ΔH_m^0 = 6.1 ± 0.1 kcal. mole⁻¹ T_b = 1769°K. ΔH_v^0 = 49.53 ± 0.22 kcal. mole⁻¹

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy, and Melting Data. C_p , T_m , and ΔH_m^0 are obtained from E. N. Rodigina, K. Z. Gmel'skii and V. P. Lugina, Zhur. Fiz. Khim., **35**, 1799 (1961). The reported heat capacity is extrapolated to an assumed glass transition temperature of 780°K., below which the heat capacity is taken to be equal to that of the crystal, PbO (c, red).

Vaporization Phenomena. T_b and ΔH_v^0 calculated from ΔH_f^0 298.15 for PbO (c, red) and functions for condensed and gaseous states.

T, °K.	C _p	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _P
0	.0000	INFINITE	2.142	12.017	12.017	INFINITE	
100	6.964	49.455	1.946	11.933	11.933	-21.731	
200	7.778	57.395	1.812	11.863	11.863	-21.731	
298	7.766	57.386	1.800	11.877	6.301	-4.619	
300	7.778	57.395	.014	11.473	6.269	-4.567	
400	8.155	59.687	1.612	11.263	4.566	-2.495	
500	8.400	61.535	1.641	11.053	2.915	-1.274	
600	8.560	63.082	1.609	10.834	1.309	-.477	
700	8.670	64.410	1.551	9.437	.022	-.022	
800	8.748	65.573	1.488	9.188	1.412	.386	
900	8.806	66.607	1.422	8.945	2.722	.661	
1000	8.850	67.537	1.358	8.709	4.005	.875	
1100	8.886	68.383	1.297	8.477	5.266	1.066	
1200	8.915	69.157	1.240	8.252	6.504	1.184	
1300	8.940	69.872	1.186	8.030	7.725	1.299	
1400	8.962	70.535	1.135	7.809	8.929	1.394	
1500	8.980	71.154	1.084	7.585	10.115	1.474	
1600	8.997	71.734	1.034	7.360	11.289	1.542	
1700	9.013	72.280	.987	7.130	12.447	1.600	
1800	9.027	72.796	.942	6.898	13.593	1.650	
1900	9.040	73.284	.899	6.661	14.725	1.694	
2000	9.052	73.748	.857	6.420	15.843	1.731	
2100	9.064	74.190	.816	6.176	16.946	1.762	
2200	9.075	74.612	.776	5.930	18.032	1.789	
2300	9.086	75.016	.737	5.681	19.100	1.812	
2400	9.096	75.402	.699	5.430	20.150	1.831	
2500	9.106	75.774	.662	5.178	21.182	1.847	
2600	9.116	76.131	.626	4.924	22.196	1.859	
2700	9.126	76.476	.591	4.668	23.192	1.868	
2800	9.135	76.808	.556	4.411	24.170	1.875	
2900	9.144	77.128	.522	4.153	25.131	1.880	
3000	9.153	77.436	.488	3.894	26.076	1.882	
3100	9.162	77.733	.454	3.634	27.006	1.882	
3200	9.171	78.020	.421	3.373	27.920	1.882	
3300	9.180	78.312	.388	3.111	28.818	1.882	
3400	9.188	78.596	.355	2.849	29.700	1.882	
3500	9.197	78.873	.322	2.586	30.567	1.882	
3600	9.205	79.142	.290	2.322	31.420	1.882	
3700	9.214	79.406	.258	2.058	32.258	1.882	
3800	9.222	79.667	.226	1.794	33.082	1.882	
3900	9.230	79.923	.194	1.529	33.892	1.882	
4000	9.238	80.174	.162	1.264	34.688	1.882	
4100	9.247	80.420	.130	1.000	35.470	1.882	
4200	9.255	80.661	.098	.735	36.238	1.882	
4300	9.263	80.897	.066	.470	36.992	1.882	
4400	9.271	81.128	.034	.205	37.732	1.882	
4500	9.279	81.354	.002	-.060	38.457	1.882	
4600	9.287	81.576	-.030	-.324	39.167	1.882	
4700	9.295	81.794	-.058	-.588	39.862	1.882	
4800	9.303	82.008	-.086	-.852	40.542	1.882	
4900	9.311	82.218	-.114	-.116	41.207	1.882	
5000	9.319	82.424	-.142	-.380	41.857	1.882	
5100	9.327	82.626	-.170	-.644	42.492	1.882	
5200	9.335	82.824	-.198	-.908	43.112	1.882	
5300	9.343	83.018	-.226	-.172	43.717	1.882	
5400	9.351	83.208	-.254	-.436	44.307	1.882	
5500	9.359	83.394	-.282	-.700	44.882	1.882	
5600	9.367	83.576	-.310	-.964	45.442	1.882	
5700	9.375	83.754	-.338	-.128	45.987	1.882	
5800	9.382	83.928	-.366	-.392	46.517	1.882	
5900	9.390	84.100	-.394	-.656	47.032	1.882	
6000	9.398	84.268	-.422	-.920	47.532	1.882	

Lead Monoxide (PbO) (Ideal Gas)

Mol. Wt. = 223.21

ΔH_f° 298.15 = 11.46 ± 0.27 kcal. mole⁻¹

S° 298.15 = 57.346 cal. deg.⁻¹ mole⁻¹

Ground State Configuration 1Σ⁺

Electronic Level and Multiplicity

ε cm. ⁻¹	g _i
0	1

ω_e = 721.8 cm.⁻¹ ω_ex_e = 3.70 cm.⁻¹

D_e = 0.5072 cm.⁻¹ α_e = 0.0019 cm.⁻¹

r_e = 1.922 Å

σ⁺ = 1

Heat of Formation. Calculated from ΔH_f° 298.15 for PbO (c, red) and ΔH_f° 298.15⁺.

Heat Capacity and Entropy. The ground state configuration, molecular and spectroscopic constants are obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950), modified for the natural isotopic abundances reported by J. R. Stein and E. F. Clancy, "Chart of the Nuclides", General Electric Co., N. Y. (1956).

T, °K.	C _p	S° - (F° - H°)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞	∞	∞	∞	∞	INFINITE
100	6.957	59.290	-2.090	1.640	1.640	∞
200	6.964	53.672	-1.392	1.818	1.818	2.757
298	7.212	53.021	-0.600	1.781	2.510	3.363
300	7.217	53.021	-0.613	1.637	2.510	3.370
400	7.543	53.308	1.751	4.626	3.642	3.642
500	7.846	56.903	5.861	8.500	6.666	3.715
600	8.087	58.356	8.492	11.879	9.708	3.728
700	8.272	59.617	10.136	14.879	12.708	3.708
800	8.413	60.731	11.576	16.071	14.879	3.613
900	8.520	61.728	12.875	16.191	14.998	3.278
1000	8.605	62.631	14.065	15.735	14.998	3.004
1100	8.672	63.454	15.118	15.355	15.118	2.775
1200	8.726	64.211	16.037	15.046	15.237	2.581
1300	8.770	64.911	16.823	14.794	15.355	2.416
1400	8.808	65.563	17.512	14.586	15.476	2.272
1500	8.840	66.171	18.105	14.380	15.596	2.146
1600	8.867	66.743	18.611	14.184	15.715	2.035
1700	8.891	67.281	19.030	13.994	15.834	1.937
1800	8.912	67.790	19.360	13.811	15.954	1.848
1900	8.931	68.272	19.600	13.636	16.071	1.769
2000	8.948	68.731	19.756	13.468	16.191	1.697
2100	8.963	69.168	19.920	13.302	16.310	1.632
2200	8.978	69.585	20.090	13.136	16.426	1.572
2300	8.991	69.984	20.260	12.970	16.543	1.517
2400	9.003	70.367	20.430	12.804	16.659	1.466
2500	9.015	70.735	20.600	12.638	16.776	1.420
2600	9.026	71.089	20.760	12.472	16.891	1.377
2700	9.036	71.430	20.920	12.306	17.007	1.336
2800	9.046	71.759	21.080	12.140	17.123	1.299
2900	9.056	72.076	21.240	11.974	17.239	1.263
3000	9.065	72.383	21.400	11.808	17.354	1.231
3100	9.074	72.681	21.560	11.642	17.469	1.200
3200	9.082	72.969	21.720	11.476	17.584	1.171
3300	9.090	73.248	21.880	11.310	17.699	1.143
3400	9.098	73.520	22.040	11.144	17.814	1.117
3500	9.106	73.784	22.200	10.978	17.929	1.093
3600	9.114	74.040	22.360	10.812	18.044	1.066
3700	9.121	74.290	22.520	10.646	18.159	1.042
3800	9.129	74.534	22.680	10.480	18.274	1.018
3900	9.136	74.771	22.840	10.314	18.389	0.994
4000	9.143	75.002	23.000	10.148	18.504	0.970
4100	9.150	75.228	23.160	9.982	18.619	0.946
4200	9.157	75.449	23.320	9.816	18.734	0.922
4300	9.164	75.664	23.480	9.650	18.849	0.898
4400	9.171	75.875	23.640	9.484	18.964	0.874
4500	9.178	76.081	23.800	9.318	19.079	0.850
4600	9.184	76.283	23.960	9.152	19.194	0.826
4700	9.191	76.481	24.120	8.986	19.309	0.802
4800	9.197	76.674	24.280	8.820	19.424	0.778
4900	9.204	76.864	24.440	8.654	19.539	0.754
5000	9.210	77.050	24.600	8.488	19.654	0.730
5100	9.217	77.232	24.760	8.322	19.769	0.706
5200	9.223	77.411	24.920	8.156	19.884	0.682
5300	9.230	77.587	25.080	7.990	19.999	0.658
5400	9.236	77.760	25.240	7.824	20.114	0.634
5500	9.242	77.929	25.400	7.658	20.229	0.610
5600	9.248	78.096	25.560	7.492	20.344	0.586
5700	9.255	78.259	25.720	7.326	20.459	0.562
5800	9.261	78.420	25.880	7.160	20.574	0.538
5900	9.267	78.579	26.040	6.994	20.689	0.514
6000	9.273	78.735	26.200	6.828	20.804	0.490

Dec. 31, 1960; June 30, 1961; Dec. 31, 1965

SULFUR MONOXIDE (SO)

(IDEAL GAS)

MOL. WT. = 48.0634

Ground State Configuration $3 \sum^-$
 $S_{298.15} = 53.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^\circ = 1.64 \pm 0.3 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ S_{298.15} = 1.64 \pm 0.3 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{E_i, \text{cm.}^{-1}}{0} \frac{g_i}{3}$$

$$\sigma = 1$$

$$r_e = 1.481 \text{ \AA}$$

$$\omega_e = 1148.19 \text{ cm.}^{-1}$$

$$\alpha_e = 0.00562 \text{ cm.}^{-1}$$

$$B_e = 0.7207 \text{ cm.}^{-1}$$

Heat of Formation

The dissociation energy of sulfur monoxide has been reported by following investigators:

D ₀ (SO) e.v.	(kcal. mole ⁻¹)	(116.5)	(119.5)	(92.3)	(123.5)	(127.1)
5.053	5.184	4.001	5.357	5.510		
Investigator						
E. V. Martin, Phys. Rev. 41 , 167 (1932).						
A. O. Gaydon, "Dissociation Energies", Chapman & Hall Ltd. London, 1953.						
O. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. 2nd Ed., 1950.						
R. G. W. Norrish and G. A. Oldershaw, Proc. Roy. Soc. A249 , 498 (1959).						
J. J. McDermott, W. D. McOrath, Proc. Roy. Soc. A278 , 490 (1964).						

E. V. Martin, loc. cit., has measured the spectrum of SO(g) in the region 2400-4000 Å, and both Herzberg's and Gaydon's data were based on Martin's spectroscopic measurement. Because of the ambiguity of defining the state of excitation of the atomic products resulting from predissociation, the dissociation energy of SO was in question. Herzberg favored D_0 (SO) = 92.3 kcal. mole⁻¹ but Gaydon D_0 (SO) = 119.5 kcal. mole⁻¹.

Norrish and Oldershaw, loc. cit., redetermined the absorption spectrum of SO by flash photolysis, and also corrected Martin's original vibrational numbering, and then obtained the dissociation energy, D_0 (SO) = 123.5 kcal. mole⁻¹, based on the assumption of predissociation into S(¹D) and O(³P). This value, D_0 = 123.5 kcal. mole⁻¹, has been selected as the dissociation energy for SO(g) and combination with JANAF values of ΔH_f° (S; g) and ΔH_f° (O; g) gives the heat of formation of sulfur monoxide, $\Delta H_f^\circ S_{298} = 1.64 \pm 0.3 \text{ kcal. mole}^{-1}$, which is adopted in this tabulation.

R. Colin, P. Goldfinger and M. Jeunehomme, Trans. Faraday Soc. **60**, 306 (1964), have confirmed the selected D_0 (SO) = 123.5 kcal. mole⁻¹ in their mass spectrometric studies on the vaporization of CuS, SiS and BaS. J. J. McDermott and W. D. McOrath, loc. cit., reported the dissociation energy to be 127.1 kcal. mole⁻¹ based on their ultraviolet spectroscopic studies. This value appears to be the D_e from the minimum of the potential curve which corresponds to D_0 (SO) = 125 ± 1.5 kcal. mole⁻¹.

Besides the spectroscopic information, G. St. Pierre and J. Chipman, J. Am. Chem. Soc. **76**, 4787 (1954), have reported $\Delta H_f^\circ S_{298} = -19 \text{ kcal. mole}^{-1}$ for the reaction $0.5 \text{ S}_2(\text{g}) + 0.5 \text{ O}_2(\text{g}) \rightarrow \text{SO}(\text{g})$ in the equilibrium study of lime-iron oxide slags with SO₂ or SO₂-CO mixtures. Using $\Delta H_f^\circ S_{298}(\text{S}_2; \text{g}) = 30.8 \text{ kcal. mole}^{-1}$, the derived heat of formation, $\Delta H_f^\circ S_{298}(\text{SO}; \text{g}) = -3.6 \text{ kcal. mole}^{-1}$ was obtained. However, this value is doubtful because the reported $\Delta H_f^\circ S_{298} = -19 \text{ kcal. mole}^{-1}$ was dependent upon many assumptions and subsidiary data. E. W. Dewing and P. D. Richardson, Trans. Faraday Soc. **54**, 675 (1958) have measured the equilibrium constants for the reaction $\text{S}_2(\text{g}) + 2\text{SO}(\text{g}) \rightarrow 4\text{SO}(\text{g})$ at 1250°C. and $\text{SO}_2(\text{g}) \rightarrow \text{SO}(\text{g}) + 1/2 \text{ O}_2(\text{g})$ at 1500°C. Using the JANAF auxiliary data, the former yields $\Delta H_f^\circ S_{298}(\text{SO}; \text{g}) = +0.13 \text{ kcal. mole}^{-1}$ and the latter -0.17 kcal. mole⁻¹, respectively. The average of these two values is $\Delta H_f^\circ S_{298} = 0 \text{ kcal. mole}^{-1}$. Although D. Meschi and R. Myers, J. Mol. Spectry. **3**, 405 (1959) and U. Blukis and R. Myers, J. Phys. Chem. **69**, 1154 (1965), have certainly concluded in their microwave spectroscopic studies that the S₂O species was one of the important products in the Sulfur - SO₂ equilibrium which was considered as unimportant by Dewing and Richardson, the value, $\Delta H_f^\circ S_{298}(\text{SO}; \text{g}) = 0 \text{ kcal. mole}^{-1}$, derived from Dewing and Richardson is still very close to the selected value, $\Delta H_f^\circ S_{298}(\text{SO}; \text{g}) = 1.64 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy

The molecular constants ω_e , $\omega_e x_e$ and α_e were obtained from R. Norrish and G. Oldershaw, loc. cit., and the values of r_e and B_e were recently measured in the microwave spectrum by F. X. Powell and D. R. Lide, Jr., J. Chem. Phys. **41**, 1413 (1964).

Disulfur Monoxide (S₂O)

(Ideal Gas) Mol. Wt. = 80.1274

OS₂

MOL. WT. = 80.1274

DISULFUR MONOXIDE (S₂O) (IDEAL GAS)

Point Group C_{2v}
 $\Delta H_f^\circ = -13 \pm 8$ kcal. mole⁻¹
 $\Delta H_f^\circ = 63.8$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^\circ = 238.15 = [-13.5 \pm 8]$ kcal. mole⁻¹

Ground State Quantum Weight = 1
 Vibrational Frequencies and Degeneracies
 ω_e , cm.⁻¹

679 (1)
 388 (1)
 1165 (1)

Bond Distance: S-S = 1.884 Å S-O = 1.465 Å
 Bond Angle: S-S-O = 118°
 Product of the Moment of Inertia: $I_A I_B I_C = 6.27441 \times 10^{-115}$ g. cm.⁶
 $\sigma = 1$

Heat of Formation.

There is no direct measurement of the standard enthalpy of formation for S₂O(g). U. Blukis and R. Myers, J. Phys. Chem., 69, 1154 (1965), have discussed the discrepancy of the values of ΔH_f° O which vary from -1 to -35 kcal. mole⁻¹. R. Hagemann, Compt. Rend., 225, 1102 (1962), reported ΔH_f° O = -17 kcal. mole⁻¹ from his ionization and appearance potential measurements by mass spectrometry. R. Steudel and P. W. Schenk, Z. Physik Chem., 43, 33 (1964), estimated the enthalpy of formation as -22.7 kcal. mole⁻¹. If the bond dissociation energies D(S-O) = 123.5 kcal. mole⁻¹ and D(S-S) = 103 kcal. mole⁻¹ were used to estimate the dissociation energy of S₂O (i.e. D(S₂O) = 224.5 kcal. mole⁻¹), one will obtain ΔH_f° O = -35.3 kcal. mole⁻¹. A. V. Jones, J. Chem. Phys., 18, 1263 (1950), reported the predissociation energy, 91 kcal. mole⁻¹, for sulfur monoxide from the infrared and ultraviolet spectra. [D. Meschi and R. Myers, J. Mol. Spectro., 3, 405 (1959), have concluded from their experiment that the so called sulfur monoxide is S₂O.] Therefore, if 30(g) + S(g), were the dissociation products, the ΔH_f° O would be -25.4 kcal. mole⁻¹; and if S₂(g) + O(g) were the products, the ΔH_f° O would be -1.2 kcal. mole⁻¹. (All JANAP auxiliary data used in calculation.)

E. Dewing and P. Richardson, Trans. Faraday Soc., 54, 679 (1958), have investigated the gas phase equilibria in the sulfur-oxygen vapor at 1250° and 1500°C respectively. U. Blukis and R. Myers (loc. cit.) recalculated their data based on the assumption that the S₂O (instead of SO) was the major product in the equilibrium, and obtained ΔH_f° O = -13 kcal. mole⁻¹ for S₂O(g) which is adopted in this table.

Heat Capacity and Entropy.

The bond distance, angle, and vibrational frequencies were obtained from the microwave and infrared spectra measurements by D. Meschi and R. Myers, loc. cit., and U. Blukis and R. Myers, loc. cit. The three principal moments of inertia are $I_A = 2.0219 \times 10^{-39}$, $I_B = 16.6342 \times 10^{-39}$, and $I_C = 18.6560 \times 10^{-39}$ g. cm.²

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	Log K _p
0	∞	∞	2.660	-13.016	INFINITE
100	9.423	72.481	1.561	-15.610	34.114
200	9.428	64.726	0.862	-13.402	34.114
298	10.534	63.776	0.800	-13.500	15.147
300	10.562	63.861	0.820	-13.507	15.086
400	11.424	67.024	1.221	-14.959	12.572
500	12.041	69.644	2.596	-16.025	10.893
600	12.477	71.880	3.523	-16.890	9.684
700	12.786	73.628	4.787	-17.615	8.772
800	13.011	75.551	6.078	-18.373	8.069
900	13.177	77.093	7.388	-19.166	7.419
1000	13.303	78.488	8.712	-19.992	6.834
1100	13.399	79.761	10.047	-20.848	6.306
1200	13.475	80.930	11.391	-21.727	5.832
1300	13.536	82.011	12.742	-22.626	5.409
1400	13.585	83.016	14.098	-23.542	5.031
1500	13.625	83.955	15.458	-24.475	4.694
1600	13.658	84.835	16.822	-25.425	4.396
1700	13.686	85.664	18.190	-26.392	4.131
1800	13.709	86.447	19.559	-27.375	3.894
1900	13.729	87.189	20.931	-28.373	3.682
2000	13.747	87.893	22.305	-29.385	3.491
2100	13.761	88.564	23.681	-30.410	3.319
2200	13.774	89.205	25.057	-31.446	3.164
2300	13.786	89.818	26.436	-32.492	3.024
2400	13.796	90.404	27.815	-33.548	2.896
2500	13.805	90.968	29.195	-34.615	2.778
2600	13.813	91.502	30.576	-35.692	2.670
2700	13.820	92.031	31.957	-36.779	2.571
2800	13.826	92.534	33.339	-37.875	2.480
2900	13.832	93.019	34.722	-38.980	2.396
3000	13.837	93.488	36.106	-40.095	2.319
3100	13.841	93.942	37.490	-41.219	2.248
3200	13.846	94.381	38.874	-42.352	2.182
3300	13.849	94.807	40.259	-43.493	2.120
3400	13.853	95.221	41.644	-44.642	2.061
3500	13.856	95.622	43.029	-45.799	2.006
3600	13.859	96.013	44.415	-46.964	1.954
3700	13.862	96.392	45.801	-48.137	1.904
3800	13.864	96.762	47.187	-49.317	1.856
3900	13.867	97.122	48.574	-50.502	1.810
4000	13.869	97.473	49.961	-51.692	1.766
4100	13.871	97.816	51.348	-52.886	1.723
4200	13.873	98.150	52.735	-54.084	1.681
4300	13.875	98.477	54.122	-55.285	1.640
4400	13.876	98.796	55.510	-56.489	1.600
4500	13.878	99.107	56.898	-57.695	1.561
4600	13.879	99.413	58.285	-58.902	1.523
4700	13.880	99.711	59.673	-60.110	1.486
4800	13.882	100.003	61.061	-61.319	1.450
4900	13.883	100.289	62.450	-62.529	1.415
5000	13.884	100.570	63.838	-63.739	1.381
5100	13.885	100.845	65.226	-64.949	1.347
5200	13.886	101.115	66.615	-66.159	1.314
5300	13.887	101.379	68.004	-67.369	1.281
5400	13.888	101.639	69.392	-68.579	1.249
5500	13.889	101.893	70.781	-69.789	1.217
5600	13.890	102.144	72.170	-70.999	1.186
5700	13.891	102.390	73.559	-72.209	1.155
5800	13.891	102.631	74.948	-73.419	1.125
5900	13.891	102.869	76.337	-74.629	1.095
6000	13.892	103.102	77.726	-75.839	1.065

Sept. 30, 1965

OS₂

Ground State Configuration $1s^2$
 $S_{298.15}^{\circ} = 50.54$ gibbs/mol
 $\Delta H_f^{\circ} = -24.3 \pm 2$ kcal/mol
 $\Delta H_f^{\circ} = -24 \pm 2$ kcal/mol

OSI

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	1
(30000)	6
42600	2

$$\omega_e X_e = 5.92$$

$$\sigma = 1$$

$$\omega_e = 1201.44$$

$$\sigma_e = 0.00508$$

$$B_e = 0.7273$$

$$r_e = 1.509 \text{ \AA}$$

Heat of Formation

The adopted value is based on equilibrium data summarized below. The more reliable results from three different reactions lie in the range from about -23 to -26 kcal/mol. Extreme values, including -20 and -32 kcal/mol, can be discounted on experimental grounds. Margrave (1) recently reported $\Delta H_f^{\circ} = 82.8 \pm 1.5$ kcal/mol for $0.5SiO_2(g) + 0.5Si(s) = SiO(g)$, but details are not yet available. Assuming that this corresponds to reaction A below, we calculate $\Delta H_f^{\circ} = -25.4$ kcal/mol. Reaction A involves the nominal composition $SiO(s)$ which is treated as an intimate mixture of $0.5Si(c) + 0.5SiO_2$ (high cristobalite). X-ray studies (13, 14) suggest that the condensed " SiO " used in (1, 2) is probably a mixture of Si and amorphous or vitreous SiO_2 . The adopted ΔH_f° corresponds to $D_0^{\circ} = 190 \pm 3$ kcal/mol. This may be compared with $D_0^{\circ} = 179$ kcal/mol obtained by linear Birge-Sponer extrapolation of the ground state vibrational constants and with $D_0^{\circ} = 185 \pm 7$ kcal/mol obtained by Barrow (15) from $D_0^{\circ}(LiX) = 77.5$ kcal/mol for the excited state at 5280 cm⁻¹. Barrow assumed $D_0^{\circ}(LiX) = 0.456$ based on related molecules.

Source	Reaction	Method	Range, T°K	Points	No. of	ΔH_f° , kcal/mol	Drift
2. Ramstad (1961)	A	Carrier gas	1510-1788	6	80.2 ± 2.3	85.08	3.0 ± 1.4
3. Bergman (1959)	A	ΔHs by explosion	---	---	---	---	---
4. Gunther (1958)	A	Knudsen wt. gain	1202-1520	18	97.0 ± 0.7	86.76	-7.6 ± 0.5
5. Porter (1955)	A*	Knudsen mass spec.	1345-1463	2	105.1	87.35	-13
6. Tombs (1952)	A	Carrier gas	1573-1920	7	65.4 ± 1.1	84.75	11 ± 1
7. Schafer (1950)	A	Knudsen wt. loss	1336-1920	21	78.7 ± 1.5	82.74	2.9 ± 1.0
8. Gel'd (1948)	A*	Knudsen wt. loss	1173-1428	11	77.2 ± 1.8	85.87	6.8 ± 1.4
2. Ramstad (1961)	B***	Carrier gas	1698-1873	4	142.6 ± 0.7	133.79	-4.9 ± 0.4
6. Tombs (1952)	B***	Carrier gas	1703-1898	---	135	132.3	-2
9. Grube (1949)	B***	Carrier gas	1501-1926	23	86 ± 3	127.3	22 ± 2
10. Nemesyanov (1960)	C**	Knudsen collection	1473-1773	4	112 ± 3	134.4	13 ± 2
11. Yang (1958)	C	Knudsen wt. loss	1653-1739	24	---	---	-20.5
5. Porter (1955)	D	Knudsen mass spec.	1818-1960	15	195.3 ± 3.4	194.5	-21.8
12. Cochran (1962)	D	Knudsen effusion	1600-1900	2	130	184.4	29
B. $0.5SiO_2$ (high cristobalite) + $0.5Si(c,l) = SiO(g)$							
C. SiO_2 (high cristobalite) + $0.5SiO_2(g) + SiO(g)$							
D. $SiO_2(l) + Mg(g) = MgO(c) + SiO(g)$							

*Starting material was " SiO "
 **Starting material was tridymite
 ***Starting material was quartz

Heat Capacity and Entropy

All constants for the ground state and the $A^1\Pi$ state at 42600 cm⁻¹ are taken from the analysis of the A-X system reported by Lagarkov (16). An intercombination transition has been observed and assigned as $1s^2 3^1\Pi$ by Verma (17). The value of the a-X excitation energy is unknown but is estimated here as 30000 ± 5000 cm⁻¹ by comparison with the A and A states of CO and ACl. Several additional excited states are known (15, 16) to lie near or above the A state, but they are omitted because their contribution to the thermal functions is negligible.

References

1. J. L. Margrave, 5th Meeting ICRPG Thermochemistry Working Group, Linden, New Jersey, March, 1957.
2. H. F. Ramstad, F. D. Richardson and P. J. Boules, Trans. AIME 221, 1021 (1961). Data given spectroscopically.
3. G. A. Bergman and V. A. Nedvedav, Shornik Trudov Gosudarst. Inst. Priklad. Khim. 1959, 158 (1959).
4. K. G. Gunther, Glaetche. Ber. 31, 9 (1958).
5. N. C. Porter, W. A. Chupka and H. G. Ingraham, J. Chem. Phys. 23, 216 (1955).
6. H. Schafer and R. Hornig, Z. Anorg. Allg. Chem. 262, 163 (1952).
7. P. V. Gel'd and M. I. Kochnev, Zhur. Priklad. Khim. 21, 1249 (1948).
8. G. Grube and H. Speidel, Z. Elektrochem. 53, 341 (1949).
9. A. N. Nemesyanov and L. P. Firsova, Russ. J. Phys. Chem. (English Transl.) 34, 906, 1237, 1279 (1960).
10. A. N. Nemesyanov and R. Miller, Physical Chemistry of Steelmaking, pp. 63-4, John Wiley and Sons, Inc., New York, 1958.
11. Data of G. Grube and L. P. Firsova.
12. C. N. Cochran and L. M. J. Phys. Chem. 66, 380 (1962).
13. A. N. Guatinskii, K. M. Kolobova and S. A. Nemmonov, Izv. Akad. Nauk SSSR, Neorg. Materialy 1 (6), 877 (1965).
14. G. W. Brady, J. Phys. Chem. 63, 1119 (1959).
15. R. F. Barrow and H. C. Rowlinson, Proc. Roy. Soc. (London) A221, 374 (1954).
16. A. Lagarkov and O. Uhler, Arkiv Fysik 5, 95 (1952).
17. R. D. Verma and R. S. Mulliken, Can. J. Phys. 33, 908 (1961).

OSI

T, °K	Cp*	$\frac{g^{\circ}(T) - g^{\circ}(T_{ref})}{T}$	$H^{\circ} - H_{298}^{\circ}$	ΔH_f°	Log Kp
0	0.000	INFINITE	---	---	INFINITE
100	6.980	42.430	1.386	24.276	37.064
200	6.980	51.189	1.992	24.276	37.064
298	7.146	50.542	1.000	24.000	22.100
300	7.151	50.586	-0.13	24.002	22.192
400	7.441	52.682	1.742	24.136	22.597
500	7.735	54.174	1.502	24.286	15.165
600	7.982	55.407	2.288	24.445	13.390
700	8.177	57.053	3.096	24.611	12.114
800	8.328	58.155	3.922	24.784	10.817
900	8.445	59.433	4.761	24.964	10.396
1000	8.538	60.038	5.610	25.152	9.767
1100	8.611	60.455	6.468	25.349	9.286
1200	8.671	60.797	7.332	25.554	8.864
1300	8.720	62.103	8.201	25.768	8.505
1400	8.761	62.951	9.075	25.991	8.194
1500	8.795	63.556	9.953	26.224	7.922
1600	8.825	64.125	10.834	26.466	7.683
1700	8.850	64.661	11.716	26.711	7.455
1800	8.873	65.167	12.604	26.960	7.178
1900	8.893	65.648	13.493	27.213	6.929
2000	8.911	66.104	14.383	27.470	6.703
2100	8.927	66.539	15.275	27.732	6.498
2200	8.942	66.950	16.168	28.000	6.310
2300	8.955	67.353	17.063	28.274	6.138
2400	8.968	67.734	17.959	28.554	5.979
2500	8.979	68.101	18.857	28.840	5.833
2600	8.989	68.453	19.755	29.132	5.696
2700	9.000	68.792	20.655	29.430	5.570
2800	9.010	69.120	21.558	29.734	5.451
2900	9.020	69.436	22.457	30.044	5.340
3000	9.029	69.742	23.359	30.359	5.236
3100	9.038	70.038	24.262	30.679	5.138
3200	9.047	70.326	25.167	31.004	5.046
3300	9.056	70.604	26.072	31.334	4.959
3400	9.065	70.875	26.978	31.668	4.877
3500	9.074	71.137	27.885	32.006	4.799
3600	9.084	71.393	28.793	32.348	4.726
3700	9.094	71.642	29.702	32.694	4.658
3800	9.105	71.885	30.612	33.044	4.596
3900	9.117	72.122	31.523	33.398	4.537
4000	9.129	72.353	32.435	33.756	4.481
4100	9.142	72.578	33.349	34.118	4.427
4200	9.154	72.799	34.263	34.484	4.375
4300	9.172	73.014	35.180	34.854	4.325
4400	9.184	73.225	36.098	35.228	4.276
4500	9.207	73.432	37.018	35.606	4.230
4600	9.226	73.635	37.939	36.000	4.187
4700	9.247	73.833	38.863	36.400	4.145
4800	9.270	74.028	39.789	36.806	4.104
4900	9.294	74.219	40.717	37.218	4.064
5000	9.320	74.407	41.648	37.636	4.025
5100	9.348	74.592	42.581	38.060	3.987
5200	9.374	74.774	43.517	38.490	3.950
5300	9.410	74.953	44.457	38.924	3.914
5400	9.444	75.129	45.399	39.362	3.879
5500	9.479	75.303	46.345	39.804	3.844
5600	9.517	75.474	47.295	40.250	3.809
5700	9.557	75.643	48.249	40.700	3.774
5800	9.599	75.809	49.207	41.154	3.739
5900	9.642	75.974	50.169	41.612	3.704
6000	9.688	76.136	51.135	42.074	3.669

Dec. 31, 1960; Sept. 30, 1963; Sept. 30, 1967

Titanium Monoxide, Alpha (α-TiO)
(Crystal)

GFW = 63.8994

TITANIUM MONOXIDE, ALPHA (α-TiO)

(CRYSTAL)

OPW = 63.8994

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	.000	.000	INFINITE	- 1.476	- 123.476	- 123.476	INFINITE
100	3.051	5.259	19.036	- 1.378	- 123.859	- 122.118	266.800
200	7.333	8.811	13.012	.840	- 124.128	- 120.354	131.408
298	9.550	12.200	12.200	.000	- 124.190	- 118.358	86.744
300	9.574	12.259	12.200	.018	- 124.190	- 118.302	86.183
400	10.787	15.192	12.592	1.040	- 124.141	- 116.344	63.567
500	11.610	17.692	13.368	2.162	- 124.030	- 114.407	50.007
600	12.238	19.866	14.274	3.355	- 123.881	- 112.495	40.977
700	12.705	21.525	15.146	4.613	- 123.695	- 110.535	34.535
800	13.120	22.801	16.000	5.804	- 123.516	- 108.555	29.710
900	13.502	23.704	16.835	7.244	- 123.319	- 106.522	25.964
1000	13.970	24.556	17.653	8.623	- 123.117	- 105.110	22.972
1100	14.314	27.904	18.779	10.037	- 122.912	- 103.319	20.588
1200	14.600	32.168	20.372	11.582	- 122.703	- 101.280	18.758
1300	14.848	36.848	22.320	13.275	- 122.493	- 99.030	17.078
1400	15.255	41.487	24.675	14.475	- 122.293	- 97.974	15.279
1500	15.548	42.529	21.852	16.016	- 122.593	- 96.096	14.001
1600	15.935	33.542	22.552	17.585	- 122.226	- 94.341	12.866
1700	16.315	35.439	23.827	19.180	- 121.876	- 92.601	11.837
1800	16.683	37.460	25.460	20.408	- 121.476	- 90.901	10.907
1900	16.663	36.333	24.512	22.460	- 121.098	- 89.213	10.262
2000	16.931	37.194	25.124	24.140	- 125.166	- 87.390	9.550
2100	17.197	38.027	25.719	25.847	- 124.762	- 85.511	8.999
2200	17.750	38.813	26.300	27.587	- 124.384	- 83.614	8.484
2300	18.200	39.557	26.859	29.339	- 123.884	- 81.814	7.778
2400	17.960	40.375	27.406	31.124	- 123.410	- 79.994	7.284
2500	18.237	41.114	27.940	32.934	- 122.914	- 78.196	6.836

Dec. 31, 1960; Mar. 31, 1967

$S_{298.15}^{\circ} = [12.2] \text{ gbbu/mol}$
 $T^{\circ} = 1264^{\circ}\text{K}$
 $\Delta H_f^{\circ} = -123.48 \pm 1 \text{ kcal/mol}$
 $\Delta H_f^{\circ}{}_{298.15} = -124.19 \pm 1 \text{ kcal/mol}$
 $\Delta H^{\circ} = 0.83 \text{ kcal/mol}$
 $\Delta H_{298.15}^{\circ} = 128 \pm 10 \text{ kcal/mol}$

Heat of Formation.
O. L. Humphrey, *J. Am. Chem. Soc.* **73**, 1587 (1951), determined the heat of combustion $\Delta H_{298}^{\circ} = -101.61 \pm 0.12$ kcal/mol for the reaction $\text{TiO}(\alpha) + 1/2\text{O}_2(\text{g}) = \text{TiO}_2(\text{rutile})$. Based on this result and on $\Delta H_{298}^{\circ}(\text{rutile}) = -225.8 \pm 1$ kcal/mol, the adopted ΔH_f° for $\text{TiO}(\alpha)$ is calculated to be -124.19 ± 1 kcal/mol. A value of -125.4 ± 0.4 kcal/mol was reported by S. M. Ariya, M. P. Morozova and E. Vol'f, *Russ. J. Inorg. Chem. (English Transl.)* **2**, 16 (1957), who measured the heats of combustion of various compositions in the Ti-O system. Ariya et al. used an estimated correction for the formation of $\text{TiO}_2 \cdot x$ while Humphrey obtained values of $0.2 - 0.4$ kcal/mol by grinding the product and returning it with white oil. Most of the assigned uncertainty arises from this problem of non-stoichiometry [see $\text{TiO}_2(\text{rutile})$ for further details].

Heat Capacity and Entropy.
The low temperature heat capacities, $52.6 - 296.3^{\circ}\text{K}$, were measured by C. H. Shomate, *J. Am. Chem. Soc.* **68**, 310 (1946). The high temperature enthalpies, $357.0 - 1771^{\circ}\text{K}$, were determined by B. F. Naylor, *J. Am. Chem. Soc.* **69**, 1077 (1946), by use of drop calorimetry. The high temperature Cp's, $357 - 1200.5^{\circ}\text{K}$, derived from the enthalpy data, are joined smoothly with the low temperature heat capacities at 298°K . The Cp values above 1200°K are obtained by extrapolation. The entropy is obtained from Cp° using $S_0^{\circ} = 4.13$ eu; this extrapolation includes 0.23 , 1.7 and 2.2 eu for contributions of the lattice, of vacancies and of spin magnetic effects, respectively.

P. W. Ollies, *J. Chem. Phys.* (in press), discussed the inconsistencies in the thermodynamic properties of TiO as derived from widely different measurements. These inconsistencies include (1) a difference of 10 kcal/mol in H_0° values for $\text{TiO}(\text{g})$ obtained from vaporization of TiO and Ti_2O_3 , (2) a difference of about 10 kcal/mol between the calorimetric data for $\text{TiO}(\beta)$ and a recent re-assessment of the partial free energy of dissociation for the TiO system, and (3) emf. data which suggest that the entropy of $\text{TiO}(\beta)$ should be increased relative to those of Ti and Ti_2O_3 . In order to minimize these discrepancies, we tentatively increase the experimental value of S_{298}° by addition of estimated contributions due to vacancies in the crystal lattice and to spin-magnetic effects of Ti^{3+} ion.

P. Enrich, *Z. Elektrochem.* **45**, 362 (1959) and Z. Anorg. Chem. **247**, 53 (1941), concluded from the difference in pycnometric and x-ray densities of $\text{TiO}(\beta)$ that about 25 percent of the Ti and O lattice sites are vacant. This was confirmed later by S. Anderson, B. Collen, U. Kuylenstierna and A. Magnelli, *Acta. Chem. Scand.* **11**, 1641 (1957), A. D. Pearson, *J. Phys. Chem. Solids* **5**, 316 (1958), and M. E. Strueman and H. W. Li, *Z. Anorg. Allgem. Chem.* **305**, 143 (1960). Anderson et al. noted that there may be a "close structural kinship" between the α and β forms, based on the similarity of their densities and the pronounced relationship between their powder diffraction patterns. The authors suggested that the (presumably) random vacancies in $\text{TiO}(\beta)$ may occur in an ordered way in $\text{TiO}(\alpha)$. Recent electron diffraction studies by J. M. Cowley, *Acta Cryst.* (to be published), may provide an answer to this problem. Assuming the vacancies to be randomly arranged, we estimate the residual entropy of $\text{TiO}(\alpha)$ due to vacancies as $-2R(0.85 \ln 0.85 + 0.15 \ln 0.15) = 1.7$ eu, based on the method proposed by M. Hoch, A. S. Iyer and J. Neiken, *J. Phys. Chem. Solids* **23**, 1463 (1962). An alternative possibility for increasing the entropy of $\text{TiO}(\beta)$ is discussed in the Transition Data section of the table for $\text{TiO}(\beta)$.

Metallic-type conductivity of $\text{TiO}(\alpha)$ at temperatures $80 - 1000^{\circ}\text{K}$ was reported by A. D. Pearson, loc. cit., and P. J. Morin, *Phys. Rev. Letters* **3**, 34 (1959). This led J. B. Goodenough, *Phys. Rev.* **117**, 1442 (1960), to suggest the existence of strong cation-cation interactions and the possibility of a low temperature transformation of the martensitic or antiferromagnetic type. Goodenough noted that the isolectric compound VN becomes superconducting below 8.2°K . We approximate the entropy contribution of these various possibilities at 50°K by a spin-magnetic term of $R \ln 3 = 2.2$ eu.

Transition Data.
See $\text{TiO}(\beta)$ table.

Heat of Sublimation.
The difference between ΔH_{298}° for $\text{TiO}(\text{g})$ and $\text{TiO}(\alpha)$ is ΔH_{298}° .

Titanium Monoxide, Beta (β - TiO)
(Crystal) GFW = 63.8994

T. K	Cp ^a	S ^b	-(C ^a -H ²⁹⁸)/T	H ^c -H ²⁹⁸	ΔH ^f	ΔG ^f	Log Kp
100							
150							
200							
250							
300	9.550	12.372	12.372	.000	-123.872	-119.071	86.549
350	9.574	12.431	12.372	.014	-123.872	-119.035	85.099
400	10.787	12.764	12.764	1.040	-123.823	-119.005	83.431
450	11.610	13.540	13.540	2.162	-123.712	-119.175	80.906
500							
600	12.238	20.038	14.486	3.355	-123.563	-112.291	40.899
700	12.755	21.965	15.395	4.606	-123.387	-110.415	34.473
800	13.261	23.627	16.319	5.908	-123.176	-108.575	29.661
900	13.756	25.091	17.257	7.284	-122.930	-106.773	25.462
1000	14.240	26.467	18.114	8.783	-122.630	-105.073	22.042
1100	15.688	28.383	18.981	10.342	-122.289	-103.323	20.509
1200	15.987	29.756	19.852	11.924	-122.895	-101.567	19.480
1300	16.086	31.036	20.636	13.526	-122.436	-99.701	18.761
1400	16.185	32.258	21.377	15.177	-121.916	-97.720	18.027
1500	16.488	33.565	22.181	16.777	-121.516	-96.271	
1600	16.683	34.436	22.914	18.435	-121.058	-94.603	12.922
1700	16.882	35.453	23.622	20.113	-120.603	-92.964	11.951
1800	17.081	36.424	24.306	21.811	-120.155	-91.352	11.052
1900	17.279	37.351	25.000	23.526	-119.721	-89.685	10.221
2000	17.679	38.244	25.610	25.267	-119.221	-88.045	9.461
2100	17.678	39.102	26.232	27.025	-123.266	-86.272	8.978
2200	17.877	39.929	26.836	28.803	-122.794	-84.523	8.397
2300	18.076	40.728	27.453	30.601	-122.304	-82.794	7.867
2400	18.274	41.501	28.084	32.424	-121.794	-81.006	7.384
2500	18.673	42.251	28.549	34.255	-121.275	-79.400	6.941

Mar. 31, 1967

TITANIUM MONOXIDE, BETA (β -TiO) (CRYSTAL) OFW = 63.8994

$S_{298}^{\circ} = 12.372$ e.u./mol
 $T_f = 1264^{\circ}\text{K}$
 $T_m = 2023^{\circ}\text{K}$

$\Delta H_f^{\circ} = -123.872$ kcal/mol
 $\Delta H^{\circ} = 0.83$ kcal/mol
 $\Delta G_m^{\circ} = [13]$ kcal/mol

Heat of Formation.
 The $\Delta H_f^{\circ} 298(\beta)$ is obtained from $\Delta H_f^{\circ} 298(\alpha)$ by adding ΔH_t° and the difference between $H_{1264}^{\circ} - H_{298}^{\circ}$ for TiO(α) and TiO(β).

Heat Capacity and Entropy.

High temperature enthalpies, 1273 - 1771°K, have been measured with a drop calorimeter by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946). The adopted heat capacities are derived from these data, assuming the final state to be TiO(α). This problem is discussed in the Transition Data section. Cp values below 900°K are assumed to be the same as those for TiO(α). The heat capacities at temperatures 900 - 1273°K and above 1771°K are obtained by extrapolation. The S_{298}° is derived in a manner analogous to that of the heat of formation.

Transition Data.

Tt and ΔH_t° are derived from the enthalpy data of Naylor, loc. cit., assuming that TiO(α) is the final state of the drop experiment. The X-ray studies of C. C. Wang and N. J. Grant, J. Metals 5, 184 (1956), and A. D. Pearson, J. Phys. Chem. Solids 5, 316 (1958), appear to contradict this assumption. These authors found that the α form of stoichiometric TiO was obtained at room temperature only by annealing the β phase for long periods below 1223°K. Samples quenched from temperatures of 1223°K or higher retained the NaCl structure of the β form. Since the drop calorimetric experiment is similar to quenching, it is possible that the final state was mostly the β form. If this is the case, then the derived values of ΔH_t° and ΔS_t° are probably much too small. This would be an alternative means for increasing the entropy of TiO(β). It is possible, however, that differences in particle size allowed Naylor's sample to drop to the α form, or that the β form was stabilized by impurities in the X-ray studies. Further experiments are desirable in order to resolve this question. Also related to the question is the fact that the structure of TiO(α) has not been reported, probably because the X-ray diffraction pattern is quite complex.

P. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. 49, 180 (1966), reviewed the phase data and presented the most current phase diagram for the Ti-O system. This diagram suggests that stoichiometric TiO(α) starts to transform near 1210°K with formation of the two phases TiO_{1+x}(β) and Ti₂O. Transformation to stoichiometric TiO(β) is complete near 1270°K, which is essentially the Tt chosen by Naylor. This behavior is consistent with Naylor's observation of "pre-transition effects" in the enthalpy between 1224 and 1264°K.

Melting Data.

See TiO(1) table for details.

OTI

OTI

Titanium Monoxide (TiO)

(Liquid) GFW = 63.8994

T, °K	C _p ^a	gibbs/mol S ^b - (G ^c - H ²⁹⁸)/T	cal/mol H ^c - H ²⁹⁸	ΔH ^f ^c	ΔG ^f	Log K _p
0						
100	16,000	14,235	14,235	0.000	-112.801	78.841
200	16,000	14,333	14,235	0.030	-112.789	78.331
298	16,000	14,362	14,235	0.030	-112.789	78.331
300	16,000	14,362	14,235	0.030	-112.789	78.331
400	16,000	14,362	14,235	0.030	-112.789	78.331
500	16,000	14,362	14,235	0.030	-112.789	78.331
600	16,000	14,362	14,235	0.030	-112.789	78.331
700	16,000	14,362	14,235	0.030	-112.789	78.331
800	16,000	14,362	14,235	0.030	-112.789	78.331
900	16,000	14,362	14,235	0.030	-112.789	78.331
1000	16,000	14,362	14,235	0.030	-112.789	78.331
1100	16,000	14,362	14,235	0.030	-112.789	78.331
1200	16,000	14,362	14,235	0.030	-112.789	78.331
1300	16,000	14,362	14,235	0.030	-112.789	78.331
1400	16,000	14,362	14,235	0.030	-112.789	78.331
1500	16,000	14,362	14,235	0.030	-112.789	78.331
1600	16,000	14,362	14,235	0.030	-112.789	78.331
1700	16,000	14,362	14,235	0.030	-112.789	78.331
1800	16,000	14,362	14,235	0.030	-112.789	78.331
1900	16,000	14,362	14,235	0.030	-112.789	78.331
2000	16,000	14,362	14,235	0.030	-112.789	78.331
2100	16,000	14,362	14,235	0.030	-112.789	78.331
2200	16,000	14,362	14,235	0.030	-112.789	78.331
2300	16,000	14,362	14,235	0.030	-112.789	78.331
2400	16,000	14,362	14,235	0.030	-112.789	78.331
2500	16,000	14,362	14,235	0.030	-112.789	78.331
2600	16,000	14,362	14,235	0.030	-112.789	78.331
2700	16,000	14,362	14,235	0.030	-112.789	78.331
2800	16,000	14,362	14,235	0.030	-112.789	78.331
2900	16,000	14,362	14,235	0.030	-112.789	78.331
3000	16,000	14,362	14,235	0.030	-112.789	78.331
3100	16,000	14,362	14,235	0.030	-112.789	78.331
3200	16,000	14,362	14,235	0.030	-112.789	78.331
3300	16,000	14,362	14,235	0.030	-112.789	78.331
3400	16,000	14,362	14,235	0.030	-112.789	78.331
3500	16,000	14,362	14,235	0.030	-112.789	78.331
3600	16,000	14,362	14,235	0.030	-112.789	78.331
3700	16,000	14,362	14,235	0.030	-112.789	78.331
3800	16,000	14,362	14,235	0.030	-112.789	78.331
3900	16,000	14,362	14,235	0.030	-112.789	78.331
4000	16,000	14,362	14,235	0.030	-112.789	78.331
4100	16,000	14,362	14,235	0.030	-112.789	78.331
4200	16,000	14,362	14,235	0.030	-112.789	78.331
4300	16,000	14,362	14,235	0.030	-112.789	78.331
4400	16,000	14,362	14,235	0.030	-112.789	78.331
4500	16,000	14,362	14,235	0.030	-112.789	78.331

TITANIUM MONOXIDE (TiO)

(LIQUID)

GFW = 63.8994

$$\Delta H_f^{298,15} = [-112.801] \text{ kcal/mol}$$

$$\Delta H_m^\circ = [13] \text{ kcal/mol}$$

$$\Delta H_v^\circ = [91.6] \text{ kcal/mol}$$

$$S_{298,15}^\circ = [14.235] \text{ gibbs/mol}$$

$$T_m = 2023^\circ \text{K}$$

$$T_b = [3934]^\circ \text{K}$$

Heat of Formation.

The value of ΔH_f^{298} for TiO(l) is obtained from that of TiO(s) by adding ΔH_m° and the difference between $H_{2023}^\circ - H_{298}^\circ$ for TiO(s) and TiO(l).

Heat Capacity and Entropy.

The heat capacity for TiO(l) is estimated on the basis of 8 cal/g-atom. S_{298}° is obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m is taken from W. Dawid and K. Schröter, Z. Anorg. Allg. Chem. 233, 178 (1937). The heat of melting is estimated by comparison with that of VO(c) reported by C. E. Wicks and P. E. Block, U. S. Bur. Mines Bull. 605, 1963.

T_m has also been reported as 2023 and 2103°K by H. Nishimura and H. Kimura, J. Japan Inst. Metals (Sendai) 20, 589 (1956), and R. DeVries, R. Roy, and E. Osborn, Trans. Brit. Ceram. Soc. 53, 525 (1954), respectively. According to the Ti-O phase diagram reported by P. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. 49, 180 (1966), TiO melts incongruently.

Vaporization Data.

T_b is calculated as the temperature at which the Gibbs energy change of the reaction TiO(l) = TiO(g) approaches zero. The difference between ΔH_f° for TiO(g) and TiO(l) at T_b is ΔH_v° .

Tungsten Monoxide (W0)
(Ideal Gas)

GFW = 199.8494

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o) ₂₉₈ /T	H ^o - H ^o ₂₉₈	ΔH ^o	Log Kp
0	4.000	INFINITE	- 2.093	101.734	INFINITE
100	51.313	55.053	1.318	101.621	29.14
200	7.017	55.876	1.015	101.795	105.291
298	7.287	56.722	0.700	101.600	68.702
300	7.294	56.722	.013	101.596	68.243
400	7.656	60.914	.761	101.390	49.756
500	7.947	62.654	1.541	101.212	38.685
600	8.176	64.124	2.348	101.031	29.138
700	8.346	65.398	3.174	100.847	21.065
800	8.472	66.521	4.015	100.656	15.065
900	8.567	67.524	4.867	100.459	10.981
1000	8.640	68.431	5.728	100.252	7.844
1100	8.698	69.257	6.595	100.036	5.284
1200	8.744	70.016	7.467	99.809	3.276
1300	8.781	70.717	8.343	99.571	1.816
1400	8.813	71.369	9.223	99.322	0.874
1500	8.839	71.978	10.106	99.061	0.376
1600	8.862	72.549	10.991	98.788	0.047
1700	8.881	73.087	11.878	98.503	- 0.283
1800	8.899	73.595	12.767	98.206	- 0.603
1900	8.915	74.077	13.658	97.896	- 0.913
2000	8.930	74.535	14.550	97.573	- 1.213
2100	8.945	74.971	15.444	97.238	- 1.503
2200	8.959	75.387	16.339	96.888	- 1.783
2300	8.974	75.786	17.236	96.527	- 2.053
2400	8.989	76.168	18.134	96.152	- 2.323
2500	9.005	76.535	19.033	95.763	- 2.593
2600	9.022	76.889	19.935	95.363	- 2.863
2700	9.040	77.230	20.838	94.944	- 3.133
2800	9.061	77.559	21.743	94.508	- 3.403
2900	9.082	77.877	22.650	94.057	- 3.673
3000	9.105	78.185	23.554	93.599	- 3.943
3100	9.132	78.484	24.471	92.918	- 4.213
3200	9.161	78.775	25.386	92.284	- 4.483
3300	9.191	79.057	26.304	91.584	- 4.753
3400	9.224	79.332	27.224	90.810	- 5.023
3500	9.259	79.600	28.148	89.950	- 5.293
3600	9.296	79.861	29.076	88.978	- 5.563
3700	9.336	80.116	30.008	87.896	- 5.833
3800	9.377	80.366	30.943	86.706	- 6.103
3900	9.420	80.610	31.883	85.406	- 6.373
4000	9.466	80.844	32.827	84.096	- 6.643
4100	9.513	81.083	33.776	82.676	- 6.913
4200	9.561	81.313	34.730	81.146	- 7.183
4300	9.611	81.539	35.689	79.506	- 7.453
4400	9.663	81.760	36.652	77.756	- 7.723
4500	9.715	81.978	37.621	75.896	- 7.993
4600	9.768	82.192	38.595	73.926	- 8.263
4700	9.822	82.403	39.575	71.846	- 8.533
4800	9.876	82.610	40.560	69.656	- 8.803
4900	9.931	82.814	41.550	67.356	- 9.073
5000	9.985	83.016	42.546	64.946	- 9.343
5100	10.040	83.214	43.547	62.426	- 9.613
5200	10.095	83.409	44.554	59.796	- 9.883
5300	10.149	83.602	45.565	57.056	- 10.153
5400	10.203	83.792	46.584	54.206	- 10.423
5500	10.256	83.980	47.612	51.246	- 10.693
5600	10.309	84.165	48.635	48.176	- 10.963
5700	10.360	84.348	49.668	45.006	- 11.233
5800	10.411	84.529	50.707	41.726	- 11.503
5900	10.460	84.707	51.750	38.336	- 11.773
6000	10.509	84.883	52.799	34.826	- 12.043

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

TUNGSTEN MONOXIDE (W0)

(IDEAL GAS)

GFW = 199.8494

Ground State Configuration [$5s^2$] gibbs/mol
 $S_{298.15}^o = [58.7]$ gibbs/mol
 $\Delta H_{298.15}^o = 101.6 \pm 10$ kcal/mol
 $\Delta H_{298.15}^o = 101.6 \pm 10$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_1 , cm ⁻¹	g_1
[0]	[3]
[14160]	[1]
[17211]	[2]
[19189]	[6]

$w_e = 1055$ cm⁻¹
 $B_e = [0.3498]$ cm⁻¹
 $w_e x_e = [3.85]$ cm⁻¹
 $a_e = [0.0016]$ cm⁻¹
 $r_e = [1.81]$ Å

Heat of Formation

The heat of formation, $\Delta H_{298}^o(WO, g) = 101.6$ kcal/mol, was derived from the heat of reaction, $\Delta H_{298}^o = -42.0$ kcal/mol for $WO(g) \rightarrow W(c) + O(g)$ with all JANAF auxiliary data. The value of ΔH_{298}^o was calculated by the third law method from the partial pressure data, which were determined mass-spectrometrically in the temperature range 2188° to 2475°K, by G. DeMaris, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. **32**, 1373 (1960). The drift in the third law analysis was $\pm 20 \pm 7$ eu.

Heat Capacity and Entropy

The fundamental vibrational frequency, the ground state configuration, and the probable electronic levels for tungsten monoxide (g) were obtained from the infrared and ultraviolet spectroscopic investigations by matrix isolation by W. Weitzer, Jr., and D. McLeod, J. Mol. Spectry. **17**, 276 (1965). The rotational constant B_e was calculated from an estimated bond distance, $r_e = 1.81$ Å. The value of x_e was calculated from the relation $x_e u^2/2 = 0.014$ which was given by R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) **219A**, 120 (1953). The constant, 0.014, was estimated, based on those for $ZrO(g)$ and $VO(g)$. The value of a_e was calculated from the Morse potential function.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(H°-H° ₂₉₈)/T	cal. mole ⁻¹	log K _p
0	0.000	INFINITE	14.255	INFINITE
100	46.678	14.255	14.255	14.255
200	7.048	51.463	14.217	10.858
298	7.373	54.332	14.000	5.777
300	7.380	54.332	13.996	5.714
400	7.274	56.553	13.763	5.184
500	8.006	58.318	13.510	4.693
600	8.343	59.813	13.257	4.217
700	8.644	61.121	12.992	3.758
800	9.010	62.299	12.717	3.314
900	9.450	63.385	12.436	2.884
1000	9.948	64.406	12.150	2.466
1100	10.471	65.378	11.861	2.061
1200	10.980	66.311	11.571	1.668
1300	11.443	67.209	11.281	1.294
1400	11.833	68.072	11.000	0.938
1500	12.159	68.894	10.729	0.600
1600	12.358	69.690	10.467	0.280
1700	12.494	70.444	10.214	0.000
1800	12.557	71.160	9.969	-0.280
1900	12.561	71.839	9.734	-0.561
2000	12.517	72.465	9.509	-0.842
2100	12.440	73.042	9.294	-1.123
2200	12.340	73.668	9.089	-1.404
2300	12.226	74.244	8.894	-1.685
2400	12.102	74.772	8.709	-1.966
2500	11.968	75.254	8.534	-2.247
2600	11.866	75.691	8.369	-2.528
2700	11.784	76.137	8.214	-2.809
2800	11.651	76.563	8.069	-3.090
2900	11.557	76.970	7.934	-3.371
3000	11.473	77.350	7.809	-3.652
3100	11.400	77.705	7.694	-3.933
3200	11.337	78.096	7.589	-4.214
3300	11.283	78.444	7.494	-4.495
3400	11.239	78.750	7.409	-4.776
3500	11.204	79.017	7.334	-5.057
3600	11.176	79.257	7.269	-5.338
3700	11.156	79.472	7.214	-5.619
3800	11.143	80.024	7.169	-5.900
3900	11.135	80.313	7.134	-6.181
4000	11.133	80.595	7.109	-6.462
4100	11.135	80.870	7.084	-6.743
4200	11.141	81.138	7.059	-7.024
4300	11.151	81.401	7.034	-7.305
4400	11.163	81.657	7.009	-7.586
4500	11.178	81.908	6.984	-7.867
4600	11.195	82.154	6.959	-8.148
4700	11.214	82.395	6.934	-8.429
4800	11.233	82.631	6.909	-8.710
4900	11.254	82.863	6.884	-8.991
5000	11.276	83.091	6.859	-9.272
5100	11.297	83.314	6.834	-9.553
5200	11.318	83.534	6.809	-9.834
5300	11.340	83.750	6.784	-10.115
5400	11.361	83.961	6.759	-10.396
5500	11.382	84.167	6.734	-10.677
5600	11.402	84.376	6.709	-10.958
5700	11.421	84.578	6.684	-11.239
5800	11.440	84.776	6.659	-11.520
5900	11.459	84.971	6.634	-11.801
6000	11.474	85.165	6.609	-12.082

June 30, 1961; Sept. 30, 1961; Dec. 31, 1965

ZIRCONIUM MONOXIDE (ZrO)

(IDEAL GAS)

MOL. WT. = 107.2194

Ground State Configuration $1\Sigma^+$ $\Delta H_f^0 = 14.26 \pm 12 \text{ kcal. mole}^{-1}$ $S_{298.15}^0 = 54.33 \pm 2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^0 = 14.0 \pm 12 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

E_i , cm. ⁻¹	g_i	E_i , cm. ⁻¹	g_i
0	1	(18000)	2
(4000)	6	(22000)	6
(6000)	2	(25500)	2
15500	2	27500	1
(15700)	6	(28500)	6
(17500)	6		

 $\omega_e x_e = 4 \text{ cm.}^{-1}$ $r_e = 1.711 \text{ \AA}$ $\omega_e = 978 \text{ cm.}^{-1}$ $\sigma = 1$ $\omega_e x_e = 0.0023 \text{ cm.}^{-1}$ $B_e = 0.4142 \text{ cm.}^{-1}$

Heat of Formation.

The ΔH_f^0 298.15 = 14.0 ± 12 kcal. mole⁻¹ was calculated from the ΔH_f^0 298.15 = 290.342 ± 12.8 kcal. mole⁻¹ for the reaction $\text{Zr(c)} + \text{ZrO}_2(\text{c}) = \text{ZrO(g)}$. The value of ΔH_f^0 298.15 was obtained by the third law analysis from the mass spectrometric studies of M. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 28, 1207 (1957). They observed the variation of the ZrO⁺ ion intensity over the system Zr + ZrO₂ and reported equilibrium constants for the reaction $\text{Zr} + \text{ZrO}_2 \rightarrow \text{ZrO} + \text{ZrO}_2$ in the range 2124-2322°K. The third law drift is $-58 \pm 28 \text{ a.u.}$

Heat Capacity and Entropy.

The ground state of ZrO(g) was assumed to be $1\Sigma^+$ as determined from the matrix isolation spectra of W. Weltner, Jr., and D. McLeod, Jr., J. Phys. Chem. 69, 3488 (1965). Previously this had been described as the lower state in the A band system reported by V. Uhler and L. Akerlind, Arkiv Fysik 10, 431 (1955).

All molecular constants were obtained from Uhler and Akerlind, loc. cit., except $\omega_e = 978 \text{ cm.}^{-1}$ and $\omega_e x_e = 4 \text{ cm.}^{-1}$ which were calculated from ω and $\omega_e = 0.0023 \text{ cm.}^{-1}$ using the equations

$$\omega_e x_e = \frac{6 \sqrt{\omega_e x_e} \cdot B_e^3}{\omega_e} - \frac{6 B_e^2}{\omega_e} \quad \text{and} \quad \omega_e = \omega_e - 2 \omega_e x_e = 969.76 \text{ cm.}^{-1}$$

The higher electronic levels were obtained or estimated from the correlation diagram given by Weltner and McLeod, loc. cit.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(H°-H° ₂₉₈)/T	cal. mole ⁻¹	log K _p
0	0.000	INFINITE	14.255	INFINITE
100	46.678	14.255	14.255	14.255
200	7.048	51.463	14.217	10.858
298	7.373	54.332	14.000	5.777
300	7.380	54.332	13.996	5.714
400	7.274	56.553	13.763	5.184
500	8.006	58.318	13.510	4.693
600	8.343	59.813	13.257	4.217
700	8.644	61.121	12.992	3.758
800	9.010	62.299	12.717	3.314
900	9.450	63.385	12.436	2.884
1000	9.948	64.406	12.150	2.466
1100	10.471	65.378	11.861	2.061
1200	10.980	66.311	11.571	1.668
1300	11.443	67.209	11.281	1.294
1400	11.833	68.072	11.000	0.938
1500	12.159	68.894	10.729	0.600
1600	12.358	69.690	10.467	0.280
1700	12.494	70.444	10.214	0.000
1800	12.557	71.160	9.969	-0.280
1900	12.561	71.839	9.734	-0.561
2000	12.517	72.465	9.509	-0.842
2100	12.440	73.042	9.294	-1.123
2200	12.340	73.668	9.089	-1.404
2300	12.226	74.244	8.894	-1.685
2400	12.102	74.772	8.709	-1.966
2500	11.968	75.254	8.534	-2.247
2600	11.866	75.691	8.369	-2.528
2700	11.784	76.137	8.214	-2.809
2800	11.651	76.563	8.069	-3.090
2900	11.557	76.970	7.934	-3.371
3000	11.473	77.350	7.809	-3.652
3100	11.400	77.705	7.694	-3.933
3200	11.337	78.096	7.589	-4.214
3300	11.283	78.444	7.494	-4.495
3400	11.239	78.750	7.409	-4.776
3500	11.204	79.017	7.334	-5.057
3600	11.176	79.257	7.269	-5.338
3700	11.156	79.472	7.214	-5.619
3800	11.143	80.024	7.169	-5.900
3900	11.135	80.313	7.134	-6.181
4000	11.133	80.595	7.109	-6.462
4100	11.135	80.870	7.084	-6.743
4200	11.141	81.138	7.059	-7.024
4300	11.151	81.401	7.034	-7.305
4400	11.163	81.657	7.009	-7.586
4500	11.178	81.908	6.984	-7.867
4600	11.195	82.154	6.959	-8.148
4700	11.214	82.395	6.934	-8.429
4800	11.233	82.631	6.909	-8.710
4900	11.254	82.863	6.884	-8.991
5000	11.276	83.091	6.859	-9.272
5100	11.297	83.314	6.834	-9.553
5200	11.318	83.534	6.809	-9.834
5300	11.340	83.750	6.784	-10.115
5400	11.361	83.961	6.759	-10.396
5500	11.382	84.167	6.734	-10.677
5600	11.402	84.376	6.709	-10.958
5700	11.421	84.578	6.684	-11.239
5800	11.440	84.776	6.659	-11.520
5900	11.459	84.971	6.634	-11.801
6000	11.474	85.165	6.609	-12.082

June 30, 1961; Sept. 30, 1961; Dec. 31, 1965

Oxygen, Diatomic (O_2)

(Reference State - Ideal Gas) Mol. Wt. = 31.9988

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	.000	INFINITE	- 2.075	.000	.000	.000
100	6.958	41.395	55.705	1.381	.000	.000
200	6.961	46.218	49.643	.685	.000	.000
298	7.020	49.004	49.004	.000	.000	.000
300	7.023	49.047	49.004	.013	.000	.000
400	7.196	51.091	49.282	.724	.000	.000
500	7.431	52.722	49.812	1.455	.000	.000
600	7.670	54.098	50.414	2.210	.000	.000
700	7.893	55.297	51.028	2.988	.000	.000
800	8.063	56.361	51.629	3.786	.000	.000
900	8.212	57.320	52.209	4.600	.000	.000
1000	8.336	58.192	52.765	5.427	.000	.000
1100	8.439	58.991	53.295	6.266	.000	.000
1200	8.527	59.729	53.801	7.114	.000	.000
1300	8.604	60.415	54.283	7.971	.000	.000
1400	8.674	61.055	54.744	8.835	.000	.000
1500	8.738	61.656	55.185	9.706	.000	.000
1600	8.800	62.222	55.608	10.583	.000	.000
1700	8.858	62.757	56.013	11.465	.000	.000
1800	8.916	63.265	56.401	12.354	.000	.000
1900	8.973	63.749	56.776	13.249	.000	.000
2000	9.029	64.210	57.136	14.149	.000	.000
2100	9.084	64.652	57.483	15.054	.000	.000
2200	9.139	65.076	57.819	15.966	.000	.000
2300	9.194	65.483	58.143	16.882	.000	.000
2400	9.248	65.876	58.457	17.804	.000	.000
2500	9.301	66.254	58.762	18.732	.000	.000
2600	9.354	66.620	59.057	19.664	.000	.000
2700	9.405	66.974	59.344	20.602	.000	.000
2800	9.455	67.317	59.622	21.545	.000	.000
2900	9.503	67.650	59.893	22.493	.000	.000
3000	9.551	67.973	60.157	23.446	.000	.000
3100	9.596	68.287	60.415	24.403	.000	.000
3200	9.640	68.592	60.665	25.365	.000	.000
3300	9.682	68.889	60.910	26.331	.000	.000
3400	9.723	69.179	61.149	27.302	.000	.000
3500	9.762	69.461	61.383	28.276	.000	.000
3600	9.799	69.737	61.611	29.254	.000	.000
3700	9.835	70.006	61.834	30.236	.000	.000
3800	9.869	70.269	62.053	31.221	.000	.000
3900	9.901	70.525	62.267	32.209	.000	.000
4000	9.932	70.776	62.476	33.201	.000	.000
4100	9.961	71.022	62.682	34.196	.000	.000
4200	9.988	71.262	62.885	35.193	.000	.000
4300	10.015	71.498	63.081	36.193	.000	.000
4400	10.039	71.728	63.275	37.196	.000	.000
4500	10.062	71.954	63.465	38.201	.000	.000
4600	10.084	72.176	63.652	39.208	.000	.000
4700	10.104	72.393	63.836	40.218	.000	.000
4800	10.123	72.606	64.016	41.229	.000	.000
4900	10.140	72.814	64.194	42.242	.000	.000
5000	10.156	73.019	64.368	43.257	.000	.000
5100	10.172	73.221	64.540	44.274	.000	.000
5200	10.187	73.418	64.708	45.292	.000	.000
5300	10.200	73.613	64.875	46.311	.000	.000
5400	10.213	73.803	65.038	47.332	.000	.000
5500	10.225	73.991	65.199	48.353	.000	.000
5600	10.237	74.175	65.358	49.377	.000	.000
5700	10.247	74.356	65.514	50.401	.000	.000
5800	10.258	74.535	65.668	51.426	.000	.000
5900	10.267	74.710	65.820	52.452	.000	.000
6000	10.276	74.883	65.970	53.479	.000	.000

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

OXYGEN, DIATOMIC (O_2)

MOL. WT. = 31.9988

Ground State Configuration $3 \Sigma_g^-$ $\Delta H_f^\circ O = 0$

$S_{298.15}^\circ = 49.00 \pm 0.01$ cal. deg.⁻¹ mole⁻¹ $\Delta H_f^\circ 298.15 = 0$

$\omega_e x_e = 12.071$ cm.⁻¹ $\sigma^- = 2$

$B_e = 1.445$ cm.⁻¹ $r_e = 1.2074$ Å

Heat of Formation.

The heat of formation (ΔH_f°) for $O_2(g)$ is zero at all temperatures, by definition.

Heat Capacity and Entropy.

The functions adopted here are based on those of H. W. Woolley, J. Research, Nat. Bur. Standards 40, 163 (1948), who used a direct summation to 5000°K. The spectroscopic constants used were the same as those listed by O. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand Co., 1950. Raman measurements of rotation-vibration levels by A. Haber and E. A. McGinnis, J. Molec. Spect., 4, 195 (1960), support the constants selected by Herzberg which were changed on this table to apply to the naturally occurring isotopic composition given by D. Strominger, J. M. Hollander, and T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

The entropies listed by Woolley were reduced by 0.0065 cal. deg.⁻¹ mole⁻¹ which was added by Woolley to account for the contribution due to the presence of both odd and even rotational levels in O_2^{16} and O_2^{18} molecules. This correction is not necessary when isotope mixing entropy is neglected, cf. W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. 55, 1731 (1933).

Diatomic Oxygen Uninegative Ion (O_2^-)

(Ideal Gas) GFW = 31.99935

T, °K	C _p ^a	S ^b	-(C _p ^a - H ^o - H _{298.15})/T	H ^o - H _{298.15}	ΔH ^o	ΔG ^o	Log K _p
0							
100							
200							
298	7.202	49.913	49.913	0.000	-11.390	-10.174	7.458
300							
400	7.097	49.037	49.013	-0.111	-11.399	-10.166	7.506
500	7.029	50.074	50.190	0.710	-11.480	-10.166	7.506
600	7.013	51.168	50.751	1.514	-12.330	-9.084	3.971
700							
800	6.079	55.218	51.181	2.314	-12.786	-8.192	3.057
900	6.264	56.499	52.024	3.137	-13.262	-7.623	2.380
1000	6.526	58.610	53.542	4.884	-13.702	-7.054	1.835
1100	6.815	59.514	53.492	5.671	-14.633	-6.954	1.083
1200							
1300	6.066	60.138	54.396	6.536	-15.104	-3.964	0.788
1400	6.744	61.096	54.923	7.404	-15.577	-2.930	0.534
1500	6.792	61.796	55.425	8.285	-16.053	-1.956	0.312
1600	6.867	62.361	55.891	9.166	-16.531	-0.937	0.058
1700							
1800	6.898	63.635	56.798	10.939	-17.502	1.575	-0.215
1900	6.924	64.175	57.216	11.830	-17.990	2.783	-0.358
2000	6.948	64.696	57.617	12.724	-18.461	4.019	-0.486
2100	6.969	65.197	58.000	13.621	-18.926	5.280	-0.600
2200							
2300	6.990	65.631	58.372	14.518	-19.387	6.570	-0.714
2400							
2500	6.908	66.070	58.728	15.414	-19.878	7.947	-0.821
2600	6.925	66.490	59.072	16.319	-20.406	9.223	-0.916
2700	6.941	66.891	59.403	17.223	-20.984	10.587	-1.006
2800							
2900	6.957	67.284	59.718	18.126	-21.610	11.972	-1.090
3000	6.970	67.646	60.033	19.034	-22.287	13.375	-1.169
3100							
3200	6.983	68.002	60.332	19.941	-22.949	14.803	-1.244
3300	6.994	68.345	60.623	20.850	-23.650	16.248	-1.315
3400	6.998	68.674	60.905	21.761	-24.394	17.715	-1.383
3500	6.999	68.994	61.178	22.674	-25.175	19.207	-1.448
3600	6.999	69.305	61.448	23.595	-25.994	20.707	-1.508
3700							
3800	6.999	69.605	61.702	24.498	-26.849	22.228	-1.567
3900	6.999	69.896	61.954	25.413	-27.759	23.761	-1.623
4000	6.999	70.177	62.199	26.339	-28.706	25.319	-1.677
4100	6.999	70.457	62.440	27.266	-29.689	26.892	-1.728
4200	6.999	70.717	62.670	28.185	-30.700	28.480	-1.776
4300							
4400	6.997	70.974	62.897	29.084	-31.744	30.086	-1.826
4500	6.998	71.224	63.119	30.004	-32.821	31.709	-1.873
4600	6.999	71.464	63.336	30.925	-33.930	33.343	-1.916
4700	6.999	71.694	63.548	31.846	-35.069	34.983	-1.956
4800	6.999	71.914	63.755	32.771	-36.211	36.633	-2.003
4900							
5000	6.999	72.126	63.957	33.696	-37.366	38.293	-2.043
5100	6.999	72.339	64.156	34.621	-38.534	40.024	-2.083
5200	6.999	72.547	64.350	35.546	-39.714	41.773	-2.121
5300	6.999	72.746	64.536	36.471	-40.906	43.540	-2.156
5400	6.999	72.939	64.727	37.405	-42.100	45.315	-2.194
5500							
5600	6.999	73.123	64.910	38.335	-43.305	46.934	-2.230
5700	6.999	73.298	65.089	39.266	-44.521	48.687	-2.264
5800	6.999	73.468	65.261	40.197	-45.748	50.461	-2.298
5900	6.999	73.632	65.428	41.127	-46.986	52.253	-2.330
6000	6.999	73.791	65.589	42.057	-48.234	54.031	-2.362
6100							
6200	6.999	74.207	65.775	43.001	-49.493	55.839	-2.393
6300	6.999	74.369	65.939	43.940	-50.762	57.649	-2.423
6400	6.999	74.524	66.100	44.879	-52.041	59.484	-2.453
6500	6.999	74.674	66.256	45.818	-53.329	61.332	-2.483
6600	6.999	74.816	66.414	46.761	-54.626	63.171	-2.510
6700							
6800	6.999	75.086	66.567	47.701	-55.931	65.031	-2.538
6900	6.999	75.253	66.718	48.644	-57.244	66.895	-2.565
7000	6.999	75.416	66.864	49.584	-58.566	68.785	-2.592
7100	6.999	75.574	67.017	50.524	-59.897	70.699	-2.618
7200	6.999	75.729	67.167	51.464	-61.236	72.639	-2.644
7300	6.999	75.879	67.317	52.404	-62.582	74.603	-2.669
7400	6.999	76.024	67.464	53.344	-63.934	76.591	-2.694
7500	6.999	76.164	67.609	54.284	-65.291	78.603	-2.719
7600	6.999	76.304	67.754	55.224	-66.652	80.637	-2.744
7700	6.999	76.444	67.899	56.164	-68.017	82.693	-2.769
7800	6.999	76.584	68.044	57.104	-69.386	84.769	-2.794
7900	6.999	76.724	68.189	58.044	-70.759	86.865	-2.819
8000	6.999	76.864	68.334	58.984	-72.136	88.981	-2.844
8100	6.999	76.999	68.479	59.924	-73.517	91.117	-2.869
8200	6.999	77.139	68.624	60.864	-74.901	93.273	-2.894
8300	6.999	77.279	68.769	61.804	-76.288	95.449	-2.919
8400	6.999	77.419	68.914	62.744	-77.678	97.645	-2.944
8500	6.999	77.559	69.059	63.684	-79.071	99.861	-2.969
8600	6.999	77.699	69.204	64.624	-80.467	102.097	-2.994
8700	6.999	77.839	69.349	65.564	-81.866	104.353	-3.019
8800	6.999	77.979	69.494	66.504	-83.267	106.629	-3.044
8900	6.999	78.119	69.639	67.444	-84.671	108.925	-3.069
9000	6.999	78.259	69.784	68.384	-86.078	111.241	-3.094
9100	6.999	78.399	69.929	69.324	-87.487	113.577	-3.119
9200	6.999	78.539	70.074	70.264	-88.898	115.933	-3.144
9300	6.999	78.679	70.219	71.204	-90.311	118.309	-3.169
9400	6.999	78.819	70.364	72.144	-91.726	120.705	-3.194
9500	6.999	78.959	70.509	73.084	-93.143	123.121	-3.219
9600	6.999	79.099	70.654	74.024	-94.562	125.557	-3.244
9700	6.999	79.239	70.799	74.964	-95.983	128.013	-3.269
9800	6.999	79.379	70.944	75.904	-97.406	130.489	-3.294
9900	6.999	79.519	71.089	76.844	-98.831	132.985	-3.319
10000	6.999	79.659	71.234	77.784	-100.258	135.501	-3.344

Sept. 30, 1965; Dec. 31, 1966

DIATOMIC OXYGEN UNINEGATIVE ION (O_2^-) (IDEAL GAS)

OFW = 31.99935

Ground State Configuration [$^2\Pi_g$]

$S_{298.15}^o = 49.91 \pm 0.1$ gibb/mol

$\Delta H_{f,0}^o = -9.92 \pm 0.5$ kcal/mol

$\Delta H_{f,298.15}^o = -11.39 \pm 0.5$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_1, \text{ cm}^{-1}$

g_1

0 [4]

29400 [4]

$w_e x_e = 8.5 \text{ cm}^{-1}$

$\sigma = 2$

$a_e = [0.013] \text{ cm}^{-1}$

$r_e = 1.50 \text{ \AA}$

$w_e = 1170 \text{ cm}^{-1}$

$B_e = 1.247 \text{ cm}^{-1}$

Heat of Formation

The electron affinity of $O_2(g)$ has been measured in the electron detachment experiments of J. L. Pack and A. V. Phelps, J. Chem. Phys. 44, 1870 (1966). The value reported is $0.43 \pm 0.02 \text{ eV}$ ($9.92 \pm 0.48 \text{ kcal/mol}$) which is in good agreement with the value $0.46 \pm 0.10 \text{ eV}$ selected by C. W. Beckett and E. C. Casady, Natl. Bur. Std. Report 8628, Jan. 1, 1965.

Heat Capacity and Entropy

J. Rolfe, J. Chem. Phys. 40, 1664 (1964), has deduced from fluorescence emission spectra of O_2^- in alkali halides, the vibrational constants and an excited electronic level. The $^2\Pi$ ground state is that predicted by molecular orbital theory and the first excited state should also be $^2\Pi$. By analogy with Cl_2^+ , which is isoelectronic, the first excited level is estimated to lie in the 20000 - 30000 cm^{-1} region. Thus, the level observed by Rolfe is assumed to be the first excited $^2\Pi_u$ state. The bond length is taken from F. R. Olmstead, The Rand Corporation, Memo- randum RM-4034-1-PR, AD 630997. B_e was calculated from the bond length, and a_e was estimated from the above quantities using the Morse potential function relation.

The enthalpy at 0°K is -2.086 kcal/mol .

Phosphorus Dioxide (PO₂)

(Ideal Gas) Mol. Wt. = 62.975

INTERIM TABLE

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	70.611	70.611	INFINITE
100	8.016	51.132	68.657	70.619	71.431	156.105
200	8.802	56.890	71.476	70.782	72.190	78.882
298	9.497	60.607	74.834	71.000	72.834	53.387
300	9.517	60.668	74.834	71.004	72.846	53.065
400	10.913	63.663	81.009	71.204	73.429	40.118
500	11.659	66.183	86.178	71.376	73.964	32.328
600	12.189	68.358	90.714	71.538	74.468	27.123
700	12.559	70.125	94.784	71.690	74.942	23.246
800	12.837	71.664	98.496	71.832	75.386	20.046
900	13.038	73.088	101.909	71.965	75.800	17.244
1000	13.188	74.470	105.125	72.090	76.186	14.704
1100	13.304	75.812	108.250	72.208	76.546	12.404
1200	13.395	77.120	111.290	72.320	76.886	10.304
1300	13.467	78.399	114.250	72.428	77.210	8.386
1400	13.525	79.656	117.140	72.532	77.520	6.626
1500	13.573	80.894	120.000	72.632	77.816	5.016
1600	13.612	82.118	122.830	72.728	78.100	3.546
1700	13.642	83.332	125.640	72.820	78.372	2.216
1800	13.673	84.538	128.430	72.908	78.632	1.016
1900	13.697	85.728	131.200	72.992	78.880	0.000
2000	13.717	86.900	133.960	73.072	79.116	-0.916
2100	13.735	88.060	136.710	73.148	79.340	-1.760
2200	13.753	89.210	139.450	73.220	79.552	-2.540
2300	13.769	90.350	142.180	73.288	79.752	-3.260
2400	13.775	91.480	144.900	73.352	79.940	-3.920
2500	13.786	92.600	147.610	73.412	80.116	-4.520
2600	13.795	93.710	150.310	73.468	80.280	-5.080
2700	13.803	94.810	153.000	73.520	80.432	-5.600
2800	13.811	95.900	155.680	73.568	80.572	-6.080
2900	13.818	96.980	158.350	73.612	80.700	-6.520
3000	13.824	98.060	161.000	73.652	80.816	-6.920
3100	13.829	99.130	163.640	73.688	80.920	-7.280
3200	13.834	100.200	166.270	73.720	81.012	-7.600
3300	13.839	101.260	168.890	73.748	81.092	-7.880
3400	13.843	102.310	171.500	73.772	81.160	-8.120
3500	13.847	103.360	174.100	73.792	81.216	-8.320
3600	13.850	104.400	176.690	73.808	81.260	-8.480
3700	13.853	105.440	179.270	73.820	81.292	-8.600
3800	13.856	106.480	181.840	73.828	81.312	-8.680
3900	13.859	107.510	184.400	73.832	81.320	-8.720
4000	13.862	108.540	186.960	73.832	81.316	-8.720
4100	13.864	109.570	189.510	73.828	81.300	-8.680
4200	13.866	110.600	192.060	73.812	81.272	-8.600
4300	13.868	111.630	194.600	73.792	81.232	-8.480
4400	13.870	112.660	197.140	73.768	81.180	-8.320
4500	13.872	113.690	199.680	73.740	81.116	-8.120
4600	13.873	114.720	202.220	73.708	81.040	-7.880
4700	13.875	115.750	204.760	73.672	80.952	-7.600
4800	13.877	116.780	207.300	73.632	80.852	-7.280
4900	13.878	117.810	209.840	73.588	80.740	-6.920
5000	13.879	118.840	212.380	73.540	80.616	-6.520
5100	13.880	119.870	214.920	73.488	80.480	-6.080
5200	13.882	120.900	217.460	73.432	80.332	-5.600
5300	13.883	121.930	220.000	73.372	80.172	-5.080
5400	13.884	122.960	222.540	73.308	79.992	-4.520
5500	13.885	123.990	225.080	73.240	79.800	-3.920
5600	13.886	125.020	227.620	73.168	79.592	-3.260
5700	13.887	126.050	230.160	73.092	79.368	-2.540
5800	13.887	127.080	232.700	73.012	79.128	-1.760
5900	13.888	128.110	235.240	72.928	78.872	-0.916
6000	13.889	129.140	237.780	72.840	78.600	0.000

Dec. 31, 1960; Sept. 30, 1962

Phosphorus Dioxide (PO₂)

(Ideal Gas)

Mol. Wt. = 62.975

ΔH_f^o 298.15 = [-71] kcal. mole⁻¹S_{298.15}^o = [60.6] cal. deg.⁻¹ mole⁻¹Point Group = C_{2v}

Ground State Degeneracy = 2

Vibrational Frequencies and Degeneracies

 $\omega, \text{ cm.}^{-1}$
 [960] (1)
 [515] (1)
 [1044] (1)

Angle O-P-O = 134° 4'

P-O distance = 1.485 Å

I_A = [10.81 X 10⁻³⁹] g. cm.²I_B = [9.933 X 10⁻³⁹] g. cm.²I_C = [0.977 X 10⁻³⁹] g. cm.²Heat of Formation. ΔH_f^o 298.15 was calculated from an estimated heat of dissociation (270 ± 25 kcal. mole⁻¹) reported by L. Brewer and O. M. Rosenblatt, Chem. Reviews, **61**, 257 (1961).

Heat Capacity and Entropy. The molecular constants selected for this table were estimated by J. S. Gordon. The molecular constants for PO₂(g) have been estimated by (1) J. S. Gordon, "Thermodynamic Data for Combustion Products," January 1960, Thiokol Chemical Corp., Reaction Motor Division, Denville, N. J. (2) R. L. Potter, V. N. DiStefano and S. N. Fox, "The Thermodynamic Functions of Some Combustion Products Containing Phosphorus-I," American Cyanamid Company and (3) C. B. Henderson and R. S. Scheffer, "Survey of Thermochemical Data," January 1960, Atlantic Research Corp., Alexandria, Virginia. The entropies at 3000° calculated from these three estimates differ by less than 0.8 cal. deg.⁻¹ mole⁻¹.

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0	7.000	INFINITE	2.762	63.590	63.590	INFINITE
100	7.533	79.883	2.411	64.375	59.916	130.980
200	12.720	19.593	1.372	64.541	55.769	137.213
298	14.871	14.277	.000	64.537	55.769	37.213
300	14.890	14.369	.028	64.544	50.684	36.921
400	15.820	22.794	1.558	64.367	46.069	25.160
500	16.600	26.408	3.189	64.150	41.244	16.156
600	17.380	29.508	4.888	63.896	37.045	13.493
700	18.160	32.247	6.665	64.767	32.402	10.116
800	18.940	34.717	8.520	64.831	27.802	7.595
900	19.720	36.993	10.453	64.026	23.246	5.685
1000	20.500	39.111	12.464	63.548	18.739	4.095
1100	21.280	41.102	14.553	62.997	14.285	2.838
1200	22.060	42.987	16.720	62.369	9.883	1.800
1300	22.840	44.783	18.965	61.667	5.537	.931
1400	23.620	46.505	21.288	60.893	1.249	.195
1500	24.400	48.161	23.689	60.047	2.983	-.435
1600	25.180	49.760	26.168	59.132	7.155	-.977
1700	25.960	51.310	28.725	58.146	11.270	-.1445
1800	26.740	52.816	31.360	57.094	15.321	1.860
1900	27.520	54.283	34.073	55.974	19.314	2.221

March 31, 1962

Lead Dioxide (PbO₂) (crystal)

Mol. Wt. = 239.21

ΔH°_f 298.15 = -64.55 ± 0.16 kcal. mole⁻¹S°_{298.15} = 18.3 ± 0.5 cal. deg.⁻¹ mole⁻¹

Heat of Formation. Recalculated from ΔH°_{298.15} = 12.14 kcal. mole⁻¹ for the reaction: PbO(c) + 1/2O₂(g) = PbO₂(c) reported by M. Tschelizow, Compt. rend., 100, 1458 (1885).

Heat Capacity and Entropy. C_p (69.9° to 297.2°K.) reported by R. W. Miller, J. Am. Chem. Soc. 51, 207 (1929). Above 298.15°K., the heat capacity value estimated by K. K. Kelley, U. S. Bur. Mines Bull. 594 (1960) was used. The two heat capacity curves were joined smoothly at 298.15°K. by graphical extrapolation.

Sulfur Dioxide (SO₂)
(Ideal Gas) Mol. Wt. = 64.066

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T kcal. mole ⁻¹	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞
100	8.033	49.432	2.522	70.341	INFINITE
200	8.033	49.432	1.863	70.866	175.088
298	8.530	50.258	1.663	70.821	175.088
300	8.530	50.258	1.663	70.821	52.585
350	8.537	50.298	1.018	71.766	52.264
400	8.537	50.298	1.016	71.764	39.308
450	8.537	50.298	2.093	72.356	31.436
500	11.723	66.707	3.237	72.824	26.148
600	12.160	68.550	4.433	73.206	22.342
700	12.532	70.200	5.669	73.593	19.825
800	12.806	71.693	6.937	73.982	17.197
900	13.022	73.054	8.229	74.376	15.095
1000	13.194	74.303	9.540	74.766	13.376
1100	13.335	75.458	10.866	75.152	11.943
1200	13.451	76.530	12.206	75.532	10.732
1300	13.549	77.530	13.564	75.906	9.694
1400	13.632	78.468	14.915	76.273	8.795
1500	13.704	79.350	16.282	76.631	8.009
1600	13.767	80.183	17.656	76.988	7.315
1700	13.822	80.971	19.035	77.344	6.699
1800	13.872	81.720	20.420	77.699	6.148
1900	13.917	82.433	21.809	78.051	5.653
2000	13.958	83.113	23.203	78.400	5.204
2100	13.995	83.763	24.601	78.746	4.797
2200	14.030	84.386	26.002	79.089	4.425
2300	14.063	84.984	27.407	79.430	4.084
2400	14.093	85.558	28.815	79.768	3.771
2500	14.122	86.112	30.225	80.106	3.482
2600	14.149	86.645	31.639	80.442	3.214
2700	14.175	87.160	33.055	80.776	2.966
2800	14.200	87.658	34.474	81.108	2.735
2900	14.224	88.140	35.895	81.438	2.519
3000	14.247	88.607	37.319	81.766	2.317
3100	14.270	89.059	38.745	82.092	2.128
3200	14.291	89.499	40.173	82.416	1.950
3300	14.312	89.926	41.603	82.738	1.783
3400	14.333	90.341	43.035	83.058	1.625
3500	14.353	90.745	44.469	83.376	1.476
3600	14.373	91.138	45.906	83.692	1.335
3700	14.392	91.522	47.344	84.006	1.201
3800	14.411	91.896	48.784	84.318	1.075
3900	14.430	92.261	50.226	84.628	0.954
4000	14.448	92.618	51.670	84.936	0.840
4100	14.467	92.966	53.116	85.242	0.731
4200	14.485	93.307	54.563	85.546	0.627
4300	14.502	93.640	56.013	85.848	0.528
4400	14.520	93.966	57.464	86.148	0.433
4500	14.537	94.285	58.917	86.446	0.342
4600	14.554	94.598	60.371	86.742	0.255
4700	14.572	94.905	61.828	87.036	0.172
4800	14.588	95.205	63.286	87.328	0.092
4900	14.605	95.500	64.745	87.618	0.015
5000	14.622	95.790	66.207	87.906	0.059
5100	14.639	96.074	67.670	88.192	0.130
5200	14.655	96.353	69.134	88.476	0.198
5300	14.672	96.627	70.601	88.758	0.264
5400	14.688	96.896	72.069	89.038	0.327
5500	14.704	97.161	73.538	89.316	0.388
5600	14.720	97.421	75.010	89.592	0.447
5700	14.736	97.677	76.482	89.866	0.504
5800	14.753	97.930	77.957	90.138	0.559
5900	14.769	98.178	79.433	90.408	0.613
6000	14.785	98.421	80.910	90.676	0.663

June 30, 1961

SULFUR DIOXIDE (SO₂) (IDEAL GAS)

MOL. WT. = 64.066

ΔH°₁₀ = -70.341 ± 0.05 kcal. mole⁻¹
Point Group C_{2v}
ΔH°_f 298.15 = -70.947 ± 0.05 kcal. mole⁻¹
S_{298.15} = 59.30 ± 0.02 cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω, cm. ⁻¹
1151.36 (1)
517.69 (1)
1361.76 (1)

Bond Lengths and Angles S-O = 1.432 ± 0.003 Å.

OSO = 119.53 ± 0.4°

Moments of Inertia I_A = 1.38046 × 10⁻³⁹ g. cm.²

σ = 2

I_B = 8.13067 × 10⁻³⁹ g. cm.²

I_C = 9.53376 × 10⁻³⁹ g. cm.²

Heat of Formation

J. R. Eickman and P. D. Rossini, J. Research Nat. Bur. Standards **53**, 597 (1929), measured the heat of combustion of rhombic sulfur to SO₂. Changes due to different atomic weights and electrical constants though negligible have been made.

Heat Capacities and Entropies

The functions were calculated by J. Gordon, private communication, Feb. 2, 1961, using the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. **22**, 1442 (1954). Structural parameters are given by M. H. Sirlatz, J. Chem. Phys. **19**, 938 (1951), obtained from microwave measurements. Frequencies were measured by R. D. Shelton, A. H. Nielsen, W. H. Fletcher, J. Chem. Phys. **21**, 2178 (1953) and **22**, 1791 (1954). A third law value of S_{298.15} = 59.24 cal. deg.⁻¹ mole⁻¹ was obtained by W. F. Clauqua and C. C. Stevenson, J. Am. Chem. Soc. **80**, 1389 (1958).

02S

02S

QUARTZ (SiO₂)

(CRYSTAL)

GFW = 60.0848



$$\begin{aligned}\Delta H_f^\circ &= -216.5 \pm 0.4 \text{ kcal/mol} \\ \Delta H_{298.15}^\circ &= -217.7 \pm 0.4 \text{ kcal/mol} \\ \Delta H_1^\circ &= 0.174 \pm 0.04 \text{ kcal/mol} \\ \Delta H_2^\circ &= 0.48 \pm 0.15 \text{ kcal/mol} \\ \Delta H_m^\circ &= 1.84 \pm 0.2 \text{ kcal/mol}\end{aligned}$$

$$\Delta H_{298.15}^\circ = 9.91 \pm 0.03 \text{ gibbs/mol}$$

$$T_1 = 847 \pm 1.5^\circ \text{K (low quartz} \rightarrow \text{high quartz)}$$

$$T_2 = 1079 \pm 250^\circ \text{K (high quartz} \rightarrow \text{high cristobalite)}$$

$$T_m = 1696 \pm 50^\circ \text{K (high quartz} \rightarrow \text{liquid)}$$

Heat of Formation

The heat of formation is based on data of Wise (1) for combustion of SiO₂ (low quartz) and Si(c) in F₂ to form SiF₄(g). Good (2) burned a mixture of Si(c) and vinylidene fluoride polymer in oxygen in the presence of HF(aq) to form H₂SiF₆(aq HF). Combining this result with a previous heat of solution of quartz (3), the authors derived $\Delta H_{298}^\circ = -217.5 \pm 0.5 \text{ kcal/mol}$. Agreement with the adopted value is excellent, considering the complexity of the latter scheme. Both schemes are independent of ΔH_f° (HF), although the polymer-Si scheme depends on the heat of dilution of HF(aq). Wise (1) has reviewed other data which confirm the adopted value rather than the oxygen combustion value (4) of -209.9 kcal/mol . Pertinent equilibrium data are analyzed on the table for SiO₂ (low cristobalite), while the calorimetric results are summarized below.

Reaction
 $\text{SiO}_2(\text{low quartz}) + 2\text{F}_2(\text{g}) \rightarrow \text{SiF}_4(\text{g}) + \text{O}_2(\text{g})$
 See text.
 $\text{Si(c)} + 2\text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{low quartz})$

$$\begin{aligned}\Delta H_{298}^\circ, \text{ kcal/mol} & -188.26 \pm 0.28 \\ \Delta H_{298}^\circ, \text{ kcal/mol} & -217.72 \pm 0.34 \\ \Delta H_{298}^\circ, \text{ kcal/mol} & -217.5 \\ \Delta H_{298}^\circ, \text{ kcal/mol} & -209.9\end{aligned}$$

$$\text{SiO}_2(\text{low quartz}) + 2\text{F}_2(\text{g}) \rightarrow \text{SiF}_4(\text{g}) + \text{O}_2(\text{g})$$

See text.

$$\text{Si(c)} + 2\text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{low quartz})$$

Heat Capacity and Entropy

Heat capacities below 300°K are based on data of Jones (5) and Westrum (6). Earlier data of Anderson (7) are in good agreement. The entropy is obtained from Cp using $S_2^\circ = 0.00001 \text{ eu}$. Cp° from 300° to 847°K is derived from adiabatic calorimetric data of Moser (8) and Sineil'nikov (9). The adopted Cp° is discontinuous at 847°K and $\Delta C_p^\circ = -2.17 \text{ gibbs/mol}$. Values above the transition temperature are based on data of Moser and on data up to 1473°K obtained with a thermal analysis method by Leonidov (10). Cp° is extrapolated linearly to higher temperatures.

From a review of data available before 1953, Kelley (11) selected almost identical enthalpies below 847°K but a value higher by 96 cal/mol at 900°K. The higher value, due to use of a larger ΔH_{298}° , was presumably based on Roth (12), Wietzel (13) and White (14) whose enthalpy data were given the most weight by Kelley. Near 900°K these three sets of data deviate from the adopted function by -150 ± 30 , $+130 \pm 40$ and $+1535 \text{ cal/mol}$, respectively; however, a recent enthalpy datum (15) obtained by transposed temperature drop calorimetry deviates by $+75 \text{ cal/mol}$ at 968°K.

Transition Data

T₁ is taken as $847 \pm 1.5^\circ \text{K}$ based on thermal analysis of many specimens by Kieth and Tuttle (16). Wide variations in T₁ for some specimens were attributed by the authors to small amounts of impurities. The discontinuity in the volume curve (17) during inversion from trigonal low quartz to hexagonal high quartz suggests that the transition should be treated as first order. Thus, the heat of transition is derived as $(1011-854)/17 = 174 \text{ cal/mol}$, where 1011 ± 6 is $(H_{298.15}^\circ - H_{823.15}^\circ)$ measured by Moser (8), 854 is the corresponding increment calculated from the JANAF Cp°, and 17 is an endpoint correction for the difference between the observed and adopted curves below 823.15°K. Some of the more recent data which confirm the adopted ΔH_1° are summarized below.

Source	Method	ΔH_1° , kcal/mol
8. Moser (1936)	H and Cp from adiabatic calorimetry	0.174
9. Sineil'nikov (1953)	Integration of Cp from adiabatic calorimetry	0.143
10. Leonidov (1964)	Thermal analysis	0.198
17. Berger (1964)	ΔV with $dT/dP = 0.026^\circ \text{K/atm}$	0.12
18. Berger (1965)	Microcalorimetric thermal analysis	0.156, 0.165, 0.178 ± 0.010
	Single crystal	0.124 to 0.193
	Various crushed samples	

Additional polymorphism of SiO₂ is discussed on the table for high cristobalite. Quartz has been superheated through the cristobalite region to some 300° above its metastable melting point. This melting point is calculated from the adopted tables as $1895 \pm 50^\circ \text{K}$, which agrees well with the range $1673 - 1723^\circ \text{K}$ indicated by the data of Mackenzie (18). The adopted tables predict the inversion of high quartz to high cristobalite at $1079 \pm 250^\circ \text{K}$. Holmquist (20) tentatively placed this inversion at $1298 \pm 25^\circ \text{K}$. ΔH_2° and ΔH_m° are calculated from the differences in heats of formation of the appropriate phases at T₂ and T_m.

References

1. S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, *J. Phys. Chem.*, **67**, 815 (1963). ΔH_f° .
2. W. D. Good, J. L. Lacina, B. L. DePrater and J. P. McCullough, *J. Phys. Chem.*, **68**, 579 (1964); **68**, 380 (1962). ΔH_f° .
3. E. C. King, *J. Am. Chem. Soc.*, **73**, 856 (1951). ΔH_f° .
4. L. J. Moore and R. C. H. Hallett, *Can. J. Phys.*, **38**, 696 (1960). Cp, 2-4°K.
5. G. H. Sorensen and R. C. H. Hallett, *Can. J. Phys.*, **38**, 696 (1960). Cp, 2-4°K.
6. E. F. Westrum, Jr., et al., private comm. Univ. Michigan, May 19, 1960; see also A. J. Leadbetter and J. A. Morrison, *Phys. Chem. Glasses*, **4**, 188 (1963). Cp, 5-300°K.
7. C. T. Anderson, *J. Am. Chem. Soc.*, **58**, 568 (1936). Cp, 53-296°K.
8. Moser, *Physik. Z.*, **37**, 737 (1936). Cp, 317-949°K.
9. V. Sineil'nikov, *Dokl. Akad. Nauk SSSR*, **22**, 483 (1953). Cp, 300-900°K, given graphically.
10. V. Ya. Leonidov, Yu. P. Barakki and N. I. Mitrova, *Geochemistry (English Transl.)*, **1964**, 409 (1964).
11. K. K. Kelley, U. S. Bur. Mines Bull. 584, 1960.
12. W. A. Roth and W. M. Bertram, *Z. Elektrochem.*, **35**, 297 (1929). H₂, 369-1171°K.
13. R. Wietzel, *Z. Anorg. Allgem. Chem.*, **115**, 71 (1921). H₂, 373-1673°K.
14. J. L. White, *Am. J. Sci.*, **25**, 1-13 (1916).
15. J. L. Holm, O. J. Kleppa, and F. Westrum, *J. Res. Natl. Bur. Stand.*, **70A**, 1-13 (1966).
16. M. L. Kieth and O. F. Tuttle, *Am. J. Sci.*, **25**, 203 (1952). T₁.
17. C. Berger, L. Eyraud, M. Richard and R. Riviére, *Bull. Soc. Chim. France*, **1956**, 628 (1956). Transition data.
18. C. Berger, M. Richard and L. Eyraud, *Bull. Soc. Chim. France*, **1955**, 1491 (1955). ΔH_1° .
19. C. D. Mackenzie, *J. Am. Ceram. Soc.*, **43**, 615 (1960). T_m.
20. S. B. Holmquist, *J. Am. Ceram. Soc.*, **51**, 82 (1961). T₂.



Cristobalite, Low (SiO₂)

(Crystal)

GFW = 60.0848

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	-0.000	-0.000	INFINITE	-	-215.938	-215.938	INFINITE
100	1.424	2.488	17.868	-1.518	-212.570	-212.570	644.571
200	7.886	6.663	11.268	-0.921	-208.443	-208.443	227.776
298	10.744	10.372	10.372	-0.000	-204.241	-204.241	149.712
300	10.790	10.439	10.372	-0.202	-204.141	-204.141	149.731
400	12.702	13.826	10.821	1.202	-217.138	-199.839	109.187
500	14.023	16.808	11.726	2.541	-217.074	-195.519	85.461
600	15.050	19.461	12.799	3.998	-216.940	-191.220	69.652
700	15.700	21.923	13.821	5.530	-216.769	-186.762	56.362
800	16.080	23.962	14.782	7.070	-216.569	-182.242	45.362
900	16.500	25.682	15.646	8.763	-216.362	-178.078	33.340
1000	16.800	27.637	17.208	10.428	-216.148	-174.281	38.089

CRISTOBALITE, LOW (SiO₂)

(CRYSTAL)

GFW = 60.0848

O₂Si

$$\Delta H_f^\circ = -215.9 \pm 0.5 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -217.1 \pm 0.5 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 0.321 \pm 0.06 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 10.372 \pm 0.03 \text{ gibbs/mol}$$

$$T_t = 543 \pm 3^\circ \text{K (Low cristobalite + high cristobalite)}$$

Heat of Formation

The heat of formation is calculated from that of quartz using $\Delta H_f^\circ = 0.45 \pm 0.15 \text{ kcal/mol}$ for high quartz + high cristobalite, as determined by Holm(1) from ΔH_{soln} in an oxide melt. This value reduces to $\Delta H_f^\circ = 0.60 \text{ kcal/mol}$ for low quartz + low cristobalite. Kracek(2) obtained essentially the same value, $\Delta H_f^\circ = 0.63 \text{ kcal/mol}$, from ΔH_{soln} in HF(aq, 74.7°C), while Hummel(3) found $\Delta H_f^\circ = 1.80 \text{ kcal/mol}$ from ΔH_{soln} in HF(aq, 26.5°C). The larger ΔH_f° corresponds to a less negative ΔH_f° (i.e., less stable) and suggests that the sample of Hummel has disorder approaching that of vitreous silica. Presumably, this disagreement arises from different methods of preparation of cristobalite from quartz. Holm heated for 24 hours at 1743°K, while Hummel heated for 4 hours at 1793°K. Hummel's sample was then ground and treated with dilute HF to remove amorphous surface layers created by grinding; particles smaller than 2.5 microns were used in order to obtain adequate rates of dissolution. Neither author gave X-ray or DTA evidence to confirm that the samples were the more stable, ordered form of cristobalite(13).

The calorimetric data are summarized below along with equilibrium data which confirm the adopted values of ΔH_f° for cristobalite and quartz. Data from Matoba(5) and Rein(6) were reduced to the standard state of Si(l) using activity coefficients from the curves of (10).

Source	Method	Reaction	Range, °K	No. of Points	ΔH_f° , kcal/mol	ΔH_f° , kcal/mol	Drift, eu	ΔH_f° , kcal/mol
1. Holm (1967)	ΔH_{soln} in oxide melt	A	970	3	0.45±0.15	0.6	-	-217.10
2. Hummel (1959)	ΔH_{soln} in HF(aq, 26.5°C)	A	299-65	8	1.80±0.2	1.80	-	-215.90
3. Kracek (1953)	ΔH_{soln} in HF(aq, 74.7°C)	A	298-348	6	-	0.63±0.05	-	-217.07
4. Humphrey (1952)	ΔH_{soln} in HF(aq, 73.7°C)	B	1843-1953	3	104.5±0.6*	112.48*	0.8	-216.77
5. Matoba (1959)	Keq + Y(Si)	C	1773-1798	5	-	175.42*	32.37	-217.17
6. Rein (1963)	Keq + Y(Si)	D	1703-1823	6	-	146.92*	-2.96	-217.94
7. Kay (1960)	Keq + Y(Si)	E	1673-1853	15	145.9±1.3*	147.43*	-1.9±1.9	-218.45
8. Baird (1958)	Kp	E	1673-1853	15	145.8±3.5*	147.43*	-1.9±1.9	-218.45

*Values at T are from second law analysis while those at 298.15°K are from third law.

A. SiO_2 (quartz, low or high) = SiO_2 (cristobalite, low or high)
 B. SiO_2 (high cristobalite) + $2\text{H}_2(\text{g}) = \text{Si}(\text{l}) + 2\text{H}_2\text{O}(\text{g})$
 C. SiO_2 (high cristobalite) + $2\text{C}(\text{graph}) = \text{Si}(\text{l}) + 2\text{CO}(\text{g})$
 D. SiO_2 (high cristobalite) + $2\text{SiC}(\text{g}) = 3\text{Si}(\text{l}) + 2\text{CO}(\text{g})$
 E. SiO_2 (high cristobalite) + $3\text{C}(\text{graph}) = 3\text{SiC}(\text{g}) + 2\text{CO}(\text{g})$

Heat Capacity and Entropy

Cp° below 300°K is based on data of Westrum(11). Earlier data of Anderson(12) are in satisfactory agreement. The entropy is obtained from Cp° using $S_0^\circ = 0.0007 \text{ eu}$. Cp° above 300°K is derived from enthalpy data of Moesman(13) and White(14). The former deviate from the adopted functions by -0.7 to 0.5 and the latter by +0.44. Although the functions above 300°K appear to be reliable, it would be desirable to have new data for a well-characterized sample (see Transition Data).

Transition Data

Low cristobalite is metastable with respect to quartz but persists up to Tt. Tt is taken as the temperature at the peak in the heating curve for well-ordered cristobalite; however, see (15, 16) for detailed discussions of temperatures about 25° lower which were found from cooling curves. ΔH_t° is derived from enthalpy data(13, 14) for high cristobalite using the adopted enthalpy for the low form. The enthalpy data of Moesman(13) gave a lower Tt which suggests that the sample was less well-ordered than desirable. ΔH_t° is confirmed, however, by other data which are summarized below. Additional polymorphism is discussed on the table for high cristobalite.

Source	Method	ΔH_t° , kcal/mol
13. Moesman (1941)	Enthalpy data	0.321
17. Berger (1965)	Microcalorimetric thermal analysis	0.318±0.018
18. Majumdar (1964)	SV and dT/dP	0.27
19. Sabatier (1957)	Differential thermal analysis	0.26±0.01

References	Method	ΔH_t° , kcal/mol
1. J. L. Holm, O. J. Kleppa and E. F. Westrum, Jr., <i>Geochim. Cosmochim. Acta</i> , to be published. ΔH_{soln} .		
2. J. L. Holm and H. E. Schwiete, <i>Glaetche. Ber.</i> , 32, 327 (1959). ΔH_{soln} , 1215. 69 (1953). ΔH_{soln} .		
3. F. C. Humphrey and E. G. King, <i>Am. Chem. Soc.</i> , 74, 2091 (1952); 73, 656 (1951). ΔH_{soln} .		
4. S. Matoba, K. Gunji and T. Kuwana, <i>Tetsu to Hagane</i> , 45, 229 (1955); <i>Stahl Eisen</i> , 80, 299 (1960). Keq.		
5. R. H. Rein and J. Chipman, <i>J. Phys. Chem.</i> , 67, 819 (1963). Keq.		
6. D. A. R. Kay and J. Taylor, <i>Trans. Faraday Soc.</i> , 58, 1372 (1960). Kp.		
7. D. A. R. Kay and J. Taylor, <i>Trans. Faraday Soc.</i> , 58, 1372 (1960). Kp.		
8. N. E. Baird and J. Taylor, <i>Trans. Faraday Soc.</i> , 58, 1372 (1960). Kp.		
9. J. Chipman and R. Baschowitz, <i>Trans. AIME</i> , 227, 473 (1963); 233, 415 (1965). Si act. coeff.		
10. J. Chipman and R. Baschowitz, <i>Trans. AIME</i> , 227, 473 (1963); 233, 415 (1965). Si act. coeff.		
11. E. F. Westrum, Jr., et al., private comm., Univ. Michigan, May 19, 1960; see also <i>Phys. Chem. Glasses</i> , 4, 188 (1963).		
12. C. T. Anderson, <i>J. Am. Chem. Soc.</i> , 58, 568 (1936). Cp, 55-297°K.		
13. E. F. Moesman and K. S. Pitzer, <i>J. Am. Chem. Soc.</i> , 53, 2348 (1941). H, 367-499°K.		
14. H. P. White, <i>J. Am. Chem. Soc.</i> , 74, 3713 (1952). H, 367-499°K.		
15. V. G. Hill and R. Roy, <i>J. Am. Ceram. Soc.</i> , 41, 532-7 (1958). Transition data.		
16. R. F. Walker, S. Zerfoss, S. F. Holley and L. J. Gross, <i>J. Res. Natl. Bur. Std.</i> , 61, 251 (1958). Tt.		
17. C. Berger, M. Richard and L. Eyraud, <i>Bull. Soc. Chim. France</i> , 1965, 1491 (1965). ΔH_t° .		
18. A. J. Majumdar, H. A. McKinstry and R. Roy, <i>J. Phys. Chem. Solids</i> , 25, 1487 (1964). ΔH_t° .		
19. G. Sabatier, <i>Bull. Soc. Franc. Mineral. Crist.</i> , 80, 444 (1957). ΔH_t° .		

June 30, 1967

O₂Si

T, °K	Cp*	S*	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH*	ΔG*	Log Kp
100							
200							
298	6.353	11.963	11.963	.000	-216.417	-204.032	149.560
300	6.400	12.003	11.963	.012	-216.427	-203.956	148.581
400	6.752	12.408	11.963	.044	-216.460	-203.844	146.444
500	13.589	17.429	13.039	2.195	-216.737	-199.492	85.449
600	14.930	20.026	13.991	3.621	-216.634	-191.252	69.663
700	15.500	22.373	15.023	5.145	-216.473	-187.033	56.384
800	16.094	24.490	16.077	6.731	-216.285	-182.842	49.950
900	16.712	26.406	17.157	8.387	-216.093	-178.672	43.387
1000	17.350	28.156	18.268	10.117	-215.893	-174.522	37.469
1100	16.915	29.757	19.422	11.699	-215.688	-170.402	33.856
1200	17.076	31.236	20.670	13.399	-215.461	-166.296	30.287
1300	17.208	32.608	20.983	15.113	-215.259	-162.207	27.269
1400	17.320	33.886	21.259	16.840	-215.061	-158.134	24.666
1500	17.416	35.088	22.501	18.577	-214.860	-154.074	22.449
1600	17.500	36.213	23.511	20.323	-214.666	-150.027	20.493
1700	17.575	37.276	24.290	22.076	-214.503	-145.985	18.755
1800	17.642	38.282	25.039	23.837	-214.281	-141.948	17.138
1900	17.698	39.239	25.762	25.605	-214.058	-137.926	15.693
2000	17.762	40.147	26.458	27.374	-213.835	-133.913	14.393
2100	17.816	41.015	27.131	29.157	-213.611	-129.912	13.218
2200	17.866	41.845	27.781	30.941	-213.389	-125.923	12.152
2300	17.914	42.641	28.410	32.730	-213.166	-121.946	11.179
2400	17.960	43.404	29.019	34.524	-212.944	-117.984	10.266
2500	18.005	44.138	29.609	36.322	-212.724	-114.034	9.409
2600	18.047	44.845	30.182	38.125	-212.503	-110.081	8.713
2700	18.089	45.527	30.738	39.931	-212.285	-106.018	8.015
2800	18.129	46.186	31.278	41.742	-212.067	-102.067	7.367
2900	18.168	46.832	31.801	43.577	-211.850	-98.151	6.764
3000	18.206	47.459	32.314	45.376	-211.634	-94.253	6.202

June 30, 1967

CRISTOBALITE, HIGH (SiO₂)

(CRYSTAL)

GFW = 60.0848

$S_{298.15}^{\circ} = 11.963$ gibbs/mol
 $\Delta H_{298.15}^{\circ} = -216.417$ kcal/mol
 $\Delta H^{\circ} = 0.321 \pm 0.06$ kcal/mol
 $\Delta H^{\circ} = 0.48 \pm 0.15$ kcal/mol
 $\Delta H^{\circ} = 2.29 \pm 0.5$ kcal/mol

Heat of Formation

The heat of formation is calculated from that of low cristobalite by addition of $\Delta H^{\circ} = 0.321$ kcal/mol and the difference between $H_{543}^{\circ} - H_{298}^{\circ}$ for low and high forms.

Heat Capacity and Entropy

C_p° is derived from enthalpies of Nossaman (1) and White (2), whose data deviate from the adopted functions by -0.6 to $+0.5\%$ and $+0.9$ to 0.0% , respectively. White's deviations for cristobalite have a magnitude and trend similar to his deviations for quartz and vitreous silica. Data of Wietzel (3) for his sample prepared at 1600°C deviate by $+3\%$ at 673°K and $+1.6\%$ at 1773°K . C_p° below 543°K is smoothly extrapolated to give the proper trend in the Gibbs energy, but the heat capacity at 298°K is not realistic. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data

Literature on the polymorphism of SiO₂ is voluminous but is summarized in detail in recent books by Sosman (4) and Eitel (5). The known phases of SiO₂ include quartz, tridymite(?), cristobalite, vitreous silica and the more recently discovered high pressure phases. Muan (6) concisely reviewed the still controversial question of whether tridymite is stabilized only by the presence of foreign ions or whether it is a stable phase of SiO₂ intermediate between quartz and cristobalite. Transitions among the different phases are generally sluggish because of large energy barriers to the structural change and small differences in Gibbs free energies. As a result, the phases often persist far into metastable regions. In contrast, transitions within a particular phase are rapid and reversible (i.e., the low + high inversions of quartz or cristobalite).

High cristobalite is the stable phase near T_m . It becomes metastable with respect to quartz at lower temperatures but persists down to the high + low inversion at 543°K (see table for low cristobalite). The high form is cubic and the low form tetragonal (12, 13).

The adopted tables give 1079.250°K as the temperature at which $\Delta G^{\circ} = 0$ for high quartz + high cristobalite; $\Delta H^{\circ} = 0.48 \pm 0.15$ kcal/mol is the corresponding enthalpy difference. The uncertainty in T_t is derived from that in ΔH° which, in turn, is taken from $\Delta H_{970}^{\circ} = 0.45 \pm 0.15$ kcal/mol obtained by Holm (7) from ΔH_{soln} measurements in an oxide melt. It is apparent that T_t is extremely sensitive to small changes in G or H . Holmquist (8) tentatively placed this inversion at 1298.25°K but did observe cristobalite formation at temperatures as low as 1171°K .

Melting Data

Melting point data were reviewed by Schneider (9) and adjusted to the 1948 International Temperature Scale. The adopted melting point for cristobalite is based on Greig (10). ΔH_m° is calculated as the difference in ΔH_f° for liquid and crystal at T_m . Mackenzie et al. (11) showed that cristobalite may be superheated by as much as 40° above T_m due to its slow rate of fusion.

References

1. M. A. Nossaman and K. S. Pitzer, *J. Am. Chem. Soc.* **63**, 2308 (1941). H, 542 - 622°K.
2. M. P. White, *Am. J. Sci.* **47**, 1 (1919). H, 573-1673°K.
3. R. Wietzel, *Z. Anorg. Allgem. Chem.* **116**, 71 (1921). H, 673 - 1973°K.
4. R. B. Sosman, "Phases of Silica," 388 pp., Rutgers Univ. Press, New Brunswick, N. J., 1965.
5. W. Eitel, "Silicate Science," Vol. III, pp. 44-157, Academic Press, New York, 1965.
6. A. Muan and E. F. Osborn, "Phase Equilibria among Oxides in Steelmaking," pp. 17-20, Addison-Wesley Publishing Co., Reading, Mass., 1965.
7. J. L. Holm, O. J. Kleppa and E. F. Westrum, Jr., *Geochim. Cosmochim. Acta*, to be published. ΔH_{soln} .
8. S. B. Holmquist, *J. Am. Ceram. Soc.* **44**, 82 (1961). Tt.
9. S. J. Schneider, *U. S. Natl. Bur. Std. Monograph* **68**, 1963.
10. J. W. Greig, *Am. J. Sci.* **13**, 1 (1927). Tm.
11. N. G. Ainslie, J. D. Mackenzie and D. Turnbull, *J. Phys. Chem.* **65**, 1718 (1961); *J. Am. Ceram. Soc.* **43**, 615 (1960).
12. C. Barger, L. Eyraud, M. Richard and R. Riviere, *Bull. Soc. Chim. France* **1966**, 628 (1966). Crystal structure.
13. W. A. Dollase, *Z. Krist.* **121**, 369 (1965). Crystal structure.

Silicon Dioxide (SiO₂)

(Liquid) GFW = 60.0848

SILICON DIOXIDE (SiO₂)

(LIQUID)

GFW = 60.0848

$$\Delta H_{298.15}^\circ = 11.465 \pm 0.3 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^\circ = -215.74 \text{ kcal/mol}$$



$$\Delta H_m^\circ = 1996 \pm 5^\circ \text{K (high cristobalite} \rightarrow \text{liquid)}$$

$$\Delta H_m^\circ = 2.29 \pm 0.5 \text{ kcal/mol}$$

Heat of Formation

The heat of formation is calculated from that of quartz using $\Delta H_{970}^\circ = 1.45 \pm 0.15 \text{ kcal/mol}$ for high quartz + SiO₂(l), as determined by Holm (1) from ΔH_{soln} in an oxide melt. This value reduces to $\Delta H_{298}^\circ = 1.96 \text{ kcal/mol}$ for low quartz + SiO₂(l) and is consistent within $\pm 0.3 \text{ kcal/mol}$ with other calorimetric data summarized below. Earlier results were reviewed by Hummel (4).

Source	Method	Reaction	T, °K	ΔH_{298}° kcal/mol	ΔH_{298}° kcal/mol	ΔH_{298}° kcal/mol
1. Holm (1967)	ΔH_{soln} in oxide melt	A	970	1.45 $\pm$ 0.15	1.96	-215.74
2. Wise (1963)	ΔH_c in fluorine	B	298	1.78 $\pm$ 0.46	1.78	-215.92
3. Kracek (1953)	ΔH_{soln} in HF(aq, 74.7°C)	A	298-348	—	2.18 $\pm$ 0.05	-215.52
4. Hummel (1959)	ΔH_{soln} in HF(aq, 26.5°C)	A	300	2.27 $\pm$ 0.2	2.27	-215.43
A. SiO ₂ (quartz, low or high) + SiO ₂ (l)						
B. SiO ₂ (l) + 2F ₂ (g) + SiF ₄ (g) + O ₂ (g)						

Heat Capacity and Entropy

C_p below 300°K is based on data of Flubacher (5) and Westrum (6) for samples annealed at 1100 and 1070°C, respectively. Data of Turdakin (7) are higher by about 1 percent in the range 60-160°K and at 300°K but are in agreement elsewhere. The entropy is calculated from C_p using $S_{2.34}^\circ - S_0^\circ = 0.0001 \text{ eu}$ and $S_0^\circ = 1.098 \text{ eu}$. C_p data (8) for a different sample annealed at 1300°C yield an entropy larger by $<0.04 \text{ eu}$. Earlier data were reviewed by Kelley (9). The residual entropy is calculated from $S_0^\circ = S_{298}^\circ - (S_{298}^\circ - S_0^\circ) = 41.258 - 40.160 = 1.098 \text{ eu}$, where 40.160 is obtained from the adopted functions, while 41.258 is the sum of $\Delta S_m^\circ = 1.147 \text{ eu}$ and $S_0^\circ = 40.111 \text{ eu}$ for high cristobalite. We estimate the uncertainty as $\pm 0.3 \text{ eu}$, primarily from the uncertainty in ΔH_m° .

C_p above 300°K is based on adiabatic calorimetric data of Moser (5) up to 900°K. Enthalpy data of White (10) and Fischer (11) are in excellent agreement. C_p from 900 to 1500°K is derived from enthalpy data of Southard (12) and White (10). Maximum deviation of the data from the adopted values in this range is 0.5 percent. Enthalpy data of Egan (13) and Kelley (14) deviate from the adopted values by less than 1 percent in the range 1000-1500°K, although large positive deviations appear at lower temperatures.

In the region 1500-1700°K, the adopted C_p shows a rapid, sigmoidal rise which is suggested by the enthalpy data of Wiestel (15). This is presumed to be the glass transition region in which C_p rises to that of the stable liquid. C_p above 1700°K is estimated as 20.5 gibbs/mol or 6.83 gibbs/g-atom. This value is consistent with the enthalpy data (15) and with liquid heat capacities of Al₂O₃, Na₂SiO₃ and Na₂SiO₃.

Melting Data

The melting point of high cristobalite is $1996 \pm 5^\circ \text{K}$, while the metastable melting point of high quartz is $1696 \pm 50^\circ \text{K}$. ΔH_m° is the difference between ΔH_f° for liquid and high cristobalite at T_m . Values ranging from 1.6 to 3.6 kcal/mol have been derived from various interpretations of phase diagrams (1).

References

1. J. L. Holm, O. J. Kleppa and E. F. Westrum, Jr., *Geochim. Cosmochim. Acta*, to be published. ΔH_{soln} .
2. S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, *J. Phys. Chem.* **67**, 815 (1963). ΔH_r .
3. F. C. Kracek, *Ann. Rept. Director of the Geophysical Laboratory*, No. 1215, 69 (1953). ΔH_{soln} .
4. C. Hummel and H. E. Schwiete, *Glastech. Ber.* **32**, 327 (1959). ΔH_{soln} .
5. P. Flubacher, A. J. Leadbetter, J. A. Morrison and B. P. Stoicheff, *Phys. Chem. Solids* **13**, 53 (1959). C_p , 2.3-19°K.
6. E. F. Westrum, Jr., et al., private comm., Univ. Michigan, May 19, 1960. C_p , 5-300°K.
7. V. V. Tarasov, *Phys. Status Solidi* **20**, 37 (1967). C_p , 50-300°K measured by Turdakin.
8. K. K. Kelley and E. G. King, U. S. Bur. Mines Bulletin 592, 1961.
9. H. Moser, *Physik. Z.* **37**, 737 (1936). C_p , 324-936°K.
10. W. P. White, *J. Am. Chem. Soc.* **55**, 1047 (1933). H , 573-1173°K.
11. W. Fischer, *Z. Anorg. Allgem. Chem.* **200**, 335 (1931). H , 321-577°K.
12. J. C. Southard, *J. Am. Chem. Soc.* **63**, 3142 (1941). H , 506-1522°K.
13. E. Egan, Jr., Z. T. Wakefield and K. L. Elmore, *J. Am. Chem. Soc.* **72**, 2418 (1950). H , 763-1470°K.
14. K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686, 1946. H , 400-1500°K.
15. R. Wiestel, *Z. Anorg. Allgem. Chem.* **116**, 71 (1921). H , 373-1973°K.

Silicon Dioxide (SiO₂)
(Ideal Gas)

GFW = 60.0848

T, °K	C _p ^a	S° ^b - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0	∞	INFINITE	- 2.529	- 72.685	- 72.685	INFINITE
100	7.510	44.948	43.180	- 72.737	- 73.001	159.543
200	6.320	50.742	55.262	- 72.868	- 73.215	80.005
298	10.514	54.699	∞	- 73.000	- 73.377	53.772
300	10.537	54.765	58.700	- 73.003	- 73.340	53.442
400	11.474	57.929	55.125	- 73.118	- 73.460	40.137
500	12.207	60.572	55.957	- 73.208	- 73.534	32.142
600	12.767	62.849	56.920	- 73.281	- 73.593	26.806
700	13.166	64.651	57.813	- 73.345	- 73.640	22.991
800	13.500	66.039	58.644	- 73.397	- 73.678	19.699
900	13.790	67.044	59.440	- 73.440	- 73.708	16.808
1000	13.938	67.694	60.158	- 73.476	- 73.730	14.114
1100	14.085	71.033	61.632	- 73.509	- 73.746	14.652
1200	14.203	72.264	62.468	- 73.527	- 73.755	13.433
1300	14.303	73.343	63.028	- 73.541	- 73.763	12.513
1400	14.374	74.267	63.465	- 73.549	- 73.769	11.743
1500	14.438	75.061	63.758	- 73.555	- 73.774	11.070
1600	14.491	75.735	64.000	- 73.559	- 73.778	10.461
1700	14.536	76.326	64.126	- 73.562	- 73.781	9.905
1800	14.575	76.846	64.186	- 73.564	- 73.782	9.395
1900	14.610	77.296	64.218	- 73.566	- 73.783	8.925
2000	14.634	77.680	64.245	- 73.567	- 73.784	8.495
2100	14.658	80.160	64.553	- 73.568	- 73.785	8.105
2200	14.679	81.042	64.761	- 73.569	- 73.786	7.755
2300	14.698	81.714	64.881	- 73.570	- 73.787	7.445
2400	14.714	82.122	64.920	- 73.571	- 73.788	7.175
2500	14.728	82.422	64.953	- 73.572	- 73.789	6.945
2600	14.741	83.500	71.136	- 73.573	- 73.790	6.755
2700	14.753	84.037	71.604	- 73.574	- 73.791	6.605
2800	14.763	84.512	72.000	- 73.575	- 73.792	6.485
2900	14.771	84.913	72.329	- 73.576	- 73.793	6.385
3000	14.781	85.245	72.599	- 73.577	- 73.794	6.305
3100	14.789	85.597	73.346	- 73.578	- 73.795	6.235
3200	14.796	85.867	73.752	- 73.579	- 73.796	6.175
3300	14.802	86.064	74.032	- 73.580	- 73.797	6.125
3400	14.808	86.198	74.232	- 73.581	- 73.798	6.085
3500	14.813	87.494	74.508	- 73.582	- 73.799	6.055
3600	14.818	88.311	75.274	- 73.583	- 73.800	6.035
3700	14.823	88.711	75.632	- 73.584	- 73.801	6.025
3800	14.828	89.098	75.923	- 73.585	- 73.802	6.020
3900	14.831	89.478	76.158	- 73.586	- 73.803	6.015
4000	14.834	89.873	76.457	- 73.587	- 73.804	6.010
4100	14.838	90.239	76.944	- 73.588	- 73.805	6.005
4200	14.841	90.596	77.304	- 73.589	- 73.806	6.000
4300	14.844	90.944	77.548	- 73.590	- 73.807	5.995
4400	14.846	91.288	77.824	- 73.591	- 73.808	5.990
4500	14.849	91.621	78.025	- 73.592	- 73.809	5.985
4600	14.851	91.948	78.320	- 73.593	- 73.810	5.980
4700	14.853	92.260	78.609	- 73.594	- 73.811	5.975
4800	14.855	92.566	78.891	- 73.595	- 73.812	5.970
4900	14.857	92.866	79.171	- 73.596	- 73.813	5.965
5000	14.859	93.166	79.444	- 73.597	- 73.814	5.960
5100	14.861	93.461	79.713	- 73.598	- 73.815	5.955
5200	14.862	93.762	80.176	- 73.599	- 73.816	5.950
5300	14.864	94.058	80.430	- 73.600	- 73.817	5.945
5400	14.865	94.350	80.681	- 73.601	- 73.818	5.940
5500	14.867	94.603	80.941	- 73.602	- 73.819	5.935
5600	14.868	94.871	81.187	- 73.603	- 73.820	5.930
5700	14.869	95.144	81.425	- 73.604	- 73.821	5.925
5800	14.870	95.417	81.658	- 73.605	- 73.822	5.920
5900	14.872	95.687	81.893	- 73.606	- 73.823	5.915
6000	14.873	95.957	82.134	- 73.607	- 73.824	5.910

Dec. 31, 1960; Dec. 31, 1962; Sept. 30, 1967

SILICON DIOXIDE (SiO₂)

(IDEAL GAS)

Point Group [D_{2h}]

S°_{298.15} = [54.7] gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
[980] (1)
[370] (2)
[1430] (1)

Bond Distance: Si-O = [1.55] Å

Bond Angle: O-Si-O = [180°]

Rotational Constant: B₀ = [0.2193] cm⁻¹

Heat of Formation

The adopted value is based on the data summarized below. Margrave (1) has reported a value of ΔH°₂₉₈ = 140.9 ± 1 kcal/mol but details are not yet available. Assuming that this corresponds to reaction A below, we calculate ΔH°₂₉₈ = -75.5 kcal/mol. Firssova (2) reported two values of the sublimation pressure which were derived from Knudsen effusion data using auxiliary data for SiO(g). Porter (4) derived two pressures from a mass spectrometric study and also obtained a 2nd Law value for ΔH°₂₉₈ from ion intensities. The resulting range for ΔH°₂₉₈, 136 to 141 kcal/mol, is consistent with the lower limit of 130 kcal/mol obtained by Bergman (3) from a method involving explosion in a spherical bomb. An alternative analysis of the mass spectrometric data (4) using the gas phase reaction B suggests an even higher ΔH°₂₉₈ of 148 kcal/mol. The adopted ΔH°₂₉₈ corresponds to ΔH°₂₉₈ = 143.4 ± 4 kcal/mol and to ΔH°_{atom} = 297.3 ± 8 kcal/mol.

Source	Reaction	Method	Range, °K	ΔH° ₂₉₈ , kcal/mol	Drift
Margrave (1967)	A	-	-	- 140.9 ± 1	-
Firssova (1960)	A	Knudsen, calculation	1600-1800	-	- 75.5
Bergman (1959)	A	Explosion	-	- 137.0 ± 2	-
Porter (1955)	A	Knudsen mass spec.	1800-1900	128	- 86
	A	Ion intensities	1750-1980	136 ± 8	- 76.8
	B	Knudsen mass spec.	1800-1900	- 2	- 80
	A. SiO ₂ (high cristobalite) = SiO ₂ (g)			- 44.8 ± 1.2	- 23
	B. SiO(g) + 1/2 O ₂ (g) = SiO ₂ (g)			- 68.8	-

Heat Capacity and Entropy

Point group, ground state quantum weight and the linear symmetrical configuration are estimated by analogy with the properties of CO₂. From the bond lengths in SiO, CO₂ and CO, the length in SiO₂ is estimated as 1.509 × 1.180/1.128. Bond lengths and atomization energies for these molecules are reasonably consistent with the existence of six-electron bonds in the monoxides and four-electron bonds in the dioxides (5). Vibrational frequencies are estimated from a valence bond calculation using force constants, k = 9 × 10⁵ and k₆/k₂ = 0.3 × 10⁵ dyne/cm, which are obtained from those of SiO, CO₂ and CO. The moment of inertia is 12.76 × 10⁻³⁹ g cm².

References

1. J. L. Margrave, 5th Meeting ICRPG Thermochemistry Working Group, Linden, New Jersey, March 1967.
2. L. P. Firssova and An. N. Nesmeyanov, Russ. J. Phys. Chem. (English Transl.) **34**, 1279, 1232, 906 (1960).
3. G. A. Bergman and V. A. Medvedev, Sbornik Trudov Gosudarst. Inst. Priklad. Khim. **1959**, 158 (1959).
4. R. F. Porter, W. A. Chupka and M. G. Inghram, J. Chem. Phys. **23**, 216 (1955).
5. J. W. Linnett, "The Electronic Structure of Molecules," pp. 43-55, Methuen and Co. Ltd., London, 1964.

O₂Si

Titanium Dioxide, Anatase (TiO₂)

(Crystal)

GFW = 79.8988

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-	221.835	-221.835	INFINITE
100	4.565	2.302	21.322	-	222.503	-218.397	477.306
200	10.009	7.293	13.048	-	222.906	-214.107	233.965
298	13.257	11.931	11.931	0.000	223.000	-209.743	153.760
300	13.312	12.013	11.931	-0.025	222.999	-209.681	152.752
400	15.246	14.144	12.481	1.445	222.868	-205.253	112.145
500	16.153	15.654	13.575	3.040	222.690	-200.947	87.799
600	16.658	16.447	14.843	4.682	222.469	-196.524	71.584
700	16.973	16.936	15.188	6.364	222.251	-192.217	60.013
800	17.149	17.254	15.566	8.799	221.874	-183.658	44.605
900	17.349	17.554	15.868	11.540	221.724	-179.452	39.219
1000	17.459	17.867	16.448	13.290	221.602	-175.231	34.815
1100	17.553	18.056	20.874	15.050	222.442	-170.982	31.140
1200	17.530	18.266	22.045	16.810	222.442	-170.982	28.140
1300	17.496	18.493	23.035	18.598	222.068	-162.437	25.358
1400	17.456	18.731	24.031	20.386	221.906	-158.184	23.047
1500	17.406	18.961	24.963	22.169	221.763	-153.939	21.027
1600	17.353	19.191	25.848	23.937	221.640	-149.705	19.246
1700	17.296	19.415	26.674	25.724	221.540	-145.482	17.628
1800	17.234	19.633	27.443	27.524	221.469	-141.253	16.248
1900	17.174	19.846	28.157	29.323	221.426	-137.024	14.958
2000	17.111	20.053	28.815	31.126	221.400	-132.795	13.762
2100	17.046	20.257	29.417	32.932	221.389	-128.566	12.618
2200	16.979	20.457	30.043	34.742	221.389	-124.337	11.524
2300	16.912	20.652	30.693	36.555	221.389	-120.108	10.480
2400	16.844	20.842	31.352	38.371	221.389	-115.879	9.486
2500	16.775	21.027	32.021	40.187	221.389	-111.650	8.542

TITANIUM DIOXIDE, ANATASE (TiO₂)

(CRYSTAL)

OPW = 79.8988



$$\Delta H_f^\circ = -221.8 \pm 1 \text{ kcal/mol}$$

$$\Delta H_{298}^\circ = -223.0 \pm 1 \text{ kcal/mol}$$

$$\Delta H^\circ = [0.0] \text{ kcal/mol}$$

$$\Delta H_m^\circ = \text{Unknown}$$

$$\Delta H_{298}^\circ = 161 \text{ kcal/mol}$$

$$S_{298}^\circ = 11.93 \text{ gibbs/mol}$$

$$T_f = 918^\circ \text{K}$$

$$T_m = \text{Unknown}$$

Heat of Formation.

The value of ΔH_f° (anatase) is obtained from J. L. Margrave and B. D. Kybett, "Thermodynamic and Kinetic Studies of Borides and Other Refractory Materials at High Temperatures," Tech. Rept. AFML-TR-65-123, August 1965, Rice University, Houston, Texas. The authors measured the heat of fluorination of anatase, according to the reaction $\text{TiO}_2 (\text{anatase}) + 2\text{P}_2(\text{g}) = \text{TiP}_4(\text{c}) + \text{O}_2(\text{g})$, but no experimental data were given.

P. W. Vahldek, J. Less-Common Metals 11, 99 (1966), studied the irreversible anatase-rutile phase transition at pressures of 3.8 to 24 kbars and temperatures 20 to 1000°C. Isothermal phase-transition studies were also carried out at 1 bar pressure and 880-950°C. From the slope, dT/dP , the enthalpy differences between rutile and anatase were calculated to be -2.79 and -2.89 kcal/mol at 1183 and 1223°K, respectively. Using these data and $\Delta H_f^\circ(\text{rutile}) = -225.8$ kcal/mol, the value of $\Delta H_f^\circ(\text{anatase})$ is derived as -223.23 kcal/mol, which is in excellent agreement with the adopted value.

Heat Capacity and Entropy.

Low temperature heat capacities, 52-296°K, were measured by C. H. Shomate, J. Am. Chem. Soc. 59, 218 (1947). Enthalpy data were determined in the range 416-1305°K by B. P. Naylor, J. Am. Chem. Soc. 58, 1077 (1946), and in the range 580 - 1000°K by J. Lietz, Hamburger Beitr. Angew. Mineral. Kristallphysik 1, 229 (1956). High temperature heat capacities are derived from the enthalpy data, subject to the constraint that there be a smooth joint at 298°K. The resulting enthalpies are higher by 1 to 3% than those measured by Lietz and lower by 1 to 4% than those measured by Naylor. Values above 1300°K are smoothly extrapolated. S_{298}° is calculated from the low temperature C_p° using $S_{50}^\circ = 0.45 \text{ eu}$.

In view of the discrepancies in the enthalpy data, a review of the anatase samples is pertinent. Those of Shomate and Lietz were prepared by precipitation of the hydrated oxide and conversion to the oxide at 550 - 565°C. Shomate's starting material was high purity Ti and the product analyzed as 99.3% TiO₂. Lietz' starting material was high purity TiCl₄. Naylor's sample, obtained from J. T. Baker Co., was dried at 1050°C; spectrographic analysis indicated 0.3% SiO₂ and 0.15% CaO. All three samples gave only the X-ray lines of anatase.

Transition Data.

$T_m = 918^\circ \text{K}$ and $\Delta H^\circ = 0.040 \text{ kcal/mol}$ have been reported by J. Lietz, loc. cit. A. Schröder, Z. Krist. 55, 493 (1928), suggested a transition temperature at 915°K on the basis of a peak in the thermal expansion curve. Lietz reported $\Delta H^\circ = 0.04 \text{ kcal/mol}$, but this value is not adopted since its magnitude is much less than the uncertainty in the selected enthalpies. Further study is desirable to confirm this transition.

Heat of Sublimation.

ΔH_{298}° is calculated as the difference between ΔH_f° for TiO₂(g) and TiO₂(anatase).

T, °K	C _p ^a	gibbs/mol S°	-(C _p ^a - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0	∞	∞	∞	∞	∞	∞	INFINITE
100	4.430	2.438	21.438	-2.085	-224.638	-224.638	INFINITE
200	10.153	7.153	33.153	-1.900	-225.501	-225.501	483.450
298	13.153	12.031	12.031	∞	-225.600	-212.551	155.834
300	13.191	12.112	12.031	-0.024	-225.600	-212.511	154.814
400	14.621	16.126	12.569	1.423	-225.730	-208.089	113.694
500	15.429	18.481	13.625	2.928	-225.602	-203.692	69.034
600	15.931	22.346	14.846	4.500	-225.451	-199.325	72.404
700	16.438	26.845	16.099	6.122	-225.293	-194.983	60.876
800	16.924	27.066	17.334	7.785	-225.138	-190.665	52.087
900	17.173	29.068	18.528	9.485	-224.988	-186.364	45.255
1000	17.500	30.494	19.675	11.219	-224.845	-182.080	39.794
1100	17.813	32.577	20.772	12.985	-224.707	-177.810	35.328
1200	18.116	34.140	21.822	14.781	-224.581	-173.515	31.401
1300	18.412	35.601	22.826	16.604	-224.464	-169.191	28.444
1400	18.703	36.977	23.788	18.464	-224.352	-164.890	25.741
1500	18.990	38.277	24.711	20.348	-224.244	-160.606	23.400
1600	19.274	39.511	25.598	22.262	-224.140	-156.339	21.355
1700	19.556	40.688	26.451	24.203	-224.038	-152.091	19.553
1800	19.836	41.814	27.271	26.173	-223.938	-147.859	17.953
1900	20.115	42.884	28.066	28.170	-223.842	-143.642	16.523
2000	20.393	43.933	28.835	30.196	-223.749	-139.487	15.221
2100	20.670	44.934	29.578	32.249	-223.657	-135.297	14.036
2200	20.946	45.902	30.298	34.330	-223.568	-131.066	12.960
2300	21.221	46.840	30.997	36.434	-223.483	-126.804	11.940
2400	21.496	47.749	31.676	38.574	-223.402	-122.517	11.003
2500	21.771	48.632	32.337	40.737	-223.324	-118.207	10.258

Dec. 31, 1960; Mar. 31, 1967

$$\Delta H_{\text{f}}^{\circ} = -224.6 \pm 1 \text{ kcal/mol}$$
$$\Delta H_{\text{f}}^{\circ}{}_{298.15} = -225.8 \pm 1 \text{ kcal/mol}$$
$$\Delta H^{\circ} = [16] \text{ kcal/mol}$$
$$\Delta H_{\text{f}}^{\circ}{}_{298.15} = 163.8 \text{ kcal/mol}$$

Heat of Formation.

The heat of formation for rutile has been determined from combustion calorimetry by many investigators. Several of the more consistent $\Delta H_{\text{f}}^{\circ}{}_{298}$ values are listed in the table below. Ariys et al.³ reported that the composition of the rutile obtained from combustion of Ti(c) was between TiO_{1.94} and TiO_{1.95}. Emf studies by R. N. Blumenthal and D. H. Whitmore, *J. Electrochem. Soc.* **110**, 92 (1963), indicate that at 1200°K there is a two-phase region beginning at about TiO_{1.99}. If this region extends to 298°K, then the non-atmospheric combustion products probably involve a mixture of two phases. Meh et al.⁴ applied an approximate energy correction for incomplete combustion which corresponds to 0.7 - 1.5 kcal/mol. In $\Delta H_{\text{f}}^{\circ}{}_{298}$. Analogous corrections were applied by Ariys et al.³ but were not mentioned by Neumann et al.¹ and Humphrey.⁵

The $\Delta H_{\text{f}}^{\circ}{}_{298}$ value reported by Margrave and Kybett⁵ was obtained by fluorine bomb calorimetry, according to the reaction $\text{TiO}_2(\text{rutile}) + 2\text{F}_2(\text{g}) = \text{TiF}_4(\text{c}) + \text{O}_2(\text{g})$. No experimental data were given.

Comparison of the fluorine result with the oxygen results indicates that the magnitude of the corrections for the oxygen data is reasonable, probably within ± 1 kcal/mol, provided that the fluorine data refer to stoichiometric TiO₂. Corresponding $\Delta H_{\text{f}}^{\circ}$ corrections for TiO_{2-x} are of the same order of magnitude when estimated from the partial molar free energy values given by P. Kofstad, *J. Phys. Chem. Solids* **23**, 1579 (1962), and J. B. Meier, R. N. Blumenthal and D. H. Whitmore, *J. Am. Ceram. Soc.* **49**, 384 (1965).

The $\Delta H_{\text{f}}^{\circ}{}_{298}$ value determined by Meh et al.⁴ is adopted.

$\Delta H_{\text{f}}^{\circ}{}_{298}$, kcal/mol	Source
-225.5 ± 0.3	1. B. Neumann, C. Kröger and H. Kunz, <i>Z. Anorg. Allgem. Chem.</i> 218 , 379 (1934).
-225.3 ± 0.2	2. O. L. Humphrey, <i>J. Am. Chem. Soc.</i> 73 , 1587 (1951).
-224.9 ± 0.4	3. S. Ariys, M. Morozova, and E. Volf, <i>Z. Neorg. Khim.</i> 13 , 1 (1957).
-225.8 ± 0.1	4. A. Meh, K. K. Kelley, N. Gellert, E. O. King, and C. O'Brien, U. S. Bur. Mines R15316 (1957).
-225 ± 1	5. J. L. Margrave and B. D. Kybett, "Thermodynamic and Kinetic Studies of Borides and Other Refractory Materials at High Temperatures," Tech. Rept. APWL-TR-65-123, Aug. 1965, Rice University, Houston, Texas.

Heat Capacity and Entropy.

The low temperature heat capacities, 10 - 297.7°K, have been measured by the following investigators: P. H. Keenan and N. Pearlman, *Phys. Rev.* **112**, 800 (1958), 10 - 20°K; J. S. Dugdale, J. A. Morrison and D. Patterson, *Proc. Roy. Soc. (London)* **A224**, 228 (1954), 20 - 50°K; H. Shomate, *J. Am. Chem. Soc.* **69**, 218 (1947), 52.5 - 297.7°K; and H. J. McDonald and H. Seltz, *J. Am. Chem. Soc.* **61**, 2405 (1939), 68.78 - 295.0°K. The first three sets of Cp data are joined smoothly and extrapolated to 298°K, yielding $S^{\circ}_{298} = 12.03$ eu, based on $S^{\circ}_0 = 0.0014$ eu. The Cp values reported by McDonald and Seltz seem too high and are not used.

The high temperature enthalpies have been determined by B. P. Naylor, *J. Am. Chem. Soc.* **68**, 1077 (1946), 393.5 - 1746°K; J. S. Arthur, *J. Appl. Phys.* **21**, 732 (1950), 293.2 - 1073.2°K; and J. Lietz, *Hamburger Beiträge Angew. Mineral u. Kristall Phys.* **1**, 229 (1956), 577.7 - 1283.0°K. The Cp values are derived from the data of Lietz and join smoothly at 298°K with the low temperature data. Deviations from the selected values are -1.6 to +1.0% for Lietz, -5.1 to +4.0% for Arthur, and +8.6 to +0.8% for Naylor. The data point of Lietz at 947.95°K is omitted as a probable typographical error. The largest deviations in the case of Naylor and Arthur are near 400 and 500°K, respectively.

The mean specific enthalpies have also been measured by L. P. Nilson and O. Patterson, *Z. Physik, Chem.* **1**, 27 (1987), 373.2 - 717.2°K.

The samples used by Keenan and Pearlman, Dugdale et al., Shomate, Arthur and Lietz were of high purity, according to chemical and spectroscopic analysis. However, the sample employed by Naylor was black-colored and chemical analysis gave 97.9% TiO₂. The main impurities were: 0.55% ZrO₂, 0.50% SiO₂, 0.27% V₂O₅, 0.15% CaO, 0.15% Fe₂O₃ and 0.12% Al₂O₃. The sample of McDonald and Seltz was obtained commercially. Therefore the results reported by Naylor and McDonald et al. are given the least weight.

Melting Data.

See TiO₂(1) table for details.

Heat of Sublimation.

The difference between $\Delta H_{\text{f}}^{\circ}{}_{298}$ for TiO₂(g) and TiO₂(rutile) is $\Delta H_{\text{f}}^{\circ}{}_{298}$.

Titanium Dioxide (TiO₂)
(Liquid) GFW = 79.8988

O₂Ti

TITANIUM DIOXIDE (TiO₂) (LIQUID) OFW = 79.8988

$S_{298.15}^{\circ} = [18.934] \text{ gibbs/mol}$
 $\Delta H_m^{\circ} = [16] \text{ kcal/mol}$
 $T_m = 2143^{\circ} \text{K}$

$\Delta H_f^{\circ} 298.15 = [-210.726] \text{ kcal/mol}$

Heat of Formation.

The $\Delta H_f^{\circ} 298(1)$ is calculated from $\Delta H_f^{\circ} 298(\text{rutile})$, c) by adding ΔH_m° and the difference between $H_{2143}^{\circ} - H_{298.15}^{\circ}$ for TiO₂(rutile, c) and TiO₂(l).

Heat Capacity and Entropy.

The heat capacity of TiO₂(l) is estimated on the basis of 7.0 gibbs/g-atom. The value of S_{298}° is obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting point of TiO₂(rutile) has been measured by many investigators. Eleven pertinent T_m values were reviewed and corrected, according to the International Temperature Scale of 1948, by S. J. Schneider, Natl. Bur. Std. Monograph 68, October 10, 1963. The adopted melting point is obtained from G. Brauer and W. Litke, J. Inorg. Nucl. Chem. 16, 67 (1960). These authors found that TiO₂ loses oxygen on heating and the solid residue consists of a non-stoichiometric compound of the composition TiO_{2-x}. The value of the coefficient x depends on the temperature and on the oxygen pressure of the gaseous phase. Under oxygen pressures greater than or equal to 300 torr, the solid residue was TiO_{2.000} within the sensitivity of chemical analysis; however, color of the residue was a more sensitive indicator of composition. At pressures of 600 torr or greater, the residue was bright yellow rather than blue-gray and the melting point was constant at the maximum value of 2143 ± 15°K. This value is adopted.

The heat of melting is calculated using an estimated entropy of melting, $\Delta S_m^{\circ} = 2.5 \text{ eu/g-atom}$.

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o)/T	H ^o -H ₂₉₈ ^o	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0							
100							
200							
298	13.153	18.934	18.934	.000	-210.726	-199.577	186.294
300							
300	13.151	19.015	18.934	.928	-210.726	-199.607	195.301
300	13.151	19.015	18.934	1.928	-210.726	-199.776	196.947
400	15.459	20.526	20.526	2.028	-210.528	-192.070	83.954
500							
600	15.991	29.249	21.749	4.500	-210.377	-186.393	68.622
700	16.438	31.748	23.002	7.122	-210.219	-184.741	56.679
800	16.824	33.724	24.439	9.685	-210.061	-183.089	46.679
900	17.173	35.491	25.631	11.219	-209.914	-181.503	38.108
1000	17.500	37.797	26.578		-209.771	-179.909	36.008
1100	17.813	39.480	27.675	12.995	-209.633	-179.329	33.681
1200	18.116	41.043	28.755	14.781	-210.437	-166.724	30.365
1300	18.412	42.584	29.729	16.608	-210.511	-153.081	24.896
1400	18.700	44.004	30.604	18.484	-210.584	-139.404	18.714
1500	19.000	45.328	31.419	20.364	-209.454	-155.493	22.714
1600	21.000	46.684	32.519	22.664	-208.974	-152.339	20.609
1700	21.000	47.937	33.300	24.764	-208.739	-148.813	19.131
1800	21.000	49.157	34.033	26.664	-208.753	-145.432	17.415
1900	21.000	50.343	34.719	28.364	-208.753	-142.247	15.104
2000	21.000	51.370	35.838	31.064	-211.853	-138.219	
2100	21.000	52.394	36.602	33.164	-211.508	-134.543	14.002
2200	21.000	53.371	37.342	35.264	-211.170	-130.888	13.003
2300	21.000	54.308	38.060	37.364	-210.806	-127.247	12.007
2400	21.000	55.206	39.430	41.564	-210.186	-120.006	10.491
2500	21.000	56.056					
2600	21.000	56.879	40.086	43.664	-209.668	-116.404	9.785
2700	21.000	57.672	40.722	45.764	-209.556	-112.815	9.132
2800	21.000	58.443	41.364	47.864	-209.444	-109.247	8.489
2900	21.000	59.193	41.944	49.964	-209.347	-105.670	7.963
3000	21.000	59.884	42.530	52.064	-209.650	-102.111	7.439
3100	21.000	60.573	43.101	54.164	-208.357	-98.565	6.949
3200	21.000	61.240	43.657	56.264	-208.069	-95.033	6.490
3300	21.000	61.896	44.200	58.364	-207.505	-91.503	6.055
3400	21.000	62.542	44.742	60.464	-207.230	-88.475	5.625
3500	21.000	63.122	45.264	62.564			
3600	21.000	63.713	45.751	64.664	-308.584	-80.704	4.899
3700	21.000	64.289	46.284	66.764	-308.288	-74.382	4.394
3800	21.000	64.834	46.794	68.864	-307.994	-68.064	3.894
3900	21.000	65.354	47.284	70.964	-307.704	-61.742	3.400
4000	21.000	65.926	47.660	73.064	-307.497	-55.449	3.030
4100	21.000	66.444	48.112	75.164	-307.266	-49.147	2.620
4200	21.000	66.950	48.584	77.264	-307.049	-42.837	2.230
4300	21.000	67.457	49.054	79.364	-306.859	-36.521	1.854
4400	21.000	67.954	49.524	81.464	-306.684	-30.204	1.484
4500	21.000	68.359	49.830	83.564	-306.484	-24.006	1.166
4600	21.000	68.661	50.238	85.664	-306.321	-17.727	.842
4700	21.000	68.932	50.639	87.764	-306.171	-11.453	.533
4800	21.000	69.198	51.044	89.864	-306.002	-5.176	.268
4900	21.000	69.454	51.454	91.964	-305.802	1.076	.068
5000	21.000	70.612	51.759	94.064	-305.786	7.339	.321

O₂Ti

Titanium Dioxide (TiO₂)
(Ideal Gas) GFW = 79.8988

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0	-0.000	INFINITE	INFINITE	-2.597	-61.370	-61.370	INFINITE
100	7.760	46.055	46.055	-1.885	-61.406	-61.406	134.966
200	9.634	52.065	52.065	-1.007	-61.762	-61.762	67.661
298	10.636	56.146	56.146	-	-62.000	-62.000	45.407
300	10.656	56.213	56.213	.020	-62.004	-61.945	45.407
400	11.520	59.474	59.474	3.326	-62.197	-61.895	33.618
500	12.588	62.194	62.194	2.734	-62.354	-61.801	27.013
600	13.079	64.531	64.531	3.359	-62.492	-61.677	22.466
700	13.064	66.578	66.578	4.053	-62.615	-61.535	18.744
800	13.746	68.395	68.395	6.345	-62.775	-61.365	16.744
900	13.957	70.027	70.027	7.734	-62.939	-61.179	14.856
1000	14.117	71.506	71.506	9.139	-63.126	-60.973	13.326
1100	14.241	72.856	72.856	10.556	-63.336	-60.744	12.069
1200	14.337	74.094	74.094	12.000	-63.564	-60.488	11.017
1300	14.417	75.252	75.252	13.423	-63.810	-60.122	10.107
1400	14.480	76.323	76.323	14.869	-64.078	-59.770	9.331
1500	14.532	77.324	77.324	16.319	-64.363	-59.406	8.655
1600	14.575	78.263	78.263	17.774	-64.638	-59.029	8.063
1700	14.611	79.144	79.144	19.244	-64.924	-58.642	7.542
1800	14.641	79.984	79.984	20.694	-65.215	-58.242	7.071
1900	14.667	80.776	80.776	22.162	-65.513	-57.827	6.652
2000	14.690	81.529	81.529	23.630	-65.817	-57.395	6.255
2100	14.709	82.246	82.246	25.099	-66.127	-56.947	5.887
2200	14.724	82.924	82.924	26.554	-66.442	-56.484	5.547
2300	14.736	83.566	83.566	28.000	-66.763	-56.009	5.224
2400	14.744	84.173	84.173	29.439	-67.089	-55.524	4.919
2500	14.749	84.744	84.744	30.869	-67.420	-55.030	4.630
2600	14.751	85.285	85.285	32.282	-67.756	-54.527	4.356
2700	14.750	85.793	85.793	33.679	-68.100	-54.015	4.095
2800	14.747	86.267	86.267	35.059	-68.450	-53.495	3.847
2900	14.740	86.707	86.707	36.426	-68.806	-52.968	3.613
3000	14.507	87.112	87.112	37.781	-69.169	-52.435	3.394
3100	14.536	87.487	87.487	39.126	-69.539	-51.897	3.190
3200	14.564	87.832	87.832	40.452	-69.915	-51.354	2.999
3300	14.592	88.146	88.146	41.760	-70.297	-50.806	2.820
3400	14.532	89.366	89.366	43.051	-70.684	-50.252	2.654
3500	14.532	89.766	89.766	44.317	-71.076	-49.694	2.500
3600	14.536	90.241	90.241	45.560	-71.474	-49.133	2.356
3700	14.540	90.681	90.681	46.781	-71.877	-48.567	2.221
3800	14.543	91.087	91.087	47.983	-72.285	-47.996	2.094
3900	14.543	91.462	91.462	49.163	-72.697	-47.420	1.975
4000	14.549	91.778	91.778	50.320	-73.114	-46.839	1.863
4100	14.552	92.115	92.115	51.456	-73.536	-46.254	1.756
4200	14.556	92.473	92.473	52.574	-73.963	-45.665	1.654
4300	14.556	92.852	92.852	53.679	-74.395	-45.072	1.556
4400	14.558	93.194	93.194	54.768	-74.832	-44.475	1.462
4500	14.560	93.528	93.528	55.844	-75.274	-43.874	1.371
4600	14.562	93.854	93.854	56.900	-75.721	-43.269	1.282
4700	14.564	94.174	94.174	57.938	-76.172	-42.660	1.195
4800	14.566	94.487	94.487	58.960	-76.627	-42.047	1.110
4900	14.567	94.794	94.794	59.967	-77.086	-41.431	1.026
5000	14.569	95.094	95.094	60.960	-77.549	-40.811	0.943
5100	14.570	95.388	95.388	61.938	-78.016	-40.187	0.861
5200	14.571	95.677	95.677	62.902	-78.487	-39.560	0.780
5300	14.572	95.960	95.960	63.852	-78.961	-38.931	0.700
5400	14.574	96.238	96.238	64.789	-79.438	-38.300	0.620
5500	14.575	96.511	96.511	65.714	-79.918	-37.667	0.540
5600	14.576	96.779	96.779	66.626	-80.399	-37.032	0.460
5700	14.577	97.043	97.043	67.526	-80.882	-36.395	0.380
5800	14.578	97.301	97.301	68.412	-81.367	-35.756	0.300
5900	14.578	97.556	97.556	69.285	-81.853	-35.113	0.220
6000	14.579	97.806	97.806	70.145	-82.341	-34.467	0.140

Dec. 31, 1960; Mar. 31, 1967

TITANIUM DIOXIDE (TiO₂) (IDEAL GAS)

OPW = 79.8988

Point Group [D_{2h}]

S_{298.15} = [56] gibbs/mol

ΔH_f⁰ = 61.4 ± 10 kcal/mol

Round State Quantum Weight = [1]

ΔH_f⁰ = -62.0 ± 10 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	
940 (1)	
[328] (2)	
[1214] (1)	

Bond Distances: Ti-O = [1.62] Å

Bond Angle: O-Ti-O = [180]°

Rotational Constant: B₀ = [0.2007] cm⁻¹

o = 2

Heat of Formation.

P. W. Gilles, K. D. Carlson, H. F. Frenzen, and P. O. Wahlbeck, *J. Chem. Phys.* **45**, 2461 (1967), studied the vaporization behavior of the titanium-oxygen system and found that Ti₃O₅ is the final residue of both higher and lower titanium oxides; hence Ti₃O₅ is the congruently vaporizing phase. This conclusion was obtained by measurement of the change in composition of the solid residue accompanying vaporization as determined by x-ray diffraction, chemical analysis, and color of sample.

From mass spectrometric studies over Ti₃O₅(s) near 2000°K, P. O. Wahlbeck and P. W. Gilles, *J. Chem. Phys.* **45**, 2465 (1967), concluded that the partial pressure of TiO₂ is probably less than 1% of the pressure of TiO produced by the main vaporization: Ti₃O₅(s) = 3 TiO(g) + 2 O(g). This yields ΔH_f⁰2000 ≥ 228 kcal for the reaction Ti₃O₅(s) = 2 TiO₂(g) + TiO(g) and ΔH_f⁰298(TiO₂, g) ≥ -62 kcal/mol, which is the value adopted. The corresponding atomization energy is D₀ ≤ 292 kcal/mol.

Earlier vaporization studies over TiO₂-x gave apparent heats of formation which are more negative by 20-35 kcal; however, the results appear to be uncertain due to lack of sufficient auxiliary data for the oxygen-deficient condensed phase. Knudsen effusion-mass spectrometric studies of J. Berkowitz, W. A. Chupka and M. O. Inghram, *J. Phys. Chem.* **61**, 1569 (1957), revealed the initial evolution of large amounts of MoO₃(g), suggesting that the reduction of TiO₂ is enhanced by the Mo cell. In order to reduce the effect of the initial high rate of evaporation, W. O. Groves, M. Hoch and H. L. Johnston, *J. Phys. Chem.* **59**, 127 (1955), conducted their Knudsen effusion-weight loss studies on TiO₂. Preferential loss of oxygen during the experiment, as indicated by a residue of TiO_{1.85}, was apparently ignored. Groves et al. estimated the activity of TiO₂(rutile) as 0.53; Berkowitz et al. assumed unit activity but did not indicate the composition of their condensed phase. These activities may be in serious error due to the presence of a series of distinct phases between TiO_{1.8} and TiO₂ [cf. S. Anderson, *Acta Chem. Scand.* **14**, 1161 (1960)] and to the possible existence of a two phase region near TiO_{1.99} [cf. R. N. Blumenthal and D. H. Whitmore, *J. Electrochem. Soc.* **110**, 82 (1963)]. Second and third law analyses of the data, using the authors' original assumptions, are summarized below. No weight is given to these results.

Investigator	Temperature, °K	No. of Points	ΔH _f ⁰ 298 kcal/mol	Drift eu
Oroven et al.	1849 - 2010	14	128.7 ± 7.5	1.1 ± 4.0
Berkowitz et al.	1891	3	142.7 ± 5**	142.8
				-85.7
				-83.0

*Calculation based on the third law ΔH_f⁰298.

**Obtained from the temperature variation experiments, reported in the original paper.

Heat Capacity and Entropy.

The molecular structure is assumed to be linear. The Ti-O bond distance is estimated as the same as that in TiO(g). The vibrational frequency 940 cm⁻¹ was observed in matrix isolation by W. Weltner, Jr., and D. McLeod, Jr., *J. Phys. Chem.* **69**, 3488 (1965). The other two frequencies are calculated, based on the valence bond method as suggested by Berkowitz, Chupka and Inghram, loc. cit. The moment of inertia is 1.3944 x 10⁻³⁸ g cm².

O₂Ti

Tungsten Dioxide (WO₂)

(Crystal) GFW = 215.8488

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	4.566	2.388	21.558	-2.081	-139.757	-139.757	INFINITE
200	10.089	7.384	13.204	-1.917	-140.462	-136.319	297.925
298	13.322	12.077	12.077	-1.164	-140.869	-131.987	144.229
				∞	-140.940	-127.603	93.535
300	13.340	12.159	12.077	-1.026	-140.939	-127.520	92.989
400	15.160	16.269	15.075	-1.57	-140.807	-123.053	67.239
500	16.290	18.781	13.713	-3.034	-140.562	-118.654	51.864
600	17.042	22.821	14.884	-4.702	-140.260	-114.300	41.634
700	17.596	25.492	15.298	-6.435	-139.926	-109.999	34.343
800	18.000	27.644	15.654	-8.244	-139.569	-105.744	28.658
900	18.398	30.017	16.861	-10.040	-139.208	-101.542	24.268
1000	18.684	31.971	20.076	-11.895	-138.834	-97.376	21.281
1100	18.911	33.763	21.240	-13.775	-138.457	-93.250	18.227
1200	19.153	35.377	22.353	-15.656	-138.079	-89.156	16.237
1300	19.355	36.854	23.417	-17.536	-137.698	-85.094	14.287
1400	19.530	38.406	24.437	-19.546	-137.302	-81.063	12.255
1500	20.340	39.792	25.415	-21.566	-136.872	-77.059	11.228
1600	21.040	41.128	26.356	-23.636	-136.398	-73.088	9.883
1700	21.760	42.425	27.263	-25.766	-135.871	-69.146	8.889
1800	22.485	44.016	28.091	-27.966	-135.296	-65.233	7.854
2000	23.270	46.108	29.817	-32.580	-134.611	-57.523	6.286
2100	23.900	47.263	30.621	-34.949	-133.924	-53.713	5.590
2200	24.740	48.775	31.403	-37.803	-133.132	-49.970	4.901
2300	25.470	50.277	32.163	-40.675	-132.247	-46.292	4.212
2400	25.150	50.537	32.909	-42.307	-131.117	-42.489	3.869
2500	25.560	51.572	33.634	-44.843	-130.333	-38.816	3.393
2600	25.960	52.582	34.344	-47.419	-129.526	-35.169	2.956
2700	26.360	53.569	35.038	-50.035	-128.694	-31.553	2.554
2800	26.760	54.534	35.722	-52.696	-127.842	-27.972	2.184
2900	27.120	55.481	36.382	-55.386	-127.022	-24.420	1.840
3000	27.510	56.406	37.034	-58.117	-126.200	-20.894	1.522

TUNGSTEN DIOXIDE (WO₂)

(CRYSTAL)

OPW = 215.8488

$\Delta H_f^\circ = -139.76 \pm 0.21$ kcal/mol
 $\Delta H_f^{298.15} = -140.94 \pm 0.21$ kcal/mol
 $\Delta H_f^{298.15} = -140.94 \pm 0.21$ kcal/mol
 $\Delta H_f^{298.15} = 159.24$ kcal/mol
 $T_d = 1997^\circ K$
 $S_{298.15}^\circ = 12.08 \pm 0.07$ gibbs/mol
 $T_d = 1997^\circ K$

Heat of Formation.

The adopted heat of formation, -140.94 ± 0.21 kcal/mol, was determined by combustion calorimetry by A. D. Mah, J. Am. Chem. Soc. **81**, 1582 (1959). R. C. Griffiths, J. Electrochem. Soc. **105**, 398 (1958), has measured the heat of combustion to WO₃(c) which yields $\Delta H_f^{298}(\text{WO}_3, c) = -139.8 \pm 1.5$ kcal/mol when recalculated with $\Delta H_f^{298}(\text{WO}_3, c) = -201.46$ kcal/mol. This result is less certain because of the incomplete characterization of the final products.

Recent equilibrium data yield essentially the same average of the heat of formation by the third law method. The results are presented as follows.

Author	Reaction*	Temp. (°K)	No. of Points	ΔH ²⁹⁸ (kcal/mol)	Drift (eu)	ΔH ²⁹⁸ (kcal/mol)
1. St. Pierre (1962) et al.	A	1275 - 1497	10	2.672	0.036	-140.62
	B	973 - 1467	6	11.994	12.076	-139.58
2. Gerasimov (1962) et al.	C	923 - 1223	7	-70.281	-67.943	-140.56
3. Vasil'eva (1960) et al.	B	1075 - 1210	5	12.949	13.051	-141.49
4. Griffiths (1959)	B	873 - 1273	30	12.550	10.295	-140.70
*Reaction	A:	1/2 WO ₂ (c) + CO(g) = 1/2 W(c) + CO ₂ (g)				
	B:	1/2 WO ₂ (c) + H ₂ (g) = 1/2 W(c) + H ₂ O(g)				
	C:	1/2 W(c) + 1/2 O ₂ (g) = 1/2 WO ₂ (c)				

- Reference 1. G. R. St. Pierre, W. T. Ebiyara, M. J. Pool and R. Speiser, Trans. AIME **224**, 259 (1962).
 2. Ya. I. Gerasimov, I. A. Vasil'eva, T. P. Chuasova, V. W. Ociderikh, and M. A. Timofeeva, Zh. Fiz. Khim. **36**, 358 (1962).
 3. I. A. Vasil'eva, Ya. I. Gerasimov and Yu. P. Smanov, Zh. Fiz. Khim. **34**, 1811 (1960).
 4. R. C. Griffiths, J. Electrochem. Soc. **106**, 418 (1959).

Heat Capacity and Entropy.

E. G. King, W. W. Weller, and A. U. Christensen, U. S. Bur. Mines RI 5664, (1960), have measured the low temperature heat capacities from 53° to 297°K and high temperature enthalpy changes from 398° to 1800°K by drop calorimetry. The low temperature and high temperature heat capacities were joined smoothly at 298.15°K. The entropy was obtained from the heat capacities based on $S_{298.15}^\circ = 0.52$ eu. It is possible that at temperatures below 50°K the entropy due to the uncoupling of the d² electrons will appear, contributing an additional 2.2 eu.

Temperature of Decomposition.

Tungsten dioxide (c) has no melting point, since disproportionation occurs to yield W(c) and WO₃(l) before melting starts. The Td is calculated as the temperature at which ΔG equals zero for $3 \text{ WO}_2(c) = 2 \text{ WO}_3(l) + \text{W}(c)$.

Heat of Sublimation.

The heat of sublimation was calculated from the difference between the heats of formation of WO₂(g) and WO₃(c).

Tungsten Dioxide (WO₂)

(Ideal Gas) GFW = 215.8488

T, °K	C _p ^o	S ^o	-(C _p ^o -H ^o)/T	H ^o -H ^o ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	0.000	INFINITE	-	2.688	18.876	18.876	INFINITE
100	6.400	58.00	76.944	-1.581	17.309	-35.025	
200	8.508	60.23	76.944	-1.581	16.853	-35.025	
298	10.471	68.209	68.209	0.000	14.901	-10.923	
300	10.489	68.274	68.209	0.019	18.205	-10.840	
400	11.355	71.415	68.631	1.113	17.774	-7.526	
500	11.999	74.022	69.456	2.483	17.497	-5.557	
600	12.454	76.252	70.407	3.507	17.785	-4.257	
700	12.776	78.197	71.384	4.769	17.648	-3.335	
800	13.006	79.919	72.345	6.059	17.507	-2.648	
900	13.176	81.461	73.274	7.368	17.360	-2.119	
1000	13.303	82.856	74.164	8.693	17.204	-1.700	
1100	13.401	84.129	75.013	10.028	17.036	-1.359	
1200	13.477	85.299	75.822	11.372	16.857	-1.078	
1300	13.538	86.380	76.593	12.723	16.665	-0.844	
1400	13.587	87.385	77.328	14.079	16.460	-0.645	
1500	13.627	88.324	78.030	15.440	16.242	-0.474	
1600	13.660	89.204	78.701	16.805	16.011	-0.328	
1700	13.688	90.033	79.344	18.172	15.765	-0.200	
1800	13.711	90.816	79.960	19.542	15.504	-0.088	
1900	13.731	91.558	80.551	20.914	15.228	-0.010	
2000	13.748	92.263	81.119	22.288	14.937	0.085	
2100	13.763	92.934	81.666	23.664	14.631	0.174	
2200	13.776	93.575	82.193	25.041	14.307	0.242	
2300	13.787	94.187	82.701	26.419	13.969	0.303	
2400	13.797	94.774	83.192	27.798	13.614	0.358	
2500	13.806	95.338	83.666	29.178	13.242	0.407	
2600	13.815	95.879	84.126	30.559	12.855	0.451	
2700	13.822	96.401	84.571	31.941	12.446	0.490	
2800	13.829	96.904	85.002	33.324	12.007	0.525	
2900	13.836	97.389	85.421	34.707	11.527	0.557	
3000	13.843	97.858	85.828	36.091	11.002	0.585	
3100	13.850	98.312	86.223	37.476	10.421	0.611	
3200	13.857	98.752	86.608	38.861	9.776	0.633	
3300	13.864	99.179	86.983	40.247	9.062	0.653	
3400	13.872	99.593	87.347	41.634	8.269	0.669	
3500	13.880	99.995	87.703	43.021	7.385	0.684	
3600	13.890	100.386	88.050	44.410	6.385	0.696	
3700	13.900	100.767	88.389	45.794	5.306	0.703	
3800	13.910	101.138	88.719	47.180	4.064	0.697	
3900	13.922	101.499	89.042	48.561	2.708	0.682	
4000	13.935	101.852	89.358	49.934	1.250	0.666	
4100	13.950	102.196	89.667	51.309	0.684	0.680	
4200	13.965	102.532	89.969	52.684	0.000	0.673	
4300	13.982	102.861	90.265	54.062	-0.788	0.667	
4400	13.999	103.183	90.555	55.442	-1.581	0.660	
4500	14.020	103.498	90.839	56.826	-2.372	0.653	
4600	14.041	103.806	91.118	58.209	-3.163	0.645	
4700	14.064	104.108	91.391	59.591	-3.954	0.638	
4800	14.088	104.405	91.659	60.974	-4.745	0.630	
4900	14.113	104.695	91.922	62.358	-5.536	0.623	
5000	14.140	104.981	92.181	63.741	-6.327	0.615	
5100	14.168	105.261	92.434	65.124	-7.118	0.607	
5200	14.198	105.536	92.684	66.507	-7.909	0.599	
5300	14.228	105.807	92.929	67.890	-8.700	0.591	
5400	14.260	106.073	93.170	69.273	-9.491	0.583	
5500	14.294	106.335	93.407	70.656	-10.282	0.575	
5600	14.328	106.593	93.640	72.039	-11.073	0.567	
5700	14.363	106.847	93.869	73.422	-11.864	0.559	
5800	14.400	107.097	94.095	74.805	-12.655	0.551	
5900	14.438	107.344	94.316	76.188	-13.446	0.543	
6000	14.475	107.587	94.537	77.571	-14.237	0.535	

June 30, 1962; Sept. 30, 1968

TUNGSTEN DIOXIDE (WO₂)

(IDEAL GAS)

OPW = 215.8488

Point Group { C_{2v} }

S_{298.15}^o = [68.2] gibbs/mol

Ground State Quantum Weight = [3]

ΔH_f^o = 18.9 ± 7 kcal/mol

ΔH_f^o_{298.15} = 18.3 ± 7 kcal/mol

Electronic Levels and Quantum Weights

ε, cm ⁻¹	g _i
0	[3]
[25,000]	[10]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O = [110°]

Product of the Moments of Inertia: I_AI_BI_C = [9.433 x 10⁻¹¹⁵] g³cm⁶

σ = [2]

Heat of Formation

G. DeMaris, R. F. Burns, J. Dromart and M. O. Inghram, J. Chem. Phys. **32**, 1373 (1960), have reported the partial pressures of WO₂(g), WO₃(g) and O(g) in a mass spectrometric study of aluminum oxide vaporized from a tungsten cell from 2188° to 2475°K. The adopted value, ΔH_f^o₂₉₈ (WO₂g) = 18.3 ± 7 kcal/mol, was calculated from ΔH_f^o₂₉₈ = -100.9 kcal/mol for W(c) + 2 O(g) → WO₂(g), which was obtained from third law treatment of their partial pressure data, using all JANAF functions. The third law drift is 15.0 ± 5.2 eu. Partial pressures of WO₂(g), WO₃(g) and O(g) at 2242°K have also been reported by W. A. Chupka, J. Berkowitz and C. F. Olene, J. Chem. Phys. **30**, 827 (1959), in a mass spectrometric study of beryllium oxide in a tungsten cell. Similar calculation gives ΔH_f^o₂₉₈ = -105.9 kcal/mol, which yields ΔH_f^o₂₉₈ (WO₂g) = 13.2 kcal/mol.

Heat Capacity and Entropy

The WO₂(g) was assumed to have a C_{2v} symmetry with a bond angle O-W-O = 110°. The bond distance W-O was estimated to be the same as that in WO(g). The asymmetric and asymmetric stretching frequencies were obtained from the infrared spectrum of WO₂ in an inert matrix by W. Weltner, Jr., and D. McLeod, Jr., J. Mol. Spectry. **11**, 276 (1965). The bending vibrational frequency (300 cm⁻¹) was estimated by comparison with other dioxides. The electronic levels and quantum weights were estimated from W⁴⁺ ion by analogy with Mo⁴⁺ ion. The three principal moments of inertia are: I_A = 4.8776 x 10⁻³⁹, I_B = 1.1680 x 10⁻³⁸ and I_C = 1.6559 x 10⁻³⁸ g cm².

Zirconium Dioxide (ZrO₂)

Mol. Wt. = 123.2188

(Crystal) (CRYSTAL)

MOL. WT. = 123.2188

O₂Zr

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	INFINITE	-2.091	-260.999	-260.999	INFINITE
100	4.524	21.604	2.268	-1.934	-257.504	-257.504	562.748
200	10.224	13.301	1.174	-1.174	-262.210	-262.210	276.490
298	13.436	12.036	0.000	-0.000	-262.500	-262.500	182.148
300	13.447	12.036	-0.025	-262.299	-248.416	-248.416	180.962
400	15.260	16.268	12.590	1.471	-243.802	-243.802	133.201
500	16.196	19.782	13.686	3.048	-262.024	-239.821	104.558
600	16.787	22.791	14.959	4.699	-261.832	-234.678	95.477
700	17.155	25.733	15.560	6.139	-261.631	-225.687	86.156
800	17.445	28.618	16.408	8.139	-261.431	-216.798	77.652
900	17.685	31.449	17.424	10.005	-261.231	-207.909	69.720
1000	18.104	34.249	18.529	11.707	-261.033	-200.059	62.816
1100	18.342	36.949	19.613	13.242	-260.790	-192.249	56.816
1200	18.581	39.549	20.662	14.614	-260.550	-184.466	51.715
1300	18.781	42.049	21.662	15.830	-260.310	-176.715	47.415
1400	18.949	44.449	22.613	16.900	-260.069	-169.000	43.815
1500	19.089	46.749	23.513	17.830	-259.829	-161.315	40.815
1600	19.200	48.949	24.363	18.630	-259.589	-153.660	38.315
1700	19.289	51.049	25.163	19.300	-259.349	-146.040	35.815
1800	19.355	53.049	25.913	19.850	-259.109	-138.460	33.315
1900	19.400	54.949	26.613	20.280	-258.869	-130.910	30.815
2000	19.430	56.749	27.263	20.600	-258.629	-123.390	28.315
2100	19.445	58.449	27.863	20.810	-258.389	-115.910	25.815
2200	19.449	60.049	28.413	20.910	-258.149	-108.460	23.315
2300	19.440	61.549	28.913	20.900	-257.909	-101.040	20.815
2400	19.419	62.949	29.363	20.850	-257.669	-93.660	18.315
2500	19.379	64.249	29.763	20.660	-257.429	-86.310	15.815
2600	19.319	65.449	30.113	20.330	-257.189	-78.990	13.315
2700	19.239	66.549	30.413	19.860	-256.949	-71.710	10.815
2800	19.139	67.549	30.663	19.250	-256.709	-64.460	8.315
2900	19.019	68.449	30.863	18.500	-256.469	-57.240	5.815
3000	18.879	69.249	31.013	17.610	-256.229	-50.060	3.315
3100	18.719	69.949	31.113	16.500	-255.989	-42.910	0.815
3200	18.539	70.549	31.163	15.270	-255.749	-35.790	-1.685
3300	18.339	71.049	31.163	13.940	-255.509	-28.710	-3.185
3400	18.119	71.449	31.113	12.510	-255.269	-21.660	-4.685
3500	17.879	71.749	31.013	10.980	-255.029	-14.640	-6.185
3600	17.619	71.949	30.863	9.350	-254.789	-7.660	-7.685
3700	17.339	72.049	30.663	7.610	-254.549	-0.710	-9.185
3800	17.039	72.049	30.413	5.760	-254.309	6.240	-10.685
3900	16.719	71.849	30.113	3.810	-254.069	13.260	-12.185
4000	16.379	71.449	29.763	1.760	-253.829	20.310	-13.685

$$\Delta H_f^0 = -261.0 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = -262.3 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 1.42 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [20.8] \text{ kcal. mole}^{-1}$$

Heat of Formation.

The ΔH_f^0 298.15 = -263.1 ± 0.5 kcal. mole⁻¹ is the average value of the ΔH_f^0 298.15 = -261.5 ± 0.2 kcal. mole⁻¹ and ΔH_f^0 298.15 = -263.1 ± 0.5 kcal. mole⁻¹ measured (by combustion calorimetry) by O. L. Humphrey, J. Am. Chem. Soc. 76, 978 (1954) and E. J. Huber, Jr., E. L. Head and C. E. Holley, Jr., J. Phys. Chem. 68, 3040 (1964) respectively. Also the heat of formation was measured calorimetrically by B. Neumann, C. Kröger and H. Kunz, Z. anorg. Chem. 218, 379 (1934), by W. A. Roth, E. Bödger, and H. Siemensen, ibid., 239, 321 (1938) and by A. Sievert, A. Gotta and S. Halberstadt, ibid., 187, 155 (1930) and was found -259.2, -259.8 and -256.1 kcal. mole⁻¹ respectively. However more weight was given to the Humphrey and Huber values.

Heat Capacity and Entropy.

The low temperature heat capacities, 54.3-295°K., were measured by K. K. Kelley, Ind. Eng. Chem. 36, 377 (1944). The heat capacities in the temperature range 298-1478°K. were calculated by using the J. P. Coughlin and E. O. King equation $C_p = 16.64 + 1.80 \times 10^{-3}T + 3.36 \times 10^{-5}T^2$ obtained from their measured enthalpy data in the range 396.8 - 1841°K., J. Am. Chem. Soc. 72, 2252 (1950). The values from the two sources join smoothly at 298°K. Above the transition 1478°K. the heat capacity was taken as constant at 17.80 cal. mole⁻¹ deg⁻¹, Coughlin and King, loc. cit. The entropy was calculated at 54.30 using the Debye and Einstein Function $D(\frac{345}{T}) + E(\frac{513}{T})$ given by Kelley, loc. cit. The value of $S_{54.3}^0 = 0.5507$ cal. deg⁻¹ mole⁻¹.

Transition Data.

T_t and ΔH_t^0 were taken from Coughlin and King loc. cit.

Melting Data.

The T_m and ΔH_m^0 were taken from Natl. Bur. Standards Circ. 500 Washington (1952).

O₂Zr

Zirconium Dioxide (ZrO₂)

(Liquid) Mol. Wt. = 123.2188

O₂Zr

MOL. WT. = 123.2188

ZIRCONIUM DIOXIDE (ZrO₂) (LIQUID)

$$\Delta H_f^{298.15} = -17.641 \text{ kcal. deg.}^{-1}$$

$$\Delta H_m^{298.15} = -244.55 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = [20.8] \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{298.15} = [149.2] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{298.15} = -17.641 \text{ cal. deg.}^{-1}$$

$$T_m = 2950^\circ \text{K.}$$

$$T_b = 4548^\circ \text{K.}$$

Heat of Formation

The $\Delta H_f^{298.15}$ (1) was obtained from $\Delta H_f^{298.15}$ (c) by adding $\Delta H_m^{298.15}$ and the difference between $H_m^{298.15}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition was assumed at 2000°K. The heat capacity below 2000°K. was obtained from the heat capacity of the crystal. Above 2000°K. the heat capacity was assumed constant and estimated to be 21.0 cal. deg.⁻¹ mole⁻¹ or 7 cal. deg.⁻¹ per g-atom as suggested by O. Kubachewski and E. L. Evans, "Metallurgical Thermochemistry" Pergamon Press, New York (1958). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data

See ZrO₂(c) table.

Vaporization Data

T_b was calculated as the temperature at which the free energy change of the reaction $\text{ZrO}_2(l) \rightarrow \text{ZrO}_2(g)$ approaches zero. The difference between $\Delta H_f^{298.15}$ for $\text{ZrO}_2(g)$ and $\text{ZrO}_2(l)$ is $\Delta H_v^{298.15}$.

O₂Zr

June 30, 1961; Dec. 31, 1965

T, °K.	C _p	S°	$-(F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _p
0						
100	13.430	17.841	17.841	0.000	-232.463	170.406
200	13.447	17.924	17.841	0.075	-232.408	169.301
298	13.460	18.000	17.841	0.147	-232.373	126.771
300	13.461	18.001	17.841	0.148	-232.373	98.069
400	13.478	18.067	17.841	0.299	-232.276	80.281
500	13.495	18.123	17.841	0.449	-232.180	64.585
600	13.512	18.179	17.841	0.600	-232.084	50.678
700	13.529	18.235	17.841	0.750	-231.988	44.769
800	13.546	18.291	17.841	0.900	-231.892	39.948
900	13.563	18.347	17.841	1.050	-231.796	35.207
1000	13.580	18.403	17.841	1.200	-231.700	30.547
1100	13.597	18.459	17.841	1.350	-231.604	25.967
1200	13.614	18.515	17.841	1.500	-231.508	21.467
1300	13.631	18.571	17.841	1.650	-231.412	17.047
1400	13.648	18.627	17.841	1.800	-231.316	12.707
1500	13.665	18.683	17.841	1.950	-231.220	8.447
1600	13.682	18.739	17.841	2.100	-231.124	4.267
1700	13.699	18.795	17.841	2.250	-231.028	0.167
1800	13.716	18.851	17.841	2.400	-230.932	-4.043
1900	13.733	18.907	17.841	2.550	-230.836	-9.243
2000	13.750	18.963	17.841	2.700	-230.740	-14.443
2100	13.767	19.019	17.841	2.850	-230.644	-19.643
2200	13.784	19.075	17.841	3.000	-230.548	-24.843
2300	13.801	19.131	17.841	3.150	-230.452	-29.943
2400	13.818	19.187	17.841	3.300	-230.356	-35.043
2500	13.835	19.243	17.841	3.450	-230.260	-40.143
2600	13.852	19.299	17.841	3.600	-230.164	-45.243
2700	13.869	19.355	17.841	3.750	-230.068	-50.343
2800	13.886	19.411	17.841	3.900	-229.972	-55.443
2900	13.903	19.467	17.841	4.050	-229.876	-60.543
3000	13.920	19.523	17.841	4.200	-229.780	-65.643
3100	13.937	19.579	17.841	4.350	-229.684	-70.743
3200	13.954	19.635	17.841	4.500	-229.588	-75.843
3300	13.971	19.691	17.841	4.650	-229.492	-80.943
3400	13.988	19.747	17.841	4.800	-229.396	-86.043
3500	14.005	19.803	17.841	4.950	-229.300	-91.143
3600	14.022	19.859	17.841	5.100	-229.204	-96.243
3700	14.039	19.915	17.841	5.250	-229.108	-101.343
3800	14.056	19.971	17.841	5.400	-229.012	-106.443
3900	14.073	20.027	17.841	5.550	-228.916	-111.543
4000	14.090	20.083	17.841	5.700	-228.820	-116.643
4100	14.107	20.139	17.841	5.850	-228.724	-121.743
4200	14.124	20.195	17.841	6.000	-228.628	-126.843
4300	14.141	20.251	17.841	6.150	-228.532	-131.943
4400	14.158	20.307	17.841	6.300	-228.436	-137.043
4500	14.175	20.363	17.841	6.450	-228.340	-142.143
4600	14.192	20.419	17.841	6.600	-228.244	-147.243
4700	14.209	20.475	17.841	6.750	-228.148	-152.343
4800	14.226	20.531	17.841	6.900	-228.052	-157.443
4900	14.243	20.587	17.841	7.050	-227.956	-162.543
5000	14.260	20.643	17.841	7.200	-227.860	-167.643
5100	14.277	20.699	17.841	7.350	-227.764	-172.743
5200	14.294	20.755	17.841	7.500	-227.668	-177.843
5300	14.311	20.811	17.841	7.650	-227.572	-182.943
5400	14.328	20.867	17.841	7.800	-227.476	-188.043
5500	14.345	20.923	17.841	7.950	-227.380	-193.143
5600	14.362	20.979	17.841	8.100	-227.284	-198.243
5700	14.379	21.035	17.841	8.250	-227.188	-203.343
5800	14.396	21.091	17.841	8.400	-227.092	-208.443
5900	14.413	21.147	17.841	8.550	-226.996	-213.543
6000	14.430	21.203	17.841	8.700	-226.900	-218.643

Zirconium Dioxide (ZrO_2)
(Ideal Gas) Mol. Wt. = 123.2188

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹ S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ H° - H° ₂₉₈	ΔH° _f	Log K _p
0	∞	INFINITE	2.870	67.878	INFINITE
100	9.000	66.413	2.870	67.878	150.415
200	10.115	66.379	1.036	68.172	76.243
298	11.009	65.402	∞	68.400	51.695
300	11.026	65.470	∞	68.404	51.376
400	11.818	68.756	1.465	68.605	38.902
500	12.578	66.705	2.376	68.798	31.395
600	12.799	73.750	6.763	68.997	26.377
700	13.022	75.738	6.924	69.210	22.782
800	13.207	77.489	6.936	69.434	20.077
900	13.342	79.053	7.564	69.665	17.966
1000	13.442	80.464	8.863	69.907	16.271
1100	13.519	81.749	10.251	70.168	14.880
1200	13.578	82.928	11.606	71.399	13.707
1300	13.625	84.017	12.767	71.669	12.705
1400	13.663	85.028	13.831	71.951	11.843
1500	13.694	85.972	14.859	72.242	11.093
1600	13.720	86.856	15.848	72.543	10.434
1700	13.741	87.689	16.840	72.855	9.850
1800	13.759	88.475	17.445	73.178	9.328
1900	13.774	89.219	17.915	73.512	8.860
2000	13.787	89.926	18.358	73.858	8.436
2100	13.798	90.599	18.763	74.214	8.051
2200	13.808	91.241	19.132	74.586	7.682
2300	13.817	91.855	19.460	74.970	7.338
2400	13.824	92.443	19.757	75.366	7.017
2500	13.831	93.009	20.016	75.774	6.718
2600	13.837	93.550	20.246	76.193	6.436
2700	13.842	94.073	20.446	76.624	6.204
2800	13.847	94.576	20.615	77.067	5.977
2900	13.851	95.062	20.758	77.523	5.746
3000	13.855	95.532	20.870	77.991	5.539
3100	13.859	95.986	20.952	78.466	5.344
3200	13.862	96.426	21.000	78.946	5.161
3300	13.865	96.853	21.024	79.431	4.988
3400	13.868	97.267	21.028	79.920	4.824
3500	13.870	97.669	21.016	80.414	4.668
3600	13.872	98.060	20.986	80.914	4.521
3700	13.874	98.440	20.938	81.419	4.381
3800	13.876	98.810	20.874	81.931	4.247
3900	13.878	99.170	20.796	82.449	4.119
4000	13.879	99.522	20.700	82.973	3.996
4100	13.881	99.864	20.598	83.501	3.881
4200	13.882	100.199	20.482	84.034	3.770
4300	13.884	100.525	20.353	84.571	3.663
4400	13.885	100.845	20.211	85.111	3.561
4500	13.886	101.157	20.058	85.654	3.463
4600	13.887	101.462	19.895	86.201	3.368
4700	13.888	101.761	19.723	86.751	3.277
4800	13.889	102.053	19.540	87.304	3.189
4900	13.890	102.339	19.348	87.860	3.103
5000	13.891	102.620	19.148	88.418	3.018
5100	13.892	102.895	18.941	88.978	2.933
5200	13.893	103.165	18.727	89.539	2.848
5300	13.894	103.429	18.507	90.101	2.763
5400	13.894	103.689	18.281	90.664	2.678
5500	13.894	103.944	18.049	91.228	2.593
5600	13.895	104.194	17.812	91.792	2.508
5700	13.895	104.440	17.570	92.357	2.423
5800	13.896	104.682	17.324	92.922	2.338
5900	13.896	104.920	17.073	93.487	2.253
6000	13.897	105.153	16.818	94.052	2.168

June 30, 1961; Dec. 31, 1965

ZIRCONIUM DIOXIDE (ZrO_2) (IDEAL GAS)

MOL. WT. = 123.2188

O_2Zr

Point Group C_{2v}
 $\Delta H_f^\circ = -67.9 \pm 11$ kcal. mole⁻¹
 $\Delta H_f^\circ 298.15 = -68.4 \pm 11$ kcal. mole⁻¹
 $S_{298.15}^\circ = 65.402$ cal. deg⁻¹ mole⁻¹
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

(ω , cm⁻¹)
 884 (1)
 1377 (1)
 818 (1)

Bond Distance: $O-Zr = 1.711$ Å
 Bond Angle: $O-Zr-O = 109^\circ$
 Product of the Moments of Inertia: $I_A I_B I_C = 5.679836 \times 10^{-115}$ g.³ cm.⁶
 $\sigma^- = 2$

Heat of Formation.

The $\Delta H_f^\circ 298.15 = -68.4 \pm 11$ kcal. mole⁻¹ was calculated from the $\Delta H_f^\circ 298.15 = 133.867 \pm 11.25$ kcal. mole⁻¹ for the reaction $ZrO_2(c) \rightarrow ZrO_2(g)$. The value of $\Delta H_f^\circ 298.15$ was obtained by the third law method using the determined vapor pressures (at the range 2331-2480°K) by W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 25, 1207 (1957). They observed the variation of the ZrO_2^+ ion intensity over ZrO_2 and reported equilibrium constants for the reaction $ZrO_2(c) \rightarrow ZrO_2(g)$ in the range 2331-2480°K. The third law drift is 80 ± 23 e.u.

Heat Capacity and Entropy.

The vibrational frequencies $\nu_1 = 884$, $\nu_2 = 1377$, $\nu_3 = 818$ and angle $O-Zr-O = 109^\circ$ were obtained from M. J. Linevsky, Spectroscopic Studies of the Vaporization of Refractory Materials, Technical Report Nr. AFML TR-64-420 Air Force Materials Lab. Research and Technology Division, Wright Patterson Air Force Base, Ohio (1965). The bond distances (r_e) $O-Zr = 1.711$ Å was obtained from U. Uhler and L. Akerlind, Arkiv Fysik 10, 431 (1955). The three principal moments of inertia are: $I_A = 1.03083 \times 10^{-38}$, $I_B = 3.8828 \times 10^{-38}$, $I_C = 1.41903 \times 10^{-38}$ g. cm.²

O_2Zr

T, °K	C _p ^a	gibbs/mol S° - (G° - H° ₂₉₈)/T	kcal/mol ΔH°	ΔG°	Log K _p
0					
100	16.320	16.354	0.000	-169.378	124.159
200	16.350	16.455	0.030	-169.271	123.314
300	16.380	17.021	1.770	-163.485	89.324
400	16.410	17.446	3.685	-157.763	68.958
500	16.440	17.833	5.718	-152.113	55.407
600	16.470	18.186	7.833	-146.531	45.749
700	16.500	18.509	10.005	-141.017	38.524
800	16.530	18.798	12.221	-135.557	32.918
900	16.560	19.056	14.474	-130.149	28.444
1000	16.590	19.287	16.762	-124.792	24.704
1100	16.620	19.494	19.083	-119.477	21.760
1200	16.650	19.678	21.438	-114.204	19.199
1300	16.680	19.841	23.829	-108.972	17.011
1400	16.710	19.984	26.252	-103.776	15.120
1500	16.740	20.108	28.705	-98.616	13.470
1600	16.770	20.214	31.188	-93.466	12.010
1700	16.800	20.302	33.701	-88.396	10.733
1800	16.830	20.373	36.244	-83.334	9.586
1900	16.860	20.428	38.817	-78.304	8.557
2000	16.890	20.468	41.420	-73.302	7.629
2100	16.920	20.494	44.053	-68.330	6.788
2200	16.950	20.509	46.716	-63.385	6.023
2300	16.980	20.515	49.409	-58.464	5.324
2400	17.010	20.512	52.132	-53.576	4.684
2500	17.040	20.500	54.885	-48.706	4.094
2600	17.070	20.479	57.668	-43.867	3.551
2700	17.100	20.449	60.481	-39.049	3.048
2800	17.130	20.411	63.324	-34.255	2.582
2900	17.160	20.366	66.197	-29.481	2.148
3000	17.190	20.315			

TUNGSTEN OXIDE (WO_{2.72}) (CRYSTAL) OPW = 227.3684

ΔH°_{298.15} = [16.35] gibbs/mol
ΔH°_{298.15} = -186.70 ± 0.5 kcal/mol
ΔH°₂₉₈ = Unknown

Heat of Formation.

The adopted heat of formation, -186.7 ± 0.5 kcal/mol, is derived from recent equilibrium data which are in excellent agreement; the results are summarized below. In addition R. C. Oriffis, J. Electrochem. Soc. 105, 398 (1958), has measured the heat of combustion to WO₃(c) which yields ΔH°₂₉₈(WO_{2.72}, c) = -185.4 ± 1 kcal/mol when recalculated with ΔH°₂₉₈(WO₃, c) = -201.48 kcal/mol. This result is less certain because of the incomplete characterization of the final products. The EMF data reported by Ya. I. Gerasimov, I. A. Vasil'eva, T. P. Chusova, V. A. Gelderikh, and M. A. Timofeeva, Zh. Fiz. Khim. 36, 358 (1962), give the value of -186.89 kcal/mol for the heat of formation at 298° K. R. J. Ackermann and E. O. Rauh, J. Phys. Chem. 67, 2596 (1963), have investigated the tungsten-oxygen system by mass effusion, mass spectroscopy, and X-ray diffraction. In the temperature range from 1300° to 1600° K, they have derived indirectly from their measurements the heat of formation, -182.2 kcal/mol (corresponding to -187.2 kcal/mol at 298° K, using the JANAF functions).

Author	Reaction*	Temp. (°K)	No. of Points	ΔH° ₂₉₈ (kcal/mol) 3rd law	2nd law	Drift (eu)	ΔH° ₂₉₈ (WO _{2.72} , c)** (kcal/mol)
1. Bouquet (1964) et al.	A	830 - 1048	5	4.095	2.951	1.2 ± 0.2	-186.65
2. St. Pierre (1962) et al.	B	1173 - 1423	-	-	-45.739	-	-186.68
3. Vasil'eva (1960) et al.	A	904 - 1066	4	4.279	2.678	1.6 ± 0.3	-186.83
4. Oriffis (1958)	A	873 - 1173	24	4.314	4.314	-0.01 ± 0.06	-186.87

*Reaction A: 100/72 WO_{2.72}(c) + H₂(g) = 100/72 WO₃(c) + H₂O (g)
B: WO₂ (c) + 0.72 O₂ (g) = WO_{2.72} (c)

** Based on the 3rd law value wherever possible.

1. J. Bouquet and O. Frechon, Compt. rend. 259, 3669 (1964)
2. O. R. St. Pierre, M. T. Ekhlara, M. J. Pool, and R. Speiser, Trans. AIME 224, 259 (1962)
3. I. A. Vasil'eva, Ya. I. Gerasimov and Yu. P. Simanov, Zh. Fiz. Khim. 34, 1811 (1960)
4. R. C. Oriffis, J. Electrochem. Soc. 105, 418 (1958).

Heat Capacity and Entropy.

The monoclinic unit cell of WO_{2.72} corresponds to W₁₀O₂₇, as shown by the x-ray diffraction studies of A. Magneli, O. Andarson, B. Blomberg and L. Kihlberg, Anal. Chem. 24, 1998 (1952). The tabulated heat capacities of WO_{2.72}(c) were estimated from those of WO₂(c) and WO₃(c), because all three have similar monoclinic structures as identified by Magneli et al.

The entropy (S°₂₉₈ = 18.35 eu) was calculated from ΔS°₂₉₈ = 7.96 ± 0.09 eu for reaction A, using all JANAF values. The value of ΔS°₂₉₈ was derived from the second law analysis of Oriffis' data, loc. cit.

Tungsten Oxide (WO_{2.90})
(Crystal) GFW = 230.2483

TUNGSTEN OXIDE (WO_{2.90})
(CRYSTAL)

OPW = 230.2483

02.90W

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100	17.060	17.536	17.536	.000	-196.000	-177.716	130.269
200	17.100	17.662	17.636	.032	-195.968	-177.603	129.383
300	17.100	17.700	17.673	.027	-195.973	-177.598	128.500
400	17.100	17.700	17.673	.027	-195.973	-177.598	127.617
500	17.100	17.700	17.673	.027	-195.973	-177.598	126.734
600	21.730	31.184	21.227	9.974	-195.043	-159.494	58.086
700	22.450	34.590	22.898	18.185	-194.581	-153.605	47.957
800	22.940	37.652	24.552	24.755	-194.100	-147.026	40.728
900	23.270	40.287	26.703	27.575	-193.619	-140.348	34.288
1000	23.720	42.877	27.703	35.174	-193.107	-133.619	29.792
1100	24.035	45.099	29.183	42.516	-192.604	-126.867	25.961
1200	24.350	47.203	30.588	49.526	-192.090	-120.057	22.776
1300	24.650	49.105	31.951	56.278	-191.567	-113.191	19.088
1400	24.940	50.740	33.251	62.771	-191.034	-106.282	15.866
1500	25.220	52.140	34.490	69.000	-190.491	-99.322	13.074
1600	25.530	54.379	35.682	75.014	-189.942	-92.316	10.719
1700	25.830	56.595	36.828	80.822	-189.384	-85.266	8.813
1800	26.130	58.740	37.931	86.436	-188.817	-78.176	7.055
1900	26.430	60.824	38.994	91.850	-188.246	-71.048	5.421
2000	26.730	62.846	40.021	97.064	-187.652	-63.876	4.863
2100	27.030	64.816	41.014	102.078	-187.053	-56.661	4.223
2200	27.330	66.740	41.974	106.892	-186.446	-49.401	3.652
2300	27.630	68.620	42.906	111.506	-185.826	-42.115	3.153
2400	27.930	70.450	43.814	115.920	-185.196	-34.802	2.716
2500	28.230	72.220	44.694	120.134	-184.559	-27.471	2.341
2600	28.530	73.940	45.561	124.148	-183.908	-20.124	2.016
2700	28.830	75.610	46.403	127.962	-183.253	-12.771	1.731
2800	29.130	77.230	47.219	131.576	-182.602	-5.418	1.486
2900	29.430	78.800	48.014	135.090	-181.943	1.935	1.281
3000	29.730	80.320	48.784	138.504	-181.284	9.180	1.116

Heat of Formation.
The adopted heat of formation, -196.0 ± 3 kcal/mol, is a weighted average of those derived from equilibrium data; in addition the following results have been reported.

R. C. Oriffia, J. Electrochem. Soc. 105, 398 (1958), has measured the heat of combustion to WO₃(c), which yields -195.6 kcal/mol when recalculated with ΔH°₂₉₈(WO₃, c) = -201.46 kcal/mol. This result is less certain because of the incomplete characterization of the final products. R. J. Ackermann and E. O. Raub, J. Phys. Chem. 67, 2596 (1963), have investigated the tungsten-oxygen system by mass effusion, mass spectroscopy, and X-ray diffraction. In the temperature range from 1300° to 1600°K, they have derived indirectly two values of ΔH°(WO_{2.90}, c) -190.9 and -188.0 kcal/mol (corresponding to -196.1 and -193.3 kcal/mol, respectively, at 298.15°K, using all JANAF functions).

Author	Reaction	Temperature (°K)	No. of Points	ΔH° ₂₉₈ (kcal/mol)	Drift (eu)	ΔH° ₂₉₈ (WO _{2.90} , c) (kcal/mol)
1. Bouquet (1963) et al.	A	775-898	5	0.270	2.168	-2.3 ± 0.07
3. Vasil'eva (1960) et al.	A	897-993	4	0.240	2.178	-2.1 ± 0.01
4. Oriffia (1959)	A	875-1073	18	0.284	1.504	-1.3 ± 0.02
1. Bouquet (1964) et al.	B	844-934	5	0.754	2.657	-2.1 ± 0.09
3. Vasil'eva (1960) et al.	B	915-1021	5	0.834	1.585	-0.76 ± 0.1
4. Oriffia (1959)	B	875-1073	18	0.589	3.368	-2.68 ± 0.02
1. Bouquet (1964) et al.	C	757-798	5	5.013	6.762	-2.3 ± 0.9
2. St. Pierre (1962) et al.	D	1023-1273	-	-	-7.97	-
2. St. Pierre (1962) et al.	E	1173-1322	-	-	-13.87	-

* Reaction A: WO₃(c) + 0.1 H₂(g) = WO_{2.90}(c) + 0.1 H₂O (g)
B: WO_{2.90}(c) + 0.18 H₂(g) = WO_{2.72}(c) + 0.18 H₂O (g)
C: WO_{2.90}(c) + 0.9 H₂(g) = WO₂(c) + 0.9 H₂O (g)
D: WO_{2.90}(c) + 0.05 O₂(g) = WO₃(c)
E: WO_{2.72}(c) + 0.09 O₂(g) = WO_{2.90}(c)

** Based on the third law value wherever possible and ΔH°₂₉₈(WO_{2.72}, c) = -186.7 kcal/mol.

- J. Bouquet and O. Perachon, Compt. rend. 258, 3869 (1964); 256, 694 (1963)
- O. R. St. Pierre, W. T. Ebihaie, M. J. Pool and R. Speiser, Trans. AIME 224, 259 (1962)
- I. A. Vasil'eva, Ya. I. Perasimov and Yu P. Simanov, Zh. Fiz. Khim. 34, 1811 (1960)
- R. C. Oriffia, J. Electrochem. Soc. 106, 418 (1959)

Heat Capacity and Entropy.

The monoclinic unit cell of WO_{2.90} corresponds to WO₃0.9 as shown by the X-ray diffraction studies of A. Magnell, O. Anderson, B. Blomberg and L. Kihlberg, Anal. Chem. 24, 1998 (1952). The tabulated heat capacities and the entropy (S°₂₉₈ = 17.536 eu) were estimated from those of WO₂(c) and WO₃(c), because all three have the similar monoclinic structure as identified by Magnell et al.

Sept. 30, 1966

02.90W

Tungsten Oxide (WO_{2.96})
(Crystal) GFW = 231.2082

O_{2.96}^W

GFW = 231.2082

(CRYSTAL)

TUNGSTEN OXIDE (WO_{2.96})

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0							
100							
200							
298	17.300	17.900	17.900	•000	-199.560	-180.946	132.637
300	17.360	18.007	17.900	•032	-199.558	-180.831	131.735
400	19.480	23.298	18.607	1.876	-199.355	-174.615	95.405
500	21.000	27.819	20.009	3.765	-199.009	-168.467	73.637
600	22.050	31.746	21.645	6.061	-198.582	-162.397	59.153
700	22.780	35.202	23.340	8.304	-198.111	-156.402	48.831
800	23.280	38.278	25.018	10.608	-197.621	-150.480	41.109
900	23.750	41.046	26.648	12.958	-197.118	-144.616	35.118
1000	24.070	43.562	28.215	15.347	-196.607	-138.808	30.336
1100	24.430	45.874	29.717	17.772	-196.087	-133.055	26.436
1200	24.740	48.013	31.154	20.231	-195.559	-127.347	23.193
1300	25.060	50.006	32.528	22.721	-195.023	-121.684	20.457
1400	25.360	51.874	33.844	25.242	-194.478	-116.064	18.118
1500	25.620	53.633	35.105	27.791	-193.926	-110.482	16.047
1600	25.880	55.294	36.315	30.366	-193.368	-104.936	14.134
1700	26.180	56.872	37.479	32.969	-192.801	-99.436	12.372
1800	26.480	58.377	38.598	35.602	-192.226	-93.951	11.407
1900	26.780	59.817	39.677	38.265	-191.640	-88.507	10.181
2000	27.080	61.198	40.719	40.958	-191.044	-83.095	9.080
2100	27.380	62.527	41.726	43.681	-190.438	-77.712	8.088
2200	27.680	63.807	42.701	46.434	-189.824	-72.360	7.188
2300	27.980	65.044	43.646	49.217	-189.196	-67.034	6.370
2400	28.280	66.241	44.562	52.030	-188.560	-61.733	5.622
2500	28.580	67.402	45.453	54.873	-187.914	-56.457	4.936
2600	28.880	68.529	46.319	57.746	-187.257	-51.220	4.305
2700	29.180	69.624	47.162	60.649	-186.595	-46.029	3.723
2800	29.480	70.691	47.983	63.582	-185.936	-40.804	3.185
2900	29.780	71.731	48.784	66.545	-185.292	-35.634	2.685
3000	30.080	72.745	49.566	69.538	-184.665	-30.480	2.220

ΔH_f^o = Unknown

ΔH_f^o_{298.15} = -199.56 ± 3 kcal/mol

S_{298.15} = [17.90] gibbs/mol

Heat of Formation.

The adopted value, ΔH_f^o₂₉₈ (WO_{2.96}, c) = -199.56 kcal/mol, was obtained by third law treatment of ΔH_f^o = 191,600 ± 54.0 T (cal/mol) in the temperature range from 1300 - 1550°K, using all JANAF functions. The equation for ΔH_f^o was reported by R. J. Ackermann and E. G. Rauh, J. Phys. Chem. **67**, 2536 (1963), based on studies by mass spectroscopy and x-ray diffraction. In this study ΔH_f^o was obtained by comparison of the Gibbs energies of sublimation (to gaseous WO₃, W₂O₆, W₂O₉, and W₄O₁₂) over the two systems W-WO₂(c) and WO_{2.96}(c); thus WO_{2.96}(c) was related to WO₂(c) through the gaseous species.

J. E. Battles, Ph. D. Thesis, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," The Ohio State University, (1964), has reported partial pressures of W₂O₉(g) and W₄O₁₂(g) in equilibrium with WO₃ - WO_{2.96}(c). In light of Ackermann and Rauh's observation, the condensed phase was presumed to have the composition of WO_{2.96}(c). The pressure data are in reasonable agreement with the studies of Ackermann and Rauh as summarized below. Values of ΔH_f^o₂₉₈ for WO_{2.96}(c) derived from the data of Battles are based on the same author's data for W₂O₉(g), and W₄O₁₂(g) in order to relate WO_{2.96} to WO₂ directly.

Investigator	Reaction	Temperature (°K)		ΔH _f ^o ₂₉₈ (kcal/mol)	Drift (cal)	ΔH _f ^o ₂₉₈ (WO _{2.96} , c) ^a (kcal/mol)
		1st law	2nd law			
1. Ackermann & Rauh	A	1300-1550	60.82	56.32	3.2 ± 0.6	-199.57
2. Ackermann & Rauh	B	1300-1550	41.37	38.35	2.094 ± 0.09	-199.58
3. Battles	B	1274-1418	40.82	43.28	-1.854 ± 0.05	-199.72
4. Ackermann & Rauh	C	1300-1550	35.81	33.58	1.551 ± 0.09	-199.60
5. Battles	C	1333-1418	35.37	38.74	-2.461 ± 0.1	-199.95

Reaction: A: WO_{2.96}(c) = 0.44 W₂O₉(g) + 0.04 W₃O₈(g)

B: WO_{2.96}(c) = 0.29333 W₂O₉(g) + 0.04 W₃O₈(g)

C: WO_{2.96}(c) = 0.22 W₄O₁₂(g) + 0.04 W₃O₈(g)

* Third law value adopted in calculation.

Heat Capacity and Entropy.

The tabulated heat capacities and the entropy at 298.15°K were estimated from those of WO₂(c) and WO₃(c). Ackermann and Rauh, loc. cit., have found that the composition WO_{2.96} probably represents the azeotropic composition of the WO₃-x solid solution and is the only single phase which evaporates congruently below 1550°K.

Sept. 30, 1966

O_{2.96}^W

Ozone (O₃)

(Ideal Gas) Mol. Wt. = 48.000

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f ^o	Log K _p
0	0.000	∞	0.000	34.739	∞
100	0.000	47.249	2.474	34.739	12.112
200	0.379	37.884	1.002	34.739	10.565
298	0.379	37.884	1.000	34.739	10.565
300	0.400	37.138	0.17	34.098	28.430
400	10.455	59.992	1.012	34.026	22.227
500	11.296	62.419	2.101	34.019	18.511
600	11.916	64.536	3.263	34.048	16.032
700	12.349	66.409	4.479	34.097	14.259
800	12.704	68.083	5.733	34.154	12.927
900	12.956	69.595	7.017	34.217	11.869
1000	13.151	70.971	8.323	34.282	11.058
1100	13.303	72.232	9.646	34.347	10.376
1200	13.422	73.392	10.982	34.411	9.807
1300	13.506	74.473	12.330	34.474	9.324
1400	13.561	75.479	13.687	34.535	8.910
1500	13.602	76.420	15.052	34.593	8.550
1600	13.743	77.305	16.423	34.649	8.235
1700	13.794	78.140	17.800	34.703	7.953
1800	13.843	78.930	19.182	34.751	7.709
1900	13.885	79.680	20.569	34.795	7.486
2000	13.922	80.393	21.959	34.835	7.286
2100	14.057	81.073	23.353	34.872	7.105
2200	14.094	81.723	24.750	34.901	6.940
2300	14.017	82.345	26.150	34.927	6.789
2400	14.045	82.943	27.554	34.948	6.651
2500	14.070	83.516	28.959	34.961	6.523
2600	14.094	84.069	30.368	34.972	6.404
2700	14.117	84.601	31.778	34.975	6.299
2800	14.139	85.115	33.191	34.973	6.196
2900	14.160	85.611	34.604	34.966	6.102
3000	14.180	86.099	36.023	34.954	6.014
3100	14.199	86.557	37.442	34.937	5.932
3200	14.216	86.986	38.861	34.915	5.857
3300	14.234	87.396	40.285	34.889	5.783
3400	14.254	87.781	41.710	34.857	5.715
3500	14.272	88.145	43.136	34.822	5.651
3600	14.288	88.487	44.564	34.783	5.590
3700	14.301	88.800	45.992	34.740	5.539
3800	14.321	89.080	47.425	34.694	5.478
3900	14.337	89.333	48.858	34.645	5.428
4000	14.353	89.566	50.293	34.591	5.380
4100	14.369	89.780	51.729	34.535	5.334
4200	14.384	89.979	53.166	34.477	5.290
4300	14.399	90.156	54.605	34.416	5.248
4400	14.414	90.316	56.046	34.352	5.208
4500	14.429	90.461	57.488	34.287	5.171
4600	14.444	90.598	58.932	34.220	5.135
4700	14.458	90.729	60.377	34.150	5.100
4800	14.473	90.853	61.824	34.080	5.067
4900	14.487	90.972	63.272	34.009	5.035
5000	14.501	91.085	64.721	33.935	5.005
5100	14.515	91.192	66.172	33.861	4.976
5200	14.529	91.292	67.624	33.786	4.948
5300	14.543	91.385	69.078	33.711	4.920
5400	14.557	91.471	70.533	33.635	4.895
5500	14.571	91.551	71.989	33.559	4.871
5600	14.585	91.627	73.447	33.481	4.847
5700	14.599	91.698	74.906	33.404	4.823
5800	14.612	91.764	76.366	33.327	4.802
5900	14.625	91.825	77.828	33.250	4.781
6000	14.639	91.881	79.292	33.173	4.760

June 30, 1961

OZONE (O₃)

(IDEAL GAS)

MOL. WT. = 48.000

ΔH_f^o = 34.8 ± 0.4 kcal. mole⁻¹
 ΔH_f^o 298.15 = 34.2 ± 0.4 kcal. mole⁻¹
 S_{298.15}^o = 57.080 cal. deg.⁻¹ mole⁻¹
 Point group C_{2v}

Vibrational Levels and Multiplicities

(ω _i , cm. ⁻¹)
1110 (1)
705 (1)
1043 (1)

Ground state multiplicity = 1

No α_1 available

σ = 2

Rotational constants: A₀₀₀ = 3.55381 cm.⁻¹ B₀₀₀ = 0.44530 cm.⁻¹ C₀₀₀ = 0.39477 cm.⁻¹
 X₁₁ = -3.8 cm.⁻¹ X₃₃ = -4.0 cm.⁻¹ X₂₃ = -3.5 cm.⁻¹
 X₁₂ = -3.5 cm.⁻¹ X₃₁ = -9.0 cm.⁻¹

Heat of Formation

P. Qunther, E. Wessmuth, and L. A. Schryver, Z. phys. Chem. 158, 297 (1932), measured ΔE for the reaction O₃(g) → 3/2 O₂(g) in a calorimeter calibrated by means of the reaction CO(g) + 1/2 O₂(g) → CO₂(g), and found the ratio of the ΔE values for these reactions to be 0.5077 ± 0.0024. The temperature of the experiments is not reported and is assumed to have been 18°C. From the above ratio, ΔH_f^o 298.15 is calculated to be 33.89 ± 0.36 cal. mole⁻¹. A. Kallen and S. Jahn, Z. anorg. Chem. 68, 243 (1910), measured ΔH at an unspecified temperature for the reaction O₃(g) → 3/2 O₂(g) in an electrically calibrated calorimeter. If the temperature of the experiments is assumed to have been 18°C and the modern joule-calorie conversion factor is used, ΔH_f^o 298.15 is found to be 34.3 ± 0.6 kcal. mole⁻¹. Variability in the O₃ content of the feed gas is allowed for in the uncertainty. The value adopted here is 34.2 ± 0.4 kcal. mole⁻¹.

Heat Capacity and Entropy

J. S. Gordon, private communication, April, 1961, has calculated the thermodynamic functions from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from L. Pierce, J. Chem. Phys. 24, 139 (1956). The functions below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.

Lead Metasilicate (PbSiO₃)

(Crystal) Mol. Wt. = 283.2742

O₃PbSi

MOL. WT. = 283.2742

(CRYSTAL)

LEAD METASILICATE (PbSiO₃)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	-	3.876	-272.011	INFINITE
100	10.680	8.883	32.343	-273.039	-266.727	582.904
200	17.343	18.523	28.116	-273.514	-260.197	284.316
298	21.520	26.273	0.000	-273.660	-253.600	185.900
300	21.580	26.406	2.040	-273.661	-253.496	184.663
400	28.776	38.776	28.422	-273.320	-246.112	104.968
600	28.380	43.806	30.992	-272.954	-233.503	85.049
700	29.500	48.269	33.148	-273.684	-226.770	70.797
800	30.250	52.260	35.282	-273.215	-220.101	60.126
900	31.150	55.818	36.724	-272.185	-208.938	43.224
1000	31.150	59.118	30.393	-272.185	-208.938	23.484
1100	31.440	62.101	41.324	-271.645	-200.441	39.822
1200	31.690	64.847	43.171	-271.089	-193.991	35.329
1300	31.890	67.392	44.938	-270.523	-187.589	31.535
1400	32.050	69.748	46.627	-269.952	-181.232	28.290
1500	32.270	71.982	48.244	-269.373	-174.914	25.484
1600	32.420	74.070	49.794	-268.792	-168.635	23.033
1700	32.550	76.039	51.280	-268.212	-162.283	20.862
1800	32.690	77.904	52.708	-267.630	-155.961	18.863
1900	32.800	79.683	54.081	-267.070	-149.672	17.077
2000	32.890	81.377	55.403	-266.534	-143.414	15.474

$$\Delta H_f^0 = -272.01 \pm 1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 298.15 = -273.66 \pm 1 \text{ kcal. mole}^{-1}$$

$$S_{298.15} = 26.273 \pm 0.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1037^\circ \text{K.}$$

Heat of Formation.

The heat of the reaction $\text{PbO}(\text{red}) + \text{SiO}_2 \rightarrow \text{PbSiO}_3(\text{c})$ was reported by K. K. Kelley, U. S. Bureau of Mines, Report Investigation 5501 (1952). This value for the heat of reaction of the oxides has been converted to the heat of formation using JANAP values for $\text{PbO}(\text{c})$ (March 31, 1962) and for $\text{SiO}_2(\text{c})$ (Dec. 31, 1962). The above $\Delta H_f^0 298.15 = -3.75 \pm 0.12 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

In the low temperature region (53.25-298.15°K.) the C_p values are those determined by E. G. King, J. Am. Chem. Soc. 81, 799-800 (1959). Above 298.15 C_p values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.25°K. using the Debye and Einstein functions $D(\frac{140}{T}) + E(\frac{215}{T}) + 2E(\frac{595}{T}) + E(\frac{1440}{T})$ given by E. G. King, J. Am. Chem. Soc. 81, 799-800 (1959). The $S_{53.25} = 3.662 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

T_m was taken from Geller, Creamer and Bunting, J. Research Natl. Bureau of Standards, 13, 237 (1934).

June 30, 1965

O₃PbSi

Sulfur Trioxide (SO₃)

(Ideal Gas) Mol. wt. = 80.0622

T, °K.	C _p	S° - (S° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.145	50.733	2.796	93.220	93.220	INFINITE
200	10.119	62.920	1.998	93.656	92.205	201.504
298	12.108	61.344	1.094	94.150	90.555	98.949
300	12.142	61.344	1.094	94.150	88.689	65.007
400	13.784	61.344	1.022	94.597	88.652	64.580
500	15.082	61.344	1.322	95.463	86.597	67.312
600	16.075	61.344	2.768	96.052	84.310	36.850
700	16.361	61.344	4.328	96.481	81.919	29.837
800	16.561	61.344	5.511	96.811	79.401	24.401
900	16.683	61.344	6.407	97.044	76.211	20.401
1000	16.732	61.344	7.067	97.188	72.423	18.025
1100	16.752	61.344	7.533	97.248	68.154	15.354
1200	16.752	61.344	7.838	97.248	63.306	13.173
1300	16.732	61.344	8.001	97.188	57.862	11.357
1400	16.683	61.344	8.063	97.044	51.862	9.508
1500	16.609	61.344	8.025	96.801	45.368	7.371
1600	16.499	61.344	7.895	96.467	38.368	5.377
1700	16.351	61.344	7.673	95.945	30.868	3.434
1800	16.179	61.344	7.368	95.280	22.868	1.643
1900	15.993	61.344	6.993	94.419	14.368	0.141
2000	15.793	61.344	6.563	93.280	5.368	-0.678
2100	15.583	61.344	6.083	91.920	-4.136	-1.829
2200	15.353	61.344	5.553	90.280	-13.636	-2.879
2300	15.103	61.344	4.983	88.380	-22.836	-3.829
2400	14.833	61.344	4.383	86.180	-31.636	-4.679
2500	14.553	61.344	3.753	83.680	-40.036	-5.429
2600	14.263	61.344	3.083	80.880	-48.036	-6.079
2700	13.963	61.344	2.483	77.780	-55.636	-6.629
2800	13.653	61.344	1.853	74.380	-62.836	-7.079
2900	13.333	61.344	1.183	70.680	-69.636	-7.429
3000	13.003	61.344	0.583	66.680	-76.036	-7.679
3100	12.663	61.344	-0.047	62.380	-82.036	-7.829
3200	12.313	61.344	-0.647	57.780	-87.636	-7.879
3300	11.953	61.344	-1.217	52.880	-92.836	-7.829
3400	11.583	61.344	-1.757	47.680	-97.636	-7.679
3500	11.203	61.344	-2.257	42.180	-102.036	-7.429
3600	10.813	61.344	-2.717	36.380	-106.036	-7.079
3700	10.413	61.344	-3.137	30.180	-109.636	-6.629
3800	10.003	61.344	-3.517	23.580	-112.836	-6.079
3900	9.583	61.344	-3.857	16.580	-115.636	-5.429
4000	9.153	61.344	-4.157	9.180	-118.036	-4.679
4100	8.713	61.344	-4.417	1.380	-120.036	-3.829
4200	8.263	61.344	-4.637	-6.820	-121.636	-2.879
4300	7.803	61.344	-4.817	-14.820	-122.836	-1.829
4400	7.333	61.344	-4.957	-22.580	-123.636	-0.679
4500	6.853	61.344	-5.057	-30.080	-124.036	0.521
4600	6.363	61.344	-5.117	-37.380	-124.036	1.671
4700	5.863	61.344	-5.137	-44.380	-123.636	2.821
4800	5.353	61.344	-5.117	-51.080	-122.836	3.971
4900	4.833	61.344	-5.057	-57.480	-121.636	5.121
5000	4.303	61.344	-4.957	-63.480	-120.036	6.271
5100	3.763	61.344	-4.817	-69.080	-118.036	7.421
5200	3.213	61.344	-4.637	-74.280	-115.636	8.571
5300	2.653	61.344	-4.417	-79.080	-112.836	9.721
5400	2.083	61.344	-4.157	-83.480	-109.636	10.871
5500	1.503	61.344	-3.857	-87.480	-106.036	12.021
5600	0.913	61.344	-3.517	-91.080	-102.036	13.171
5700	0.313	61.344	-3.137	-94.280	-97.636	14.321
5800	-0.287	61.344	-2.717	-97.080	-92.836	15.471
5900	-0.887	61.344	-2.257	-100.080	-87.636	16.621
6000	-1.487	61.344	-1.757	-103.280	-82.036	17.771

Dec. 31, 1960; Sept. 30, 1965

SULFUR TRIOXIDE (SO₃)

(IDEAL GAS)

MOL. WT. = 80.0622

Point Group D_{3h}

$$\Delta H_f^0 = -93.22 \pm 0.17 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 61.344 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$\Delta H_f^0 = -94.59 \pm 0.17 \text{ kcal. mole}^{-1}$$

Round State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm⁻¹

1068 (1)
495 (1)
1391 (2)
529 (2)

Bond Distance: S-O = 1.43 Å

Bond Angle: O-S-O = 120°

Product of the Moments of Inertia: I_AI_BI_C = 1.0813 X 10⁻¹¹⁴ g.³ cm.⁶

Q = 6

Heat of Formation.

The heat of formation was calculated from the reaction SO₂ + 1/2 O₂ → SO₃ for which three sets of equilibrium constants are available. A summary of the second and third law treatment of the data is given below.

Ref.	Temp. Range	Points	ΔH _f ⁰ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	Drift cal. mole ⁻¹ deg. ⁻¹
1	933-945°K	5	-27.67 ± 2.7	-23.608	3.7 ± 2.9
2	801-1170°K	8	-23.45 ± 0.1	-23.661	-0.8 ± 0.1
3	850-1001°K	11	-22.74 ± 0.6	-23.614	-1.5 ± 0.6
4	801-1170°K	23*	-23.40 ± 0.2	-23.638	-0.9 ± 0.2

References

1. O. B. Taylor and S. Lehnner, Z. Physik. Chem. **B30**, (1931).
2. M. Bodenstein and W. Pohl, Z. Electrochem. **11**, 373 (1905).
3. A. P. Kapustinak and L. M. Shamovskiy, Acta Physicochem. URSS **3**, 791 (1956).
4. Combination of above references, with one point omitted due to failure of a statistical test.

The combined set was adopted though it appears that the three sets are not in excellent agreement, and the combination heavily favors Ref. 2. Although there is a definite trend in all the data it cannot be considered definitive enough for use in the modification of the SO₃ functions.

Heat Capacity and Entropy.

The bond length and angles were taken from the electron diffraction data of K. J. Palmer, J. Am. Chem. Soc. **80**, 2360 (1958). The vibrational frequencies were taken from the infrared studies of R. W. Loveday, J. H. Colwell, D. F. Eggers and O. D. Halsey, J. Chem. Phys. **36**, 612 (1962), which are in excellent accord with those of R. Bent and W. R. Laidner, Spectrochim. Acta **19**, 931 (1963) using different techniques. These values differ from the assignment used by W. H. Stockmayer, O. M. Kavanagh and H. S. Mickley, J. Chem. Phys. **12**, 408 (1944) in their analysis of the thermodynamic properties of SO₃.

The individual moments of inertia were I_A=I_B = 6.148 X 10⁻³⁹ g. cm.² and I_C = 16.298 X 10⁻³⁹ g. cm.²

O₃S

Dititanium Trioxide (Ti_2O_3)
(Crystal)

GFW = 143.7982

T, °K	Cp°	S°	gibbs/mol $-(G^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	.000	.000	INFINITE	- 3.431	- 361.505	- 361.505	INFINITE
100	6.368	2.177	20.796	- 2.625	- 361.368	- 361.368	19.713
200	17.596	10.671	20.796	- 2.625	- 361.368	- 361.368	382.034
298	23.266	18.829	18.829	.000	- 361.490	- 362.820	251.294
300	23.352	18.873	18.829	.043	- 363.488	- 362.692	249.651
400	28.718	26.427	19.810	2.647	- 353.197	- 335.752	183.468
500	31.250	33.735	21.859	5.936	- 362.284	- 329.402	143.920
600	32.630	39.562	24.335	9.136	- 361.551	- 322.431	117.452
700	33.510	44.661	26.882	12.445	- 360.781	- 315.994	98.658
800	34.130	49.178	29.392	15.829	- 360.014	- 309.650	84.592
900	34.590	53.226	31.820	19.265	- 359.271	- 303.399	73.675
1000	34.960	56.890	34.146	22.743	- 358.561	- 297.229	64.959
1100	35.270	60.237	36.368	26.255	- 357.886	- 291.127	57.842
1200	35.530	63.317	38.487	29.796	- 357.121	- 285.011	51.908
1300	35.770	66.170	40.508	33.361	- 356.270	- 278.870	46.882
1400	35.980	68.829	42.437	36.948	- 355.436	- 272.766	42.595
1500	36.180	71.318	44.281	40.557	- 354.624	- 266.777	38.669
1600	36.360	73.659	46.044	44.184	- 353.839	- 260.812	35.425
1700	36.540	75.869	47.734	47.829	- 353.083	- 254.868	32.769
1800	36.710	77.962	49.356	51.491	- 352.344	- 249.025	30.236
1900	36.870	79.951	50.914	55.170	- 351.621	- 243.192	27.873
2000	37.030	81.847	52.414	58.865	- 350.912	- 237.088	25.908
2100	37.181	83.657	53.859	62.576	- 350.219	- 230.859	24.026
2200	37.330	85.390	55.253	66.301	- 349.542	- 224.666	22.316
2300	37.475	87.053	56.600	70.042	- 348.881	- 218.502	20.762
2400	37.620	88.651	57.902	73.796	- 348.234	- 212.363	19.338
2500	37.766	90.189	59.163	77.566	- 347.606	- 206.256	18.031
2600	37.910	91.673	60.385	81.350	- 346.992	- 200.176	16.826
2700	38.050	93.107	61.571	85.148	- 346.392	- 194.122	15.713
2800	38.190	94.493	62.722	88.960	- 345.804	- 188.094	14.681
2900	38.330	95.836	63.841	92.786	- 345.228	- 182.086	13.722
3000	38.470	97.137	64.929	96.626	- 344.662	- 176.106	12.829

Dec. 31, 1960; March 31, 1967; June 30, 1967

DITITANIUM TRIOXIDE (Ti_2O_3)

(CRYSTAL)

GFW = 143.7982

$S^\circ_{298.15} = 18.83$ gibbs/mol	$\Delta H^\circ_0 = -361.50 \pm 2$ kcal/mol
$T_t = 473^\circ\text{K}$	$\Delta H^\circ_{298.15} = -363.49 \pm 2$ kcal/mol
$T_m = 2112^\circ\text{K}$	$\Delta H^\circ = 0.215$ kcal/mol
	$\Delta H_m^\circ = [26.4]$ kcal/mol

Heat of Formation

G. L. Humphrey, J. Am. Chem. Soc. 73, 1587 (1951), determined the enthalpy change $\Delta H^\circ_{298} = -88.11 \pm 0.1$ kcal/mol for the reaction $\text{Ti}_2\text{O}_3(\text{c}) + 1/2\text{O}_2(\text{g}) = \text{TiO}_2(\text{rutile})$ using bomb calorimetry. Based on this result and $\Delta H^\circ_{298}(\text{rutile}) = -225.8$ kcal/mol, the adopted value of ΔH°_{298} for $\text{Ti}_2\text{O}_3(\text{c})$ is calculated to be -363.49 ± 2 kcal/mol. A value of $\Delta H^\circ_{298}(\text{Ti}_2\text{O}_3, \text{c}) = -362.8 \pm 0.6$ kcal/mol was reported by S. M. Ariya, M. P. Morozova, and E. Vol'f, Russ. J. Inorg. Chem. (Engl. Transl.) 2, 18 (1957), who measured the heat of combustion of various compositions in the Ti_2O_3 system. Ariya et al. used an estimated correction for the formation of $\text{TiO}_2 \cdot x\text{H}_2\text{O}$, while Humphrey obtained values of 0.1 - 1.3 kcal/mol by grinding the product and reburning it with white oil. Most of the assigned uncertainty arises from this problem. [See $\text{TiO}_2(\text{rutile})$ for further details.]

Heat Capacity and Entropy

The low temperature heat capacities, 53 - 296°K, were measured by C. H. Shomate, J. Am. Chem. Soc. 68, 310 (1946). The data indicate a small anomaly in Cp near 240°K. High temperature enthalpies, 375 - 1750°K, were determined by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), by drop calorimetry. The heat capacities, 298 - 473°K, derived by Naylor, loc. cit., are joined smoothly with the low temperature Cp at 298°K. Cp values above 473°K are calculated from the heat capacity equation for the β phase derived by Naylor.

S. Nomura, T. Kawakubo, and T. Yanagi, J. Phys. Soc. Japan, 16, 706 (1961), measured the specific heat in the range 70 - 750°K with a conduction-type calorimeter. A broad anomaly in the specific heat was observed from 160 to 200°K. Below this region the Cp values are unreasonably small, but near 200°K the data are closer to the adopted values. The S°_{298} is calculated from the adopted low temperature Cp based on $S^\circ_{50} = 0.442$ eu. A. D. Pearson, J. Phys. Chem. Solids, 2, 316 (1958), studied the crystal structure of Ti_2O_3 by X-ray method and found that the agreement between calculated and observed density values is good; in other words, there are no significant vacant sites in Ti_2O_3 crystal lattice. This was later confirmed by S. C. Abrahams, Phys. Rev. 130, 2230 (1963). Therefore we do not add vacancy entropy to S°_{298} . Because of the magnetic transition ($\alpha \rightarrow \beta$) at 473°K, we have assumed that no spin-magnetic entropy is likely below 50°K. See Transition Data for more information.

Transition Data

Tt and ΔH°_t were obtained from B. F. Naylor, loc. cit. S. Nomura, T. Kawakubo and T. Yanagi, J. Phys. Soc. Japan 16, 706 (1961), derived the much smaller $\Delta H^\circ_t = 0.036$ kcal/mol from their observations with a conduction-type calorimeter. These authors suggested that the discrepancy may be due to non-stoichiometry or to impurities in the sample studied by Naylor.

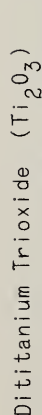
Single-crystal neutron diffraction studied by S. C. Abrahams, Phys. Rev. 130, 2230 (1963), indicate that Ti_2O_3 undergoes an antiferromagnetic ordering of small magnetic moment, associated with the Ti^{3+} cations, below a Néel temperature of about 660°K. The temperature of this transition has been reported variously as about 450 to 600°K based on other properties. A. D. Pearson, J. Phys. Chem. Solids 2, 316 (1958), found no change in the Ti_2O_3 corundum-type structure, but noted a rapid change in the lattice parameters between 430 and 473°K. Observations of corresponding changes in magnetic susceptibility, resistivity and thermoelectric power have been summarized by the same authors and by J. B. Goodenough, Phys. Rev. 117, 1442 (1960). Goodenough attempted to interpret the earlier observations in terms of strong cation-cation interactions.

The magnetic nature of the transition suggests that any spin-magnetic entropy in Ti_2O_3 would be included in ΔH°_t and in the observed Cp values for α and β phases. Magnetic contributions are thus unlikely below 50°K.

Melting Data

See $\text{Ti}_2\text{O}_3(\text{l})$ table for details.

03Ti2



(Liquid) GFW = 143.7982

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
100							
200							
298	37,500	22,952	22,952	.000	-342.087	-322.646	236.506
300	37,500	23,184	22,953	.069	-342.059	-322.526	236.960
400	37,500	33,972	24,424	3,819	-340.612	-316.235	172.782
500	37,500	42,340	27,201	7,569	-339.250	-310.301	135.632
600	37,500	49,177	30,311	11,319	-337.945	-304.633	110.943
700	37,500	54,558	32,431	15,249	-336.754	-299.425	91.407
800	37,500	59,665	34,481	18,819	-335.621	-293.886	80.286
900	37,500	64,382	36,305	22,569	-334.564	-288.732	70.114
1000	37,500	68,333	42,014	26,319	-333.582	-283.693	62.001
1100	37,500	71,907	44,571	30,069	-332.668	-278.787	55.382
1200	37,500	75,172	46,272	33,569	-331.814	-274.001	48.200
1300	37,500	78,172	48,272	37,569	-331.019	-269.321	41.211
1400	37,500	80,951	51,437	41,319	-330.282	-264.746	34.756
1500	37,500	83,538	53,492	45,069	-330.709	-259.192	28.764
1600	37,500	85,958	55,446	48,819	-329.800	-254.451	23.210
1700	37,500	88,172	57,288	52,319	-328.433	-249.517	18.160
1800	37,500	89,951	58,951	55,569	-327.137	-244.377	13.666
1900	37,500	92,402	60,787	60,069	-327.379	-240.566	9.666
2000	37,500	94,326	62,416	63,819	-335.575	-235.689	25.755
2100	37,500	95,156	63,950	67,569	-334.893	-230.710	21.010
2200	37,500	97,549	65,922	71,319	-334.251	-225.631	16.966
2300	37,500	99,666	68,322	75,069	-333.658	-220.451	12.966
2400	37,500	101,163	70,819	78,819	-332.858	-215.966	9.666
2500	37,500	102,694	72,466	82,569	-332.200	-211.112	6.655
2600	37,500	104,165	74,265	86,319	-331.588	-206.282	3.740
2700	37,500	105,588	76,111	90,069	-330.966	-201.451	0.866
2800	37,500	106,966	78,011	93,819	-330.269	-196.454	15.353
2900	37,500	108,260	79,966	97,569	-329.641	-191.929	14.464
3000	37,500	109,531	81,966	101,319	-329.021	-187.191	13.637

DITITANIUM TRIOXIDE (Ti₂O₃) (LIQUID)

S°_{298.15} = [22.952] gibbs/mol

Tm = 2112 ± 10°K

ΔHf°_{298.15} = [-342.087] kcal/mol

ΔHm° = [28.4] kcal/mol

Heat of Formation

The heat of formation, ΔHf°₂₉₈, for Ti₂O₃(l) is obtained from that of the crystal by adding ΔHm° and the difference between H°₂₁₁₂ - H°₂₉₈ for Ti₂O₃(c) and Ti₂O₃(l).

Heat Capacity and Entropy

The heat capacity of Ti₂O₃(l) is estimated on the basis of 7.5 gibbs/g-atom. The S°₂₉₈ is derived in a manner analogous to that of the heat of formation.

Melting Data

The adopted Tm was determined by P. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. 49, 18 (1966). ΔHm° is estimated based on the assumption that at Tm the entropy of melting is 2.5 eu/g-atom. Other Tm values reported are listed as follows:

Tm, °K	Source
2073	T. H. Schofield and A. E. Bacon, J. Inst. Metals 84, 47 (1956).
2093	G. Brauer and W. Lüttke, J. Inorg. Nucl. Chem. 16, 67 (1960).
2103	H. Mashimura and H. Kimura, J. Japan Inst. Metals (Sendai) 20, 524 (1956).
2173	E. Junker, Z. Anorg. Allgem. Chem. 228, 97 (1936).
2193	R. C. DeVries and R. Roy, Bull. Am. Ceram. Soc. 33, 370 (1954).



Tungsten Trioxide (WO₃)

GFW = 231.8482

(Crystal)

TUNGSTEN TRIOXIDE (WO₃)

(CRYSTAL)

OPW = 231.8482

T, °K	Cp°	q _{lib} /mol S° - (H° - H° ₂₉₈)/T	kcal/mol H° - H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	+0.00	INFINITE	- 2.951	- 200.110	- 200.110	INFINITE
100	7.277	4.508	- 2.659	- 201.014	- 195.026	426.229
200	13.909	11.826	- 1.565	- 201.444	- 188.832	206.345
298	17.481	18.143	+0.00	- 201.460	- 182.626	133.869
300	17.520	18.252	- 0.032	- 201.458	- 182.650	132.958
400	19.486	24.150	1.186	- 200.501	- 170.601	74.307
500	21.186	28.158	3.942	- 200.501	- 170.601	74.307
600	22.255	32.122	6.118	- 200.469	- 163.861	59.686
700	22.978	35.610	8.382	- 199.993	- 157.796	49.266
800	23.480	38.713	10.706	- 199.499	- 151.803	41.471
900	23.800	41.414	13.044	- 198.984	- 145.940	35.476
1000	24.300	44.040	15.483	- 198.479	- 139.994	30.596
1100	23.653	46.663	30.086	- 187.650	- 134.188	26.661
1200	24.044	48.738	31.555	- 187.212	- 128.437	23.392
1300	24.435	50.678	32.952	- 186.759	- 122.724	20.632
1400	24.827	52.497	34.286	- 186.289	- 117.047	18.272
1500	25.218	54.230	35.557	- 185.802	- 111.404	16.232
1600	25.609	55.870	36.775	- 185.295	- 105.794	14.451
1700	26.001	57.434	37.945	- 184.768	- 100.215	12.894
1800	26.400	58.931	39.069	- 184.224	- 94.668	11.494
1900	26.800	60.359	40.153	- 183.659	- 89.153	10.255
2000	27.200	61.754	41.199	- 183.074	- 83.666	9.145
2100	27.600	63.091	42.209	- 182.469	- 78.212	8.140
2200	28.000	64.384	43.188	- 181.846	- 72.788	7.231
2300	28.400	65.638	44.137	- 181.200	- 67.392	6.404
2400	28.800	66.856	45.056	- 180.535	- 62.030	5.646
2500	29.200	68.039	45.934	- 179.851	- 56.703	4.955
2600	29.600	69.192	46.766	- 179.145	- 51.368	4.318
2700	30.000	70.316	47.675	- 178.425	- 46.081	3.730
2800	30.400	71.414	48.593	- 177.698	- 40.820	3.186
2900	30.800	72.481	49.512	- 176.945	- 35.586	2.682
3000	31.200	73.539	50.402	- 176.201	- 30.379	2.215

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

$\Delta H_f^\circ = -200.11 \pm 0.2$ kcal/mol

$\Delta H_f^\circ_{298.15} = -201.46 \pm 0.2$ kcal/mol

$\Delta H_f^\circ = 0.355$ kcal/mol

$\Delta H_m^\circ = 17.55$ kcal/mol

$\Delta H_f^\circ_{298.15}$ (to monomer) = 131.46 kcal/mol

$\Delta H_f^\circ_{298.15}$ (to dimer) = 82.36 kcal/mol

$\Delta H_f^\circ_{298.15}$ (to trimer) = 40.26 kcal/mol

$\Delta H_f^\circ_{298.15}$ (to tetramer) = 33.91 kcal/mol

Heat of Formation.

The selected heat of formation, $\Delta H_f^\circ_{298}$ (WO₃, c) = -201.46 $\pm$ 0.2 kcal/mol, was determined by A. D. Mah, J. Am. Chem. Soc. **81**, 1582 (1959), using bomb calorimetry. G. Huff, E. Squitieri and P. E. Snyder, J. Am. Chem. Soc. **70**, 3380 (1948), have reviewed the literature heat of formation data and also measured calorimetrically the heat of formation, -201.84 $\pm$ 0.1 kcal/mol, which is in good agreement with the value selected. Other combustion values were reported as $\Delta H_f^\circ_{298} = -199 \pm 1$ kcal/mol by R. C. Griffiths, J. Electrochem. Soc. **105**, 398 (1958); and $\Delta H_f^\circ_{298} = -205.3$ kcal/mol by I. A. Vasil'eva, V. I. Garasimov, and Y. P. Shmanov, Zh. Fiz. Khim. **31**, 682 (1957). R. C. Griffiths, J. Electrochem. Soc. **106**, 418 (1959), also derived the heat of formation, -202.8 $\pm$ 1.4 kcal/mol from equilibrium data.

Heat Capacity and Entropy.

The low temperature (53-296.7°K) heat capacities and high temperature (399.6 - 1835.8°K) enthalpy changes have been measured by E. G. King, W. W. Kellner, and A. U. Christensen, U.S. Bur. Minea R.I. 5664 (1960); and these data have been used to derive the tabulated heat capacities. Low temperature and high temperature values were joined smoothly at 298.15°K. The entropy was calculated from the heat capacities based on $S^\circ_1 = 1.31$ eu.

King et al. were apparently unaware of the transition near 593°K which was reported by J. A. Perri, E. Banks, and B. Post, J. Appl. Phys. **28**, 1272 (1957), and they did not take sufficient points in that region to fix the precise enthalpy curve. We have adopted only one curve through the region because of the insufficiency of the data and also because the heat effects appear to be small or gradual.

Transition and Melting Data.

The heat of transition, the transition point, the heat of melting and the melting point were derived from the high temperature enthalpy data of King et al., loc. cit.

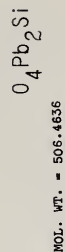
The melting point, 1746 $\pm$ 1°K, has also been quoted by S. J. Schneider, NBS Monograph **68**, "Compilation of the Melting Points of the Metal Oxides," October 10, 1963.

In the high temperature X-ray diffractometric studies, Perri et al., loc. cit., indicate that WO₃ undergoes a phase transition from monoclinic to orthorhombic at approximately 593°K and from orthorhombic to tetragonal at 933°K.

Heat of Sublimation.

The values of ΔH° at 298.15°K are calculated as the heat of sublimation of one mole of crystal to one mole of monomer, 1/2 mole of dimer, 1/3 mols of trimer and 1/4 mole of tetramer, respectively.

Lead Orthosilicate (Pb_2SiO_4)
(Crystal) Mol. Wt. = 506.4636



T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	0.000	0.000	INFINITE	6.198	-327.311	-327.311	INFINITE
100	17.636	17.210	69.708	5.250	-328.699	-320.263	699.901
200	27.239	32.672	47.489	2.963	-329.259	-311.554	340.434
298	32.740	44.654	44.654	0.000	-329.320	-302.839	221.976
300	32.800	44.857	44.655	0.061	-329.318	-302.825	220.488
400	34.330	55.794	44.655	3.951	-329.030	-298.574	146.480
500	39.140	63.212	48.610	7.301	-328.670	-285.051	124.590
600	41.430	70.561	51.669	11.335	-328.099	-276.377	100.665
700	43.030	77.077	54.862	15.564	-329.756	-267.428	83.491
800	44.020	82.313	57.982	19.821	-328.039	-258.574	70.636
900	44.450	86.733	60.940	24.048	-326.576	-248.576	59.584
1000	45.200	92.848	64.000	28.848	-327.673	-241.132	52.697
1100	45.600	97.175	66.822	33.380	-326.640	-232.540	46.199
1200	45.900	101.155	69.420	37.963	-325.782	-224.021	40.798
1300	46.300	104.856	72.097	42.773	-324.900	-215.577	36.240
1400	46.800	108.291	74.760	47.820	-324.000	-207.177	31.677
1500	47.000	111.552	76.918	51.907	-323.069	-198.680	28.977
1600	47.300	114.565	79.177	56.622	-322.133	-190.642	26.039
1700	47.570	117.441	81.344	61.365	-321.288	-182.343	23.441
1800	47.810	120.167	83.426	66.345	-320.429	-173.495	21.064
1900	48.030	122.752	85.426	71.568	-319.557	-164.529	18.864
2000	48.400	125.236	87.357	75.758	-318.682	-155.960	17.042

LEAD ORTHOSILICATE (Pb_2SiO_4)

(CRYSTAL)

$\Delta H^\circ_f 0 = -327.3 \pm 3.5 \text{ kcal. mole}^{-1}$

$\Delta H^\circ_f 298.15 = -329.3 \pm 3.5 \text{ kcal. mole}^{-1}$

$S^\circ_{298.15} = 44.654 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_m = 1016^\circ\text{K.}$

Heat of Formation.

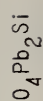
The heat of the reaction $2\text{PbO}(c) + \text{SiO}_2(c) \rightarrow \text{Pb}_2\text{SiO}_4(c)$ was reported by O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, Pergamon Press, New York (1958). This value for the heat of reaction of the oxides has been converted to the heat of formation using JANAF values for $\text{PbO}(c)$ (March 31, 1962) and for $\text{SiO}_2(c)$ (Dec. 31, 1962). The above $\Delta H^\circ_f 298.15 = -7.00 \pm 3.5 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

In the low temperature region ($53.07\text{--}298.15^\circ\text{K.}$) the C_p values are those determined by E. G. King, J. Am. Chem. Soc., 81, 799-800 (1959). Above 298.15°K. values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.07°K. using the Debye and Einstein functions $D(\frac{h\nu}{2kT}) + 2E(\frac{h\nu}{2kT}) + E(\frac{h\nu}{2kT})$ given by E. G. King, J. Am. Chem. Soc., 81, 799-800 (1959). The $S^\circ_{53.07} = 8.248 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

T_m was taken from Geller, Creamer and Bunting, J. Research Natl. Bureau of Standards, 13, 237 (1934).



Trilead Tetroxide (Pb_3O_4)
(Crystal) Mol. Wt. = 685.63

INTERIM TABLE

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	-0.070	-0.000	INFINITE	7.144	-173.373	-173.373	INFINITE
100	20.800	19.087	78.517	5.843	-174.867	-165.830	362.405
200	31.100	27.071	53.516	3.260	-175.362	-156.269	174.826
298	35.136	30.394	50.394	.000	-175.311	-147.943	107.943
300	35.150	30.411	50.395	.065	-175.308	-147.092	107.151
400	35.920	40.859	51.743	3.618	-174.133	-137.712	75.239
500	36.697	48.927	54.429	7.249	-174.983	-128.377	56.111
600	37.480	55.487	57.428	10.958	-174.856	-119.046	43.368
700	38.260	60.529	60.459	14.745	-174.233	-109.205	34.094
800	39.000	64.643	63.421	18.610	-174.127	-99.353	27.141
900	39.820	68.136	66.267	22.553	-177.954	-89.515	21.736
1000	40.600	71.562	68.988	26.574	-177.705	-79.699	17.417
1100	41.360	74.906	71.584	30.673	-177.381	-69.916	13.890
1200	42.100	78.169	74.104	34.850	-176.973	-60.166	10.956
1300	42.840	81.350	76.427	39.105	-176.490	-50.446	8.480
1400	43.720	84.471	78.681	43.438	-175.940	-40.773	6.365
1500	44.500	87.541	80.862	47.849	-175.323	-31.135	4.536
1600	45.280	90.568	82.947	52.338	-174.649	-21.545	2.943
1700	46.040	93.547	84.953	56.905	-173.913	-11.996	1.542
1800	46.840	96.480	86.887	61.550	-173.128	-2.498	.303
1900	47.620	99.365	88.754	66.273	-172.289	6.957	.800
2000	48.400	102.197	90.560	71.074	-171.397	16.366	1.769

March 31, 1962

TRILEAD TETROXIDE (Pb_3O_4) (Crystal)

Mol. Wt. = 685.63

$\Delta H^\circ_f 298.15 = -175.31 \pm 0.49$ kcal. mole⁻¹

$S^\circ_{298.15} = 50.4 \pm 1.6$ cal. deg.⁻¹ mole⁻¹

Heat of Formation. Calculated from $\Delta F^\circ_{298.15} = -147.27$ kcal. mole⁻¹ for the reaction: $3\text{Pb}(c) + 2\text{O}_2(g) = \text{Pb}_3\text{O}_4(c)$ given by R. W. Millar, J. Am. Chem. Soc., 51, 207 (1929).

Heat Capacity and Entropy. C_p (71.5° to 292.6°K.) reported by R. W. Millar, loc. cit. Above 298.15°K., heat capacity values were estimated by comparison with C_p values for the other lead oxides. The two heat capacity curves were joined smoothly at 298.15°K. by graphical extrapolation.

O_4Pb_3

O_4Pb_3

Zirconium Orthosilicate (ZrSiO₄)
(Crystal)

Mol. Wt. = 183.3036

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	0.000	INFINITE	3.562	-481.062	-481.062	INFINITE	INFINITE
100	7.513	11.889	22.058	2.034	-483.400	-483.400	106.415	106.415
200	17.513	22.058	2.034	-483.400	-483.400	-483.400	508.473	508.473
298	23.580	20.083	0.000	-483.736	-483.736	-483.736	334.874	334.874
300	23.600	20.229	0.044	-483.738	-483.738	-483.738	332.337	332.337
400	27.000	21.600	2.607	-483.740	-483.740	-483.740	241.238	241.238
500	30.100	23.019	5.489	-483.741	-483.741	-483.741	181.587	181.587
600	31.950	25.330	8.596	-483.721	-483.721	-483.721	156.174	156.174
700	33.180	27.742	11.895	-482.833	-482.833	-482.833	131.040	131.040
800	34.100	30.145	15.222	-482.402	-482.402	-482.402	112.206	112.206
900	34.720	32.488	18.664	-481.967	-481.967	-481.967	97.569	97.569
1000	35.200	34.749	22.161	-481.483	-481.483	-481.483	84.812	84.812
1100	35.550	36.919	25.700	-481.024	-481.024	-481.024	76.311	76.311
1200	35.780	38.997	29.267	-481.529	-481.529	-481.529	66.342	66.342
1300	35.890	40.985	32.851	-481.075	-481.075	-481.075	61.599	61.599
1400	35.900	42.886	36.443	-480.575	-480.575	-480.575	57.826	57.826
1500	35.900	44.705	40.041	-480.220	-480.220	-480.220	50.926	50.926
1600	36.000	46.447	43.641	-479.820	-479.820	-479.820	46.455	46.455
1700	36.000	48.116	47.241	-491.543	-491.543	-491.543	42.587	42.587
1800	36.000	49.718	50.841	-491.143	-491.143	-491.143	39.079	39.079
1900	36.000	51.256	54.441	-490.762	-490.762	-490.762	35.941	35.941
2000	36.000	52.735	58.041	-490.389	-490.389	-490.389	33.120	33.120
2100	36.000	54.159	61.641	-490.052	-490.052	-490.052	30.569	30.569
2200	36.000	55.532	65.241	-490.629	-490.629	-490.629	28.235	28.235
2300	36.000	56.856	68.841	-490.324	-490.324	-490.324	26.100	26.100
2400	36.000	58.136	72.441	-490.031	-490.031	-490.031	24.143	24.143
2500	36.000	59.373	76.041	-489.750	-489.750	-489.750	22.343	22.343
2600	36.000	60.570	79.641	-489.477	-489.477	-489.477	20.684	20.684
2700	36.000	61.730	83.241	-489.216	-489.216	-489.216	19.149	19.149
2800	36.000	62.854	86.841	-489.065	-489.065	-489.065	17.723	17.723
2900	36.000	63.946	90.441	-489.224	-489.224	-489.224	16.397	16.397
3000	36.000	65.006	94.041	-489.493	-489.493	-489.493	15.159	15.159

0.4SiZr

MOL. WT. = 183.3036

ZIRCONIUM ORTHOSILICATE (ZrSiO₄)
(CRYSTAL)

$\Delta H_f^\circ 0 = -481.1 \pm 0.7$ kcal. mole⁻¹
 $\Delta H_f^\circ 298.15 = -483.7 \pm 0.7$ kcal. mole⁻¹
 $S^\circ_{298.15} = 20.083 \pm 0.3$ cal. deg.⁻¹ mole⁻¹
 $T_d = 1811^\circ\text{K}.$

Heat of Formation.

The $\Delta H_f^\circ 298.15$ was calculated from the $\Delta H_f^\circ 298.15$ of its constituent oxides $\text{ZrO}_2(\text{c}) + \text{SiO}_2(\text{c}) = \text{ZrSiO}_4(\text{c})$ and from the $\Delta H_f^\circ 298.15$ of $\text{ZrO}_2(\text{c})$ (June 30, 1961) and $\text{SiO}_2(\text{c})$ (Dec. 31, 1962) in JANAF tables. The $\Delta H_f^\circ 298.15 = -4.736$ kcal. mole⁻¹ was based on the free energy of formation of its constituent oxides at the decomposition temperature 1811°K.

Heat Capacity and Entropy.

At low temperatures C_p were used from K. K. Kelley, J. Am. Chem. Soc. 63, 2750 (1941). From 298-940°K. C_p was calculated by using the J. P. Coughlin and E. O. King equation $C_p = 31.48 + 3.92 \times 10^{-5} T - 8.08 \times 10^{-8} T^2$, J. Am. Chem. Soc., 72, 2282 (1950), which joined smoothly with the low temperature data. Above 940°K. the data was estimated by extending the curve smoothly. The entropy was calculated at 52.7°K. using the Debye and Einstein functions $D(\frac{h\nu}{kT}) + 2E(\frac{h\nu}{kT}) + 2E(\frac{h\nu}{kT})$ given by K. K. Kelley, J. Am. Chem. Soc., 63, 2750 (1941). $S^\circ_{52.7} = 0.65404$ cal. deg.⁻¹ mole⁻¹.

Temperature of Decomposition.

T_d is the temperature at which $\Delta F^\circ = 0$ for the reaction $\text{ZrSiO}_4(\text{c}) \rightarrow \text{ZrO}_2(\text{c}) + \text{SiO}_2(\text{c})$. $T_d = 1811^\circ\text{K}.$ was taken from C. E. Curtis and H. G. Sowman, J. Am. Soc., 36, 190 (1953).

0.4SiZr

QFM = 223.697

(CRYSTAL)

TRITITANIUM PENTOXIDE, ALPHA (α -Ti₃O₅)

$\Delta H_f^\circ = -584.63 \pm 0.7$ kcal/mol
 $\Delta H_f^\circ(298.15) = -587.75 \pm 3.0$ kcal/mol
 $\Delta H^\circ = [2.81]$ kcal/mol

$S_{298.15}^\circ = 30.935$ gibbs/mol
 $T_m = 450^\circ\text{K}$

Heat of Formation

The enthalpy change, $\Delta H_f^\circ(298) = -49.65 \pm 0.05$ kcal/mol, for the reaction $\text{Ti}_3\text{O}_5(\text{c}) + 1/2 \text{O}_2(\text{g}) = 3 \text{TiO}_2(\text{rutile})$ has been measured by O. L. Humphrey, J. Am. Chem. Soc. 73, 1587 (1951), using combustion bomb calorimetry. Based on the reported $\Delta H_f^\circ(298)$ and $\Delta H_f^\circ(298)(\text{rutile}) = -225.8$ kcal/mol, the value of $\Delta H_f^\circ(298)$ for $\text{Ti}_3\text{O}_5(\text{a})$ is derived as -587.75 ± 0.7 kcal/mol. A value of -587.0 ± 1.0 kcal/mol was obtained by S. M. Araya, M. P. Morozova, and E. Vol'f, Russ. J. Inorg. Chem. (English transl.) 2, 16 (1957), from a similar calorimetric study on Ti-O compounds of various compositions. The latter authors observed that their combustion product had a composition of about $\text{TiO}_{1.9750}$ so they applied an approximate correction to their data. Presumably, the rutile in Humphrey's combustion was also deficient in oxygen, but we have not attempted to make a correction (see TiO_2 (rutile) table for further details).

Heat Capacity and Entropy

Low temperature heat capacities, 53.1 - 236.6°K, were measured by C. H. Shomate, J. Am. Chem. Soc. 68, 310 (1946). High temperature enthalpies, 360.5 - 1340°K, were determined by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), by use of drop calorimetry. The heat capacities, 298 - 450°K, derived by Naylor are too high to join smoothly at 298°K with the low temperature data, hence they are not used. The Cp values above 296.6°K are obtained by graphical extrapolation of the adopted low temperature Cp.

The samples used by both Shomate and Naylor were prepared by reduction of titanium dioxide with carbon at 1350°C. Analysis of the product gave 99.1% Ti₃O₅, 0.2% TiO and 0.7% SiO₂. X-ray lines from the sample were weak and fuzzy but no data were given. Thus comparison with subsequent studies is not possible. According to Naylor, the enthalpy measurements showed a transition at about 450°K. When Ti₃O₅ was heated above this temperature, it did not return to the original state on cooling. Enthalpies were then systematically higher by up to 10 percent. The change in the enthalpy curve seemed to depend upon both the temperature and time of heating above Tt. Regrinding was the only method found for returning the sample to its original state. Possible explanations are presented in the Transition Data.

S_{298}° is calculated from $S_{50}^\circ = 0.88$ eu using the low temperature Cp reported by Shomate, loc. cit. It is pertinent to ask if there should be entropy contributions due to vacancies in the crystal lattice or to spin-magnetic effects below 50°K. S. Asbrink and A. Megnell, Acta Cryst. 13, 575 (1959), showed that the X-ray crystallographic density is greater than the experimental density by less than 1%, thus the entropy due to the presence of vacancies is considered to be negligible. We also assume that any spin-magnetic entropy is related to the $\alpha \rightarrow \beta$ transition, by analogy with the $\alpha \rightarrow \beta$ transition of Ti₂O₃. Consistent with this assumption is the observation that the entropy of β -Ti₃O₅ is already larger than the sum of entropies for β -Ti₂O₃ and TiO₂.

Transition Data

See Ti₃O₅(β) table.

Dec. 31, 1960; Mar. 31, 1967

Trititanium Pentoxide, Beta (β -Ti₃O₅)
(Crystal) GFW = 223.697

T, °K	C _p ^a	gibbs/mol S ^b - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K _p
0						
100						
200						
298	44.165	35.913	0.00	-585.354	-552.983	405.347
300						
300	44.180	36.186	35.914	-585.338	-552.783	402.702
400	45.728	37.456	4.082	-585.311	-552.584	396.465
500	47.788	39.130	9.679	-585.278	-552.385	382.533
600	46.593	67.550	44.720	-583.004	-521.164	189.834
700	47.397	74.792	48.511	-582.308	-510.912	159.514
800	48.201	81.494	52.202	-581.612	-500.660	139.651
900	49.005	87.796	55.893	-580.916	-490.408	120.185
1000	49.809	92.102	59.584	-580.220	-480.156	105.051
1100	50.614	96.407	63.275	-579.524	-470.722	93.524
1200	51.418	101.326	66.966	-578.828	-460.709	83.906
1300	52.222	105.733	70.657	-578.132	-450.694	75.757
1400	53.026	110.140	74.348	-577.436	-440.679	68.608
1500	53.830	113.559	78.039	-576.740	-430.660	62.747
1600	54.634	116.978	81.730	-576.044	-420.649	57.474
1700	55.438	119.995	85.421	-575.348	-410.634	52.830
1800	56.242	123.012	89.112	-574.652	-400.619	48.739
1900	57.046	126.029	92.803	-573.956	-390.604	45.027
2000	57.850	129.046	96.494	-573.260	-381.322	41.669
2100	58.654	131.937	100.185	-572.564	-371.006	38.611
2200	59.458	134.684	103.876	-571.868	-360.749	35.837
2300	60.262	137.295	107.567	-571.172	-350.532	33.345
2400	61.066	139.806	111.258	-570.476	-340.315	31.119
2500	61.872	142.436	114.949	-569.780	-330.268	28.872

TRITITANIUM PENTOXIDE, BETA (β -Ti₃O₅) (CRYSTAL)

GFW = 223.697

$$\Delta H_{298.15}^{\circ} = [-585.354] \text{ kcal/mol}$$

$$\Delta H^{\circ} = [2.81] \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = [35] \text{ kcal/mol}$$

$$S_{298.15}^{\circ} = [35.913] \text{ gibbs/mol}$$

$$T_f = 450^{\circ}\text{K}$$

$$T_m = 2047 \pm 10^{\circ}\text{K}$$

Heat of Formation

The value of $\Delta H_{298}^{\circ}(\beta)$ is obtained from $\Delta H_{298}^{\circ}(\alpha)$ by adding ΔH° and the difference between $H_{450}^{\circ} - H_{298}^{\circ}$ for Ti₃O₅(α) and Ti₃O₅(β).

Heat Capacity and Entropy

The heat capacities are derived from the enthalpy data, 452 - 1340°K, measured by B. P. Naylor, J. Am. Chem. Soc. **69**, 1077 (1946). The Cp values beyond the experimental range are obtained by linear extrapolation.

The S_{298}° is calculated in a manner analogous to that of the heat of formation. For a discussion pertaining to the entropy uncertainty, see the Transition Data.

Transition Data

Tt and ΔH° are based on the β -phase enthalpy data of Naylor, loc. cit., and on the selected enthalpies of the α -phase. ΔH° is thus subject to an unknown error since the β -phase enthalpies correspond to a somewhat different state than do the α -phase values (see α -Ti₃O₅). The enthalpy data also show unusual scatter in the range 452-530°K. Because of these uncertainties, the more recent X-ray studies are summarized below.

S. Abrink and A. Magnelli, *Acta Cryst.* **12**, 575 (1959), found that monoclinic α -Ti₃O₅ transforms to a β form of the ansoovite type (slightly deformed pseudo-brookite) at about 393°K, i. e., over 50° lower than Naylor's value. P. G. Wahlbeck and P. W. Gilles, *J. Am. Ceram. Soc.* **49**, 180 (1966), confirmed that the transition occurs between 373 and 475°K but did not measure the temperature accurately. In both studies only the α form was observed on cooling the samples to room temperature. Abrink and Magnelli noted the following in X-ray studies at elevated temperatures. In a wide region around 393°K, the powder reflections of the unstable phase disappeared, while the general characteristics of the stable one formed within considerably less than one hour. Complete development of some reflections of the stable phase took several hours, while some lines appeared with anomalous intensities at temperatures approaching the transformation point, thus "forewarning" the change of structure. Small contents of Fe or Mg stabilized the β form at room temperature.

These observations suggest that the transformation may be considered as a "permt" which occurs over a range of temperatures. The anomalous enthalpy data observed by Naylor may arise from slow completion of the transition and from stabilization of part of the sample in the β form due to impurities. The latter suggestion is consistent with Naylor's observation that regrounding returned the sample to its normal α form. Correction of the enthalpy data based on these assumptions does not appear practical. Pending new data for a well-characterized sample, we must rely on the results of Naylor.

Melting Data.

P. G. Wahlbeck and P. W. Gilles, *J. Am. Ceram. Soc.* **49**, 180 (1966), found that Ti₃O₅ melts incongruently at 2047 $\pm$ 10°K which is adopted. ΔH_m° is estimated assuming that at T_m the entropy of melting is 2 eu/g-atom. Melting points of 2175 and 1983°K were reported by R. DeVries and R. Roy, *Bull. Am. Ceram. Soc.* **33**, 370 (1954), and G. Brauer and M. Litke, *J. Inorg. Nucl. Chem.* **16**, 67 (1960), respectively.

Trititanium Pentoxide (Ti₃O₅)
(Liquid) GFW = 223.697

T, °K	C _p ^a	S ^b	-(C _p ^a - H ₂₉₈ °)/T	H ^c - H ₂₉₈ °	ΔH ^c	ΔG ^c	Log K _p
0							
100							
200	56.000	38.679	38.679	.000	- 560.754	- 529.208	387.920
298							
300	56.000	38.680	38.680	.104	- 560.716	- 529.012	385.385
400	56.000	38.025	40.876	5.704	- 558.747	- 518.744	283.428
500	56.000	35.135	45.024	11.304	- 556.913	- 508.959	222.466
600	56.000	32.631	49.669	16.904	- 555.198	- 499.532	181.954
700	56.000	30.481	54.674	22.504	- 553.624	- 489.855	141.934
800	56.000	28.541	59.981	28.104	- 552.192	- 480.355	101.924
900	56.000	26.787	65.487	33.704	- 550.769	- 472.702	61.924
1000	56.000	25.200	71.144	39.304	- 549.329	- 464.095	21.924
1100	56.000	23.768	76.993	44.904	- 547.893	- 455.406	9.520
1200	56.000	22.463	82.941	50.504	- 546.454	- 446.631	1.520
1300	56.000	21.268	88.989	56.104	- 545.014	- 437.770	73.730
1400	56.000	20.161	95.179	61.704	- 543.574	- 428.829	67.187
1500	56.000	19.124	101.484	67.304	- 542.134	- 419.809	61.484
1600	56.000	18.143	107.899	72.904	- 540.694	- 410.713	56.483
1700	56.000	17.213	114.419	78.504	- 539.254	- 401.547	51.482
1800	56.000	16.331	121.041	84.104	- 537.814	- 392.311	46.481
1900	56.000	15.494	127.761	89.704	- 536.374	- 383.005	41.480
2000	56.000	14.704	134.579	95.304	- 534.934	- 373.629	36.479
2100	56.000	13.956	141.494	100.904	- 533.494	- 364.183	31.478
2200	56.000	13.243	148.504	106.504	- 532.054	- 354.667	26.477
2300	56.000	12.561	155.604	112.104	- 530.614	- 345.074	21.476
2400	56.000	11.914	162.799	117.704	- 529.174	- 335.414	16.475
2500	56.000	11.304	170.084	123.304	- 527.734	- 325.689	11.474
2600	56.000	10.724	177.461	128.904	- 526.294	- 315.899	6.473
2700	56.000	10.174	184.934	134.504	- 524.854	- 306.049	1.472
2800	56.000	9.649	192.504	140.104	- 523.414	- 296.139	27.645
2900	56.000	9.144	200.174	145.704	- 521.974	- 286.164	22.644
3000	56.000	8.654	207.944	151.304	- 520.534	- 276.124	17.643
3100	56.000	8.179	215.804	156.904	- 519.094	- 266.024	12.642
3200	56.000	7.719	223.754	162.504	- 517.654	- 255.864	7.641
3300	56.000	7.274	231.799	168.104	- 516.214	- 245.639	2.640
3400	56.000	6.844	239.934	173.704	- 514.774	- 235.344	16.807
3500	56.000	6.424	248.164	179.304	- 513.334	- 225.004	15.806
3600	56.000	6.014	256.484	184.904	- 511.894	- 214.614	14.814
3700	56.000	5.614	264.899	190.504	- 510.454	- 204.164	13.822
3800	56.000	5.224	273.404	196.104	- 509.014	- 193.654	12.830
3900	56.000	4.844	281.999	201.704	- 507.574	- 183.084	11.838
4000	56.000	4.474	290.684	207.304	- 506.134	- 172.454	10.846

Mar. 31, 1967

OPM = 223.697

(LIQUID)

TRITITANIUM PENTOXIDE (Ti₃O₅)

ΔH_{298.15}^o = [-560.754] kcal/mol

ΔH_m^o = [33] kcal/mol

S_{298.15}^o = [38.679] gibbs/mol

T_m = 2047 ± 10°K

Heat of Formation

The ΔH_{298.15(1)}^o is obtained from ΔH_{298.15(β)}^o by adding ΔH_m^o and the difference between H₂₀₄₇^o - H₂₉₈^o for Ti₃O₅(β) and Ti₃O₅(1).

Heat Capacity and Entropy

The heat capacity is estimated on the basis of 7.0 gibbs/g-atom. S₂₉₈^o is obtained in a manner analogous to that of the heat of formation.

Melting Data

See Ti₃O₅(β) table for details.

Diphosphorus Trioxide, Dimeric (Ideal Gas) Mol. Wt. = 219.90 INTERIM TABLE

T. °K.	C _p ^o	S ^o	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	INFINITE	-5.534	-508.401	-508.401	INFINITE
100	11.239	59.176	105.919	-4.674	-502.908	-502.908	1099.031
200	24.210	79.884	85.432	-2.910	-495.133	-495.133	541.051
298	34.402	82.584	82.584	∞	-486.831	-486.831	356.840
300	34.556	82.798	82.585	3.064	-486.671	-486.671	354.523
400	40.338	93.386	86.954	8.216	-469.185	-469.185	265.071
500	44.319	103.386	86.954	15.131	-451.608	-451.608	194.323
600	47.096	111.902	90.417	12.891	-431.608	-431.608	140.992
700	48.789	119.444	94.036	17.786	-409.557	-409.557	106.766
800	50.136	126.129	97.640	22.881	-383.656	-383.656	84.495
900	51.236	132.079	100.417	28.181	-355.251	-355.251	64.950
1000	52.094	137.752	104.543	33.209	-324.090	-324.090	47.297
1100	52.696	142.789	107.794	38.495	-288.894	-288.894	31.343
1200	53.085	147.427	110.506	43.825	-253.540	-253.540	17.285
1300	53.793	151.720	113.482	49.189	-218.236	-218.236	8.894
1400	54.384	155.742	115.754	54.596	-182.942	-182.942	4.286
1500	54.845	159.451	118.456	59.966	-147.677	-147.677	1.958
1600	54.406	162.958	122.065	65.428	-112.452	-112.452	1.025
1700	54.544	166.260	124.568	70.876	-87.271	-87.271	0.693
1800	54.561	169.381	126.972	76.336	-62.100	-62.100	0.437
1900	54.484	172.332	129.284	81.814	-36.935	-36.935	0.240
2000	54.845	175.150	131.506	87.288	-11.732	-11.732	0.101
2100	54.918	177.828	133.649	92.776	3.546	3.546	0.025
2200	54.981	180.384	135.716	98.271	18.894	18.894	0.000
2300	55.037	182.870	137.711	103.772	34.236	34.236	0.000
2400	55.087	185.297	139.634	109.284	39.576	39.576	0.000
2500	55.129	187.673	141.507	114.789	44.916	44.916	0.000
2600	55.168	189.986	143.315	120.304	50.256	50.256	0.000
2700	55.202	192.268	145.067	125.822	55.596	55.596	0.000
2800	55.233	194.576	146.776	131.344	60.936	60.936	0.000
2900	55.261	196.819	148.449	136.869	66.276	66.276	0.000
3000	55.289	199.002	150.092	142.396	71.616	71.616	0.000
3100	55.308	199.302	151.584	147.926	76.956	76.956	0.000
3200	55.328	201.058	153.103	153.458	82.296	82.296	0.000
3300	55.347	202.761	154.582	158.991	87.636	87.636	0.000
3400	55.366	204.414	156.025	164.527	92.976	92.976	0.000
3500	55.380	206.019	157.429	170.064	98.316	98.316	0.000
3600	55.394	207.579	158.801	175.603	103.656	103.656	0.000
3700	55.407	209.097	160.139	181.143	108.996	108.996	0.000
3800	55.419	210.575	161.447	186.684	114.336	114.336	0.000
3900	55.431	212.018	162.726	192.221	119.676	119.676	0.000
4000	55.441	213.418	163.975	197.760	125.016	125.016	0.000
4100	55.451	214.787	165.198	203.315	130.356	130.356	0.000
4200	55.460	216.123	166.395	208.861	135.696	135.696	0.000
4300	55.468	217.429	167.566	214.407	141.036	141.036	0.000
4400	55.476	218.704	168.719	219.950	146.376	146.376	0.000
4500	55.484	219.951	169.853	225.492	151.716	151.716	0.000
4600	55.490	221.170	170.942	231.031	157.056	157.056	0.000
4700	55.497	222.364	172.023	236.600	162.396	162.396	0.000
4800	55.503	223.532	173.084	242.159	167.736	167.736	0.000
4900	55.509	224.684	174.125	247.717	173.076	173.076	0.000
5000	55.514	225.798	175.146	253.282	178.416	178.416	0.000
5100	55.519	226.897	176.152	258.803	183.756	183.756	0.000
5200	55.524	227.976	177.138	264.356	189.096	189.096	0.000
5300	55.528	229.033	178.107	269.908	194.436	194.436	0.000
5400	55.532	230.071	179.060	275.461	199.776	199.776	0.000
5500	55.536	231.090	179.997	281.015	205.116	205.116	0.000
5600	55.540	232.091	180.918	286.568	210.456	210.456	0.000
5700	55.544	233.074	181.824	292.123	215.796	215.796	0.000
5800	55.547	234.040	182.716	297.677	221.136	221.136	0.000
5900	55.550	234.989	183.599	303.230	226.476	226.476	0.000
6000	55.553	235.923	184.459	308.787	231.816	231.816	0.000

Dec. 31, 1960; Sept. 30, 1961; Dec. 31, 1962

DIPHOSPHORUS TRIOXIDE, DIMERIC (P₂O₅)

(Ideal Gas)

Mol. Wt. = 219.90

ΔH_f^o 298.15 = -512.5 ± 0 kcal. mole⁻¹

S_{298.15}^o = 82.6 cal. deg.⁻¹ mole⁻¹

Point group = T_d

Vibrational Frequencies and Degeneracies

ω cm.⁻¹ ω cm.⁻¹

613 (1) 485 (2)

613 (1) 643 (3)

302 (3) 919 (3)

370 (3) 1029 (2)

407 (3) 636 (3)

Bond Lengths and Angles:

P-O-P angle = 127.5 ± 1.0° P-O distance = 1.65 ± 0.02 Å

Product of Moments of Inertia: I_AI_BI_C = 4.632 X 10⁻¹¹² g.³ cm.⁶

Heat of Formation. ΔH_f^o 298.15 for liquid P₂O₅ was measured by W. E. Koerner and P. Daniela, J. Chem. Phys. 20, 113 (1952). The measurement was made by burning samples of red phosphorus in nitric oxide in a flow calorimeter. Calculation of the heat of formation of the gas was made using ΔH_f^o 298.15 = 11.46 kcal. mole⁻¹ as reported by T. D. Farr, Tenn. Valley Authority, Chem. Engr. Report No. 6 (1950).

Heat Capacity and Entropy. The vibrational levels are from the Raman data of H. Gerding, H. van Brederode and H. C. J. de Decker, Rec. Trav. Chim. 52, 549 (1942), and infra-red spectra data of T. A. Sidorov and N. N. Sobolev, Optics and Spect. 2, 710 (1957). Bond lengths and angles are from electron diffraction data by G. C. Hampson and A. J. Stosick, J. Am. Chem. Soc. 80, 1814 (1958).

Tungsten Trioxide, Dimeric (W₂)₂
(Ideal Gas) GFW = 463.6964

TUNGSTEN TRIOXIDE, DIMERIC (W₂)₂
(IDEAL GAS)

O₆W₂

OFW = 463.6964

Point Group [D_{2h}]
S_{298.15} = [99.3] gibbs/mol
Round State Quantum Weight = [1]
ΔH_f⁰ = -276.8 kcal/mol
ΔH_f^{298.15} = -278.2 ± 10 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm⁻¹
[600] (4)
[300] (8)
[172] (6)
Bond Distance: W-O = [1.81] Å
Bond Angle: O-W-O = [109.47°], W-O₂bridge-W = [70.53°]
Product of the Moments of Inertia: I_AI_BI_C = [5.917 × 10⁻¹¹²] g³ cm⁶ σ = [4]

Heat of Formation.

The adopted value, ΔH_f²⁹⁸ (W₂O₆, g) = -278.2 kcal/mol, was reduced from ΔH_f¹⁴⁵⁰ = -272.5 kcal/mol, reported by R. J. Ackermann and E. O. Rauh, J. Phys. Chem. 67, 2596 (1963). They have studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600°K by mass spectrometry, mass effusion, and X-ray diffraction, and also have determined ΔH_f⁰ (W₂O₆, g) = -272,500 + 54,98T (cal/mol) from partial pressure measurements over the W-W₂O₃(c) system.

J. E. Battles, Ph. D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," The Ohio State University, 1964, has also studied the same system in the temperature range from 1418 to 1527° K. Third law calculation of the partial pressure data gives ΔH_f²⁹⁸ = 144.0 kcal/mol for 3 W₂O₃(c) = W₂O₆(g) + W(c) which yields ΔH_f²⁹⁸ (W₂O₆, g) = -278.8 kcal/mol, using all JANAP functions. This value is in good agreement with the value adopted.

J. H. Norman and H. G. Staley, J. Chem. Phys. 43, 3804 (1965), have obtained ΔH_f¹⁸⁰⁰ = -127 kcal/mol for 2 W₂O₃(g) = W₂O₆(g) by mass spectrometric study of the vapor over W₂O₃ dissolved in CaO-Al₂O₃-SiO₂. The value of ΔH_f⁰ was determined by the second law method from ion intensities and leads to ΔH_f²⁹⁸ (W₂O₆, g) = -275 kcal/mol, using all JANAP functions (dated Sept. 30, 1966). The absolute pressure values reported by Norman and Staley appear to be quite inconsistent with the JANAP functions, since they lead to ΔH_f²⁹⁸ (W₂O₆, g) = -246 kcal/mol by the third law method.

Investigator	Chemical Reaction	Temperature (°K)	ΔH _f ²⁹⁸ (kcal/mol)	Drift (eu)	ΔH _f ²⁹⁸ (W ₂ O ₆ , g) (kcal/mol)
Ackermann & Rauh	3 W ₂ O ₃ (c) = W ₂ O ₆ (g) + W(c)	1300-1600	144.54	0.01	-278.2*
Battles	3 W ₂ O ₃ (c) = W ₂ O ₆ (g) + W(c)	1418-1527	142.66	0.85 ± 0.40	-278.8*
Norman & Staley	2 W ₂ O ₃ (g) = W ₂ O ₆ (g)	1700-1900	-135	-106	-275 **

* Third law value adopted in calculation.
** Second law value adopted in calculation.

Heat Capacity and Entropy.

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 600 cm⁻¹ (4), 300 cm⁻¹ (8), and 172 cm⁻¹ (6) in order to give the entropy at 1450°K, S₁₄₅₀ = 164.66 eu, corresponding to ΔS_f¹⁴⁵⁰ = 54.98 eu which was reported by Ackermann and Rauh. The adopted value, S₂₉₈ (W₂O₆, g) = 99.3 eu, was reduced from the entropy at 1450°K, using JANAP functions. Second law calculation of the partial pressure data of Battles gives ΔS_f¹⁴⁷⁰ = 63.5 eu for 3 W₂O₃(c) = W₂O₆(g) + W(c). This yields S₂₉₈ (W₂O₆, g) = 97.9 eu.

The molecular configuration for W₂O₆(g) was estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and two of these tetrahedra share a common oxygen edge to form a planar four-member ring. The bond distance W-O was estimated as 1.81 Å and the bond angle O-W-O = 109.47° and W-O₂bridge-W = 70.53°. The three principal moments of inertia are: I_A = 3.481 × 10⁻³⁷, I_B = 1.363 × 10⁻³⁷ and I_C = 1.247 × 10⁻³⁷ g cm².

Sept. 30, 1966

O₆W₂

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH _f	ΔG _f	Log Kp
0	-0.00	-0.00	INFINITE	-7.462	-276.750	-276.750	INFINITE
100	19.445	67.918	127.934	-6.002	-271.907	-271.907	594.231
200	31.427	85.631	102.516	-3.377	-278.416	-265.586	290.219
298	36.726	99.298	99.298	-0.000	-278.200	-259.319	190.086
300	36.793	99.526	99.299	.068	-278.193	-259.203	188.829
400	40.814	119.469	103.649	7.910	-277.4057	-246.833	107.491
500	41.662	126.990	106.930	12.036	-276.418	-240.849	87.729
600	42.165	133.451	110.268	16.288	-275.802	-234.968	73.360
700	42.515	139.196	113.527	20.453	-275.227	-229.159	62.602
800	42.742	144.242	115.742	24.542	-274.682	-223.582	53.602
1000	42.937	148.663	119.630	29.013	-274.192	-217.783	47.557
1100	43.069	152.742	122.457	33.314	-273.736	-212.170	42.154
1200	43.171	156.494	125.139	37.626	-273.318	-206.590	37.625
1300	43.251	159.953	127.786	41.947	-272.940	-201.045	33.799
1400	43.311	163.141	130.311	46.276	-272.602	-195.546	30.461
1500	43.366	166.151	132.411	50.610	-272.292	-190.034	27.688
1600	43.408	168.951	134.068	54.948	-272.023	-184.559	25.210
1700	43.443	171.583	135.706	59.291	-271.788	-179.097	23.025
1800	43.472	174.057	137.214	63.637	-271.583	-173.652	21.084
1900	43.497	176.400	138.600	67.986	-271.406	-168.226	19.361
2000	43.519	178.650	140.000	72.336	-271.251	-162.817	17.789
2100	43.537	180.774	141.425	76.689	-271.231	-157.361	16.377
2200	43.553	182.800	142.962	81.043	-271.191	-151.946	15.094
2300	43.567	184.756	144.506	85.397	-271.181	-146.525	13.923
2400	43.579	186.555	146.066	89.752	-271.161	-141.104	12.852
2500	43.590	188.370	150.774	94.115	-271.280	-135.684	11.861
2600	43.600	190.079	152.205	98.475	-271.397	-130.251	10.949
2700	43.608	191.775	153.608	102.835	-271.557	-124.820	10.103
2800	43.615	193.411	155.027	107.196	-271.783	-119.379	9.318
2900	43.621	194.996	156.383	111.560	-272.066	-113.938	8.582
3000	43.629	196.521	157.680	115.924	-272.503	-108.466	7.902
3100	43.634	197.751	158.950	120.284	-273.029	-102.994	7.261
3200	43.640	199.137	160.184	124.648	-273.687	-97.505	6.659
3300	43.644	200.750	161.385	128.948	-274.489	-91.989	6.092
3400	43.648	202.596	162.550	133.196	-275.436	-86.450	5.550
3500	43.652	203.668	163.693	137.442	-276.506	-80.863	5.030
3600	43.656	204.278	164.804	142.107	-277.997	-75.256	4.566
3700	43.659	205.474	165.887	146.473	-279.289	-69.509	4.106
3800	43.662	206.638	166.944	150.839	-280.578	-63.368	3.645
3900	43.665	207.770	167.976	155.196	-281.866	-57.185	3.179
4000	43.668	208.878	168.995	159.572	-283.155	-51.089	2.707
4100	43.670	209.956	169.971	163.939	-284.503	-44.927	2.335
4200	43.672	211.009	170.936	168.306	-285.827	-38.767	2.017
4300	43.674	212.036	171.880	172.673	-287.100	-32.583	1.656
4400	43.676	213.040	172.801	177.034	-288.399	-26.386	1.256
4500	43.678	214.022	173.709	181.408	-289.644	-20.227	.982
4600	43.680	214.982	174.596	185.776	-290.902	-14.020	.666
4700	43.681	215.921	175.465	190.144	-292.164	-7.816	.363
4800	43.683	216.851	176.318	194.513	-293.428	-1.606	.073
4900	43.685	217.764	177.156	198.882	-294.694	4.609	.000
5000	43.686	218.624	177.975	203.249	-295.962	10.829	.473
5100	43.687	219.489	178.780	207.618	-297.232	17.070	.731
5200	43.688	220.338	179.571	211.987	-298.502	23.297	.979
5300	43.689	221.160	180.348	216.356	-299.768	29.562	1.219
5400	43.690	221.960	181.100	220.725	-301.031	35.869	1.452
5500	43.691	222.788	181.862	225.094	-302.292	42.182	1.672
5600	43.692	223.576	182.600	229.463	-303.552	48.439	1.886
5700	43.693	224.349	183.326	233.832	-304.809	54.609	2.094
5800	43.694	225.109	184.000	238.201	-306.068	60.708	2.295
5900	43.695	225.849	184.653	242.570	-307.324	66.731	2.489
6000	43.695	226.590	185.433	246.940	-308.579	72.671	2.689

Tritungsten Octaoxide (W_3O_8)
(Ideal Gas) $Q_F W = 679.5452$

$O_8 W_3$

T, °K	C_p	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log K_p
0	+0.00	INFINITE	INFINITE	- 9.552	- 406.385	- 406.385	INFINITE
100	26.940	75.456	156.609	- 8.115	- 408.192	- 388.491	870.901
200	42.309	99.703	122.349	- 4.529	- 408.830	- 384.488	428.488
298	49.301	118.036	118.036	+0.00	- 408.700	- 378.458	277.425
300	49.398	118.341	118.037	- 0.091	- 408.694	- 378.282	275.578
400	53.445	133.157	120.029	5.251	- 408.145	- 368.220	201.186
500	55.875	145.366	123.912	10.727	- 407.396	- 358.322	156.623
600	57.403	155.699	128.371	16.387	- 406.579	- 348.583	126.071
700	58.401	164.475	132.390	21.100	- 405.743	- 338.920	100.834
800	59.101	172.475	137.390	26.008	- 404.974	- 329.500	90.015
900	59.594	179.466	141.684	34.004	- 404.220	- 320.108	77.733
1000	59.956	185.765	145.783	39.982	- 403.512	- 310.798	67.925
1100	60.230	191.493	149.682	45.992	- 402.850	- 301.564	59.915
1200	60.408	196.588	153.428	52.079	- 402.232	- 292.408	52.915
1300	60.508	201.084	156.912	58.107	- 401.666	- 283.249	47.618
1400	60.741	206.084	160.265	64.147	- 401.145	- 274.142	42.799
1500	60.850	210.279	163.463	70.227	- 400.673	- 265.106	38.626
1600	60.939	214.009	166.511	76.316	- 400.249	- 256.082	34.979
1700	61.012	217.395	169.424	82.412	- 399.868	- 247.072	31.810
1800	61.076	220.469	172.218	88.518	- 399.550	- 238.106	28.910
1900	61.129	223.269	174.894	94.629	- 399.278	- 229.145	26.358
2000	61.175	225.835	177.463	100.744	- 399.058	- 220.196	24.062
2100	61.214	228.021	179.934	106.864	- 398.889	- 211.254	21.986
2200	61.248	230.077	182.305	112.987	- 398.781	- 202.332	20.060
2300	61.278	231.993	184.405	119.113	- 398.710	- 193.403	18.377
2400	61.304	233.001	186.817	125.242	- 398.714	- 184.466	16.798
2500	61.327	241.504	188.955	131.374	- 398.766	- 175.549	15.346
2600	61.348	243.010	191.023	137.508	- 398.868	- 166.613	14.005
2700	61.365	244.521	193.032	143.642	- 399.015	- 157.678	12.779
2800	61.383	246.048	194.965	149.781	- 399.313	- 148.729	11.609
2900	61.397	250.612	196.847	155.920	- 399.713	- 139.771	10.534
3000	61.411	252.694	198.674	162.060	- 400.253	- 130.799	9.529
3100	61.423	254.708	200.449	168.202	- 400.966	- 121.811	8.588
3200	61.434	256.658	202.185	174.347	- 401.757	- 112.817	7.719
3300	61.444	258.548	203.885	180.489	- 402.627	- 103.767	6.871
3400	61.453	260.383	205.491	186.633	- 403.584	- 94.658	6.085
3500	61.461	262.164	207.085	192.779	- 404.634	- 85.527	5.341
3600	61.469	263.896	208.639	198.926	- 405.803	- 76.343	4.635
3700	61.476	265.582	210.162	205.078	- 407.092	- 67.090	3.968
3800	61.483	267.221	211.635	211.221	- 408.506	- 57.826	3.378
3900	61.489	268.817	213.081	217.369	- 409.948	- 47.026	2.835
4000	61.494	270.374	214.494	223.519	- 406.416	- 37.052	2.024
4100	61.499	271.892	215.875	229.668	- 406.003	- 27.055	1.442
4200	61.503	273.371	217.221	235.818	- 405.615	- 17.038	0.958
4300	61.507	274.821	218.520	241.969	- 405.246	- 7.038	0.531
4400	61.511	276.236	219.784	248.120	- 404.894	- 2.960	+ .437
4500	61.517	277.618	221.113	254.272	- 404.559	- 12.991	+ .631
4600	61.520	278.970	222.356	260.424	- 404.239	- 23.042	- 1.095
4700	61.523	280.291	223.612	266.576	- 403.934	- 33.162	- 1.864
4800	61.527	281.589	224.770	272.728	- 403.644	- 43.267	- 2.637
4900	61.530	282.857	225.943	278.881	- 403.364	- 53.369	- 3.412
5000	61.533	284.100	227.093	285.034	- 403.095	- 63.465	- 4.195
5100	61.536	285.319	228.223	291.188	- 402.836	- 73.553	- 4.981
5200	61.539	286.511	229.333	297.341	- 402.586	- 83.641	- 5.771
5300	61.541	287.684	230.423	303.494	- 402.346	- 93.730	- 6.568
5400	61.543	288.836	231.494	309.646	- 402.116	- 103.818	- 7.371
5500	61.545	289.966	232.547	315.804	- 401.894	- 113.906	- 8.184
5600	61.547	291.075	233.582	321.959	- 401.681	- 123.994	- 8.995
5700	61.549	292.164	234.600	328.111	- 401.476	- 134.081	- 9.811
5800	61.551	293.234	235.600	334.268	- 401.279	- 144.167	- 10.641
5900	61.552	294.287	236.588	340.424	- 401.089	- 154.253	- 11.477
6000	61.554	295.321	237.558	346.579	- 400.905	- 164.340	- 12.322

Sept. 30, 1966

TRITUNGSTEN OCTAOXIDE (W_3O_8) (IDEAL GAS) $Q_F W = 679.5452$

Point Group [D_{2d}] $\Delta H^\circ_f = -406.4$ kcal/mol

$S^\circ_{298.15} = [118.0]$ gibbs/mol $\Delta H^\circ_{298.15} = -408.7 \pm 10$ kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[800] (6)	[199] (3)
[350] (4)	[150] (6)
[242] (8)	

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O = [109.47°]

Product of the Moments of Inertia: $I_A I_B I_C = [7.65 \times 10^{-111}] \text{ g}^3 \text{ cm}^6$

$\sigma = [4]$

Heat of Formation.

R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963), have studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600°K by mass spectrometry, mass effusion and X-ray diffraction, and also have determined the $\Delta H^\circ_f(W_3O_8, g) = -400,900 \pm 9054 \text{ T (cal/mol)}$ from partial pressure measurements over $W-WO_2 (c)$. The adopted value, $\Delta H^\circ_{298}(W_3O_8, g) = -408.7 \text{ kcal/mol}$, was reduced from $\Delta H^\circ_{1450}(W_3O_8, g) = -400.9 \text{ kcal/mol}$, using JANAF functions.

Investigator	Chemical Reaction	Temperature (°K)	ΔH°_{298} (kcal/mol)	Drift (eu)
Ackermann & Rauh	4 $WO_2(c) = W_3O_8(g) + W(c)$	1300-1600°	155.05	155.09
		2nd law	155.05	-0.04
		3rd law		-408.7

Heat Capacity and Entropy.

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm^{-1} (6), 350 cm^{-1} (4), 242 cm^{-1} (8), 199 cm^{-1} (3) and 150 cm^{-1} (6) in order to give the entropy at 1450°K, $S^\circ_{1450} = 208.18 \text{ eu}$, corresponding to $\Delta S^\circ_{1450} = -90.54 \text{ eu}$, which was reported by Ackermann and Rauh.

The molecular configuration for $W_3O_8(g)$ was estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, the three tetrahedra are connected by two common edges, and also the three tungsten atoms are in the same axis. The bond distance W-O was estimated as 1.81 Å and the bond angle $\angle OWO = 109.47^\circ$. The three principal moments of inertia are: $I_A = I_B = 4.060 \times 10^{-37}$ and $I_C = 4.641 \times 10^{-38} \text{ g cm}^2$.

$O_8 W_3$

T, °K	C _p ^o	gibbs/mol S ^o	-(C _p ^o - H ^o)/T	H ^o - H ^o 298	ΔH ^o	ΔG ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	26.614	76.183	161.416	- 9.546	- 480.652	- 470.652	INFINITE
200	44.668	100.980	125.233	- 8.545	- 482.822	- 471.121	1029.634
298	54.284	120.599	100.980	- 4.851	- 483.709	- 468.877	501.941
300	54.401	120.600	100.980	- 4.851	- 483.709	- 468.877	501.941
400	58.210	127.015	87.760	- 5.702	- 482.956	- 474.356	325.348
500	61.048	130.337	76.982	- 6.677	- 482.074	- 472.305	186.909
600	62.806	131.860	67.434	- 7.677	- 481.105	- 470.440	109.503
700	64.256	133.008	60.111	- 8.686	- 480.127	- 468.738	72.692
800	65.442	133.863	54.683	- 9.686	- 479.179	- 467.184	50.774
900	66.301	134.562	50.374	- 10.677	- 478.265	- 465.775	37.921
1000	66.871	135.055	46.854	- 11.654	- 477.397	- 464.387	27.037
1100	67.200	135.463	43.823	- 12.617	- 476.563	- 463.011	20.161
1200	67.428	135.798	41.171	- 13.563	- 475.767	- 461.653	15.276
1300	67.586	136.063	38.826	- 14.493	- 475.002	- 460.314	11.480
1400	67.680	136.263	36.746	- 15.410	- 474.267	- 458.990	8.648
1500	67.720	136.413	34.883	- 16.316	- 473.561	- 457.690	6.407
1600	67.720	136.518	33.213	- 17.209	- 472.883	- 456.413	4.652
1700	67.680	136.574	31.711	- 18.086	- 472.233	- 455.157	3.280
1800	67.600	136.587	30.346	- 18.946	- 471.603	- 453.921	2.235
1900	67.480	136.552	29.083	- 19.786	- 471.000	- 452.703	1.525
2000	67.320	136.475	27.909	- 20.603	- 470.423	- 451.503	1.000
2100	67.128	136.353	26.811	- 21.403	- 469.871	- 450.321	0.607
2200	66.900	136.183	25.774	- 22.183	- 469.343	- 449.157	0.380
2300	66.636	135.974	24.786	- 22.943	- 468.839	- 448.013	0.235
2400	66.336	135.726	23.843	- 23.683	- 468.359	- 446.889	0.150
2500	65.996	135.443	22.943	- 24.403	- 467.893	- 445.783	0.090
2600	65.620	135.126	22.083	- 25.103	- 467.441	- 444.693	0.050
2700	65.208	134.774	21.263	- 25.783	- 466.993	- 443.613	0.030
2800	64.756	134.393	20.483	- 26.443	- 466.559	- 442.543	0.010
2900	64.268	133.983	19.743	- 27.083	- 466.139	- 441.483	0.000
3000	63.740	133.543	19.043	- 27.693	- 465.723	- 440.433	0.000
3100	63.163	133.073	18.383	- 28.273	- 465.313	- 439.393	0.000
3200	62.536	132.583	17.753	- 28.823	- 464.903	- 438.363	0.000
3300	61.860	132.073	17.153	- 29.343	- 464.503	- 437.343	0.000
3400	61.136	131.543	16.583	- 29.833	- 464.103	- 436.333	0.000
3500	60.360	130.983	16.043	- 30.293	- 463.703	- 435.333	0.000
3600	59.536	130.403	15.533	- 30.723	- 463.303	- 434.343	0.000
3700	58.660	129.793	15.043	- 31.123	- 462.903	- 433.363	0.000
3800	57.736	129.153	14.573	- 31.493	- 462.503	- 432.393	0.000
3900	56.760	128.483	14.123	- 31.833	- 462.103	- 431.433	0.000
4000	55.736	127.783	13.693	- 32.143	- 461.703	- 430.483	0.000
4100	54.660	127.053	13.283	- 32.423	- 461.303	- 429.543	0.000
4200	53.536	126.293	12.893	- 32.673	- 460.903	- 428.613	0.000
4300	52.360	125.503	12.523	- 32.893	- 460.503	- 427.693	0.000
4400	51.136	124.683	12.173	- 33.083	- 460.103	- 426.783	0.000
4500	49.860	123.833	11.843	- 33.243	- 459.703	- 425.883	0.000
4600	48.536	122.953	11.533	- 33.373	- 459.303	- 424.993	0.000
4700	47.160	122.043	11.243	- 33.483	- 458.903	- 424.113	0.000
4800	45.736	121.103	10.973	- 33.573	- 458.503	- 423.243	0.000
4900	44.260	120.133	10.723	- 33.643	- 458.103	- 422.383	0.000
5000	42.736	119.143	10.493	- 33.693	- 457.703	- 421.533	0.000
5100	41.160	118.123	10.283	- 33.723	- 457.303	- 420.693	0.000
5200	39.536	117.073	10.093	- 33.733	- 456.903	- 419.863	0.000
5300	37.860	116.003	9.923	- 33.723	- 456.503	- 419.043	0.000
5400	36.136	114.913	9.773	- 33.693	- 456.103	- 418.233	0.000
5500	34.360	113.793	9.643	- 33.643	- 455.703	- 417.433	0.000
5600	32.536	112.643	9.533	- 33.573	- 455.303	- 416.643	0.000
5700	30.660	111.463	9.443	- 33.483	- 454.903	- 415.863	0.000
5800	28.736	110.253	9.373	- 33.373	- 454.503	- 415.093	0.000
5900	26.760	109.013	9.323	- 33.243	- 454.103	- 414.333	0.000
6000	24.736	107.743	9.293	- 33.083	- 453.703	- 413.583	0.000

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

The molecular configuration for W₃O₉(g) is estimated by assuming that the oxygen atoms are tetrahedrally located around the tungsten atoms, and that each tetrahedron shares two oxygen atoms to form a planar six-member ring. The bond distance W-O is estimated as 1.61 Å and the bond angles O-W-O = 109.47° and W-O-bridge-W = 130.53°. The three principal moments of inertia are: I_A = I_B = 2.805 × 10⁻³⁷ g cm² and I_C = 4.913 × 10⁻³⁷ g cm².

Point Group [D_{3h}]
S_{298.15}^o = [120.6] gibbs/mol
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies
ω, cm⁻¹
[800] (6)
[396] (3)
[330] (9)

Bond Distance: W-O = [1.61] Å
Bond Angle: O-W-O = [109.47]°, W-O-bridge-W = [130.53]°
Product of the Moments of Inertia: I_AI_BI_C = [3.885 × 10⁻¹¹⁰] g cm³

Heat of Formation.

The adopted value, ΔH_{f,298}^o(W₃O₉,g) = -483.6 kcal/mol, was reduced from ΔH_{f,1450}^o(W₃O₉,g) = -474.1 kcal/mol of R. J. Ackermann and E. O. Rauh, J. Phys. Chem. **67**, 2596 (1963), who studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600 °K by mass spectrometry, mass effusion, and X-ray diffraction, and determined ΔH_f^o(W₃O₉,g) = -474.100 ± 110.267 (cal/mol) from partial pressure measurements over W₂O₅(c). They reviewed the previous determinations 1, 2, 3, 4 of the thermodynamic properties of sublimation of W₃O₉(c), and also pointed out that it was not possible to make quantitative observations on stoichiometric W₃O₉ in vacuo, since it is a "bivalent" system and the ion current is not constant until the composition of the sample reaches W₂O₉. This is probably the cause of previous discrepancies in sublimation studies.

J. E. Battien, Ph. D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide", The Ohio State University, 1964, has also studied the partial pressure of W₃O₉(g) over W₂O₅(c) in the temperature range from 1399° to 1527°K. Third law calculation of the partial pressure data gives ΔH_{f,298}^o = -148.2 kcal/mol for 4.5 W₂O₅(c) = W₃O₉(c) + 1.5 W (c), which yields ΔH_{f,298}^o(W₃O₉,g) = -485.0 kcal/mol, using all JANAF functions.

J. H. Norman and H. O. Staley, J. Chem. Phys. **43**, 3804 (1965), have obtained ΔH_{f,1600}^o = -240 kcal/mol for 3 W₂O₅(c) = W₃O₉(c) by mass spectrometric study of the vapor over W₃ dissolved in CaO-Al₂O₃-SiO₂. The value of ΔH_f^o was determined by the second law method from ion intensities and leads to ΔH_{f,298}^o(W₃O₉,g) = -483.4 kcal/mol, using all JANAF functions (dated September 30, 1965). The absolute pressure values reported by Norman and Staley also appear to be quite inconsistent with the JANAF functions, since they lead to -443 kcal/mol by the third law method.

Reference 1. K. Ueno, J. Chem. Soc. Japan **82**, 990 (1961).

2. J. E. Berkowitz, W. A. Chupka, and M. O. Ingalls, J. Chem. Phys. **27**, 85 (1957).

3. P. E. Blackburn, J. Hoch, and H. L. Johnston, J. Phys. Chem. **62**, 769 (1958); P. E. Blackburn, WADC TR 59-575, part 1, Mar. 1960; and part 2, Dec. 1960.

4. G. Meyer, J. P. Oosterom, and J. L. Deleco, Rec. Trav. Chim. **78**, 412 (1959).

Investigator	Chemical Reaction	Temperature (°K)	2nd law ΔH _{f,298} ^o (kcal/mol)	3rd law ΔH _{f,298} ^o (eu)	Drift ΔH _{f,298} ^o (W ₃ O ₉ ,g) (kcal/mol)
Ackermann & Rauh	4.5 W ₂ O ₅ (c) = W ₃ O ₉ (c) + 1.5 W(c)	1300-1600	150.61	150.64	-0.05
Battien	4.5 W ₂ O ₅ (c) = W ₃ O ₉ (c) + 1.5 W(c)	1389-1527	146.20	146.20	-1.91 ± 0.24
Norman & Staley	3 W ₂ O ₅ (c) = W ₃ O ₉ (c)	1700-1900	-253.4	-233	-463.4 ± ±
* Third law value adopted in calculation					
** Second law value adopted in calculation					

Heat Capacity and Entropy.

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm⁻¹ (8), 396 cm⁻¹ (3), 330 cm⁻¹ (9), 200 cm⁻¹ (6), and 150 cm⁻¹ (c) in order to give the entropy at 1450°K, S₁₄₅₀^o = 219.14 eu, corresponding to ΔH_{f,1450}^o = 110.26 eu, reported by Ackermann and Rauh. The adopted value, S₂₉₈^o(W₃O₉,g) = 120.6 eu, was reduced from the entropy at 1450°K, using JANAF functions. Second law calculation of the partial pressure data of Battien gives ΔS₁₄₅₅^o = 71.7 eu for 4.5 W₂O₅(c) = W₃O₉(c) + 1.5 W (c). This yields S₂₉₈^o(W₃O₉,g) = 122.4 eu.

Diphosphorus Pentoxide, Dimeric ((P₂O₅)₂)
(Crystal) Mol. Wt. = 283.8892

0₁₀P₄

MOL. WT. = 283.8892

DIPHOSPHORUS PENTOXIDE, DIMERIC ((P₂O₅)₂) (CRYSTAL)

$\Delta H_f^\circ = -697.0 \pm 2.1 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -702.7 \pm 2.1 \text{ kcal. mole}^{-1}$
 $\Delta H_g^\circ 298.15 = 25.34 \pm 0.08 \text{ kcal. mole}^{-1}$
 $T_g = 631^\circ \text{K.}$

Heat of Formation.

The heat of formation ($\Delta H_f^\circ 298.15$) of P₄O₁₀(c) has been reported by many investigators. The most recent value, $\Delta H_f^\circ 298.15 = -719.4 \pm 2.0 \text{ kcal. mole}^{-1}$ for the reaction P₄(white, c) + 5O₂(g) = P₄O₁₀(hex., c), was determined by E. P. Egan, Jr. and B. B. Luff, "Heats of Formation of Phosphorus Oxides", June 1, 1963 to Nov. 30, 1963, Tennessee Valley Authority, Office of Agriculture and Chemical Development, Fundamental Research Branch, Wilson Dam, Alabama. This $\Delta H_f^\circ 298.15$ value was derived from energy of combustion, $\Delta_c H^\circ = -716.397 \text{ kcal. mole}^{-1}$, which is an average value of many measurements using three different sample forms, i.e. uncoated phosphorus, lucite-coated phosphorus and cellulose acetate-coated phosphorus. The adopted $\Delta H_f^\circ 298.15$ (P₄O₁₀, c) value was recalculated based on the P(red, V, c) as reference state.

The heat of combustion of white phosphorus was determined as $-713.2 \pm 1.0 \text{ kcal. mole}^{-1}$ by W. S. Holmes, Trans. Paraday Soc. 58, 1916 (1962), yielding $\Delta H_f^\circ 298.15$ (P₄O₁₀, c) = $-696.5 \pm 1.3 \text{ kcal. mole}^{-1}$, based on P(red, V, c) as reference state. The heat of formation of P₂O₅ from red phosphorus was reported to be $-355 \pm 2 \text{ kcal. mole}^{-1}$ by M. S. Koerner and P. Daniele, J. Chem. Phys. 20, 113 (1952). The product, P₂O₅, was considered to be a mixture of two forms, i.e. crystalline and amorphous. The other $\Delta H_f^\circ 298.15$ (P₄O₁₀, c) values reported by early investigators were reviewed by Egan and Luff, loc. cit.

Heat Capacity and Entropy.

The heat capacities (12-324°K.) and $S_{298.15}^\circ$ adopted were taken from R. J. L. Andon, J. P. Counsell, H. McKerrell and J. P. Martin, Trans. Faraday Soc. 59, 2702 (1963). The Cp values above 324°K. were obtained by graphical extrapolation. The $S_{298.15}^\circ$ value was calculated based on $S_{10}^\circ = 0.36 \text{ e.u.}$

Low temperature (15-310°K.) and high temperature (298.15-623.15°K.) heat capacities were also measured by Thermal Laboratory, The Dow Chemical Company, private communication, June 18, 1962, and M. Prandsen, J. Res. Natl. Bur. Std. 10, 35 (1933), respectively. The low temperature data were not adopted because they are less satisfactory than the data of Andon et al. The high temperature data were not used because the sample employed for enthalpy measurements was not explicitly reported as pure hexagonal form.

Sublimation Data.

The value of $\Delta H_g^\circ 298.15$ was derived from the vapor pressure data by both the second and third law analyses. See the P₄O₁₀(g) table for details. T_g is the temperature at which the free energy change of the reaction P₄O₁₀(hex. c) = P₄O₁₀(g) approaches zero. Sublimation temperature for P₄O₁₀(c) was derived to be 632°K., 636°K. (average of three determinations) and 623.7°K. (average of two determinations) by M. Prandsen, loc. cit. from the vapor pressure data reported by J. M. Hoeflaka and M. F. Scheffer, Rec. trav. chim. 45, 191 (1926); A. Saite, Z. physik. Chem. 119, 337 (1930); and A. Saite and A. J. Rutgers, J. Chem. Soc. 125, 2573 (1924), respectively.

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	- 8.417	- 396.994	- 696.994	INFINITE
100	18.550	89.040	- 7.441	- 699.947	- 680.441	1487.032
200	36.940	58.020	- 4.332	- 701.810	- 660.134	721.326
298	50.600	54.680	0.000	- 702.700	- 659.450	468.707
300	50.830	54.984	0.094	- 702.707	- 639.058	465.531
400	62.200	71.218	5.761	- 702.727	- 617.815	337.542
500	71.700	86.135	12.463	- 701.964	- 596.660	260.787
600	80.300	99.982	18.530	- 700.535	- 575.725	209.698
700	88.200	112.950	24.271	- 698.535	- 555.375	173.258
800	94.800	125.153	29.640	- 696.110	- 535.992	151.683
900	100.800	136.675	34.628	- 693.336	- 518.506	128.333
1000	105.800	147.560	39.296	- 690.292	- 501.492	109.596
1100	110.200	157.888	43.572	- 686.948	- 474.948	94.359
1200	114.200	167.598	47.266	- 683.258	- 448.857	81.729
1300	116.200	176.797	50.595	- 679.263	- 423.206	71.144
1400	118.300	185.487	53.523	- 674.966	- 397.983	62.125
1500	120.000	193.710	56.109	- 670.317	- 373.168	54.368

Diphosphorus Pentoxide, Dimeric ((P₂O₅)₂)
(Ideal Gas) Mol. Wt. = 283.8892

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	INFINITE	7.308	-670.975	-670.975	INFINITE
100	16.835	64.368	127.811	-673.850	-658.929	1440.018
200	22.446	114.161	234.862	-677.400	-646.018	459.308
298	25.126	135.882	338.255	-677.400	-626.627	
300	45.1325	96.805	-0.084	-677.417	-626.311	456.245
400	54.377	111.161	5.096	-678.092	-609.157	334.812
500	60.662	124.013	10.427	-678.260	-591.896	258.705
600	65.043	135.484	106.875	-678.141	-574.633	209.300
700	68.149	145.757	231.833	-677.895	-557.400	174.020
800	70.399	155.011	371.653	-675.284	-531.374	153.374
900	72.067	163.404	501.894	-671.970	-506.797	130.346
1000	73.329	171.066	625.959	-675.589	-512.295	111.957
1100	74.304	178.102	742.329	-675.164	-487.938	96.940
1200	75.069	184.602	848.585	-675.706	-463.710	84.449
1300	75.681	190.635	946.667	-675.228	-439.599	73.900
1400	76.175	196.263	1036.741	-674.735	-415.608	64.876
1500	76.581	201.532	1119.338	-674.235	-391.719	57.071
1600	76.918	206.486	1194.944	-673.733	-367.937	50.255
1700	77.200	211.158	1263.409	-673.266	-344.241	44.253
1800	77.439	215.577	1325.741	-672.828	-320.639	38.929
1900	77.642	219.770	1382.949	-672.416	-297.116	34.175
2000	77.817	223.757	1436.041	-672.021	-273.686	29.906
2100	77.969	227.557	1485.023	-671.643	-250.309	26.049
2200	78.101	231.188	1530.003	-671.282	-227.012	22.550
2300	78.216	234.662	1571.842	-670.937	-203.783	19.363
2400	78.318	237.993	1610.481	-670.607	-180.607	16.446
2500	78.408	241.192	1646.005	-670.289	-157.494	13.767
2600	78.489	244.269	1679.519	-669.982	-134.437	11.300
2700	78.560	247.232	1711.072	-669.691	-111.429	9.019
2800	78.625	250.091	1740.654	-669.416	-88.471	6.905
2900	78.682	252.851	1768.269	-669.147	-65.556	4.940
3000	78.735	255.519	1793.920	-668.892	-42.690	3.110
3100	78.782	258.101	1817.620	-668.650	-19.862	1.400
3200	78.825	260.603	1839.243	-668.416	2.907	-1.199
3300	78.864	263.030	1858.800	-668.188	25.646	-1.698
3400	78.900	265.384	1876.347	-667.965	48.354	-3.108
3500	78.933	267.672	1891.924	-667.746	71.018	-4.434
3600	78.963	269.896	1905.564	-667.531	93.656	-5.685
3700	78.991	272.060	1917.280	-667.320	116.258	-6.867
3800	79.017	274.167	1927.080	-667.112	138.841	-7.985
3900	79.041	276.220	1935.921	-666.907	161.375	-9.043
4000	79.063	278.221	1943.747	-666.705	183.875	-10.046
4100	79.083	280.174	1950.565	-666.505	206.366	-11.000
4200	79.102	282.080	1956.384	-666.307	228.829	-11.907
4300	79.119	283.941	1961.200	-666.112	251.266	-12.770
4400	79.137	285.760	1965.012	-665.919	273.673	-13.593
4500	79.152	287.539	1967.811	-665.728	296.055	-14.378
4600	79.167	289.279	1970.596	-665.539	318.418	-15.128
4700	79.180	290.981	1973.368	-665.352	340.759	-15.845
4800	79.193	292.649	1976.127	-665.167	363.077	-16.531
4900	79.205	294.282	1978.874	-664.984	385.357	-17.187
5000	79.216	295.882	1981.608	-664.802	407.632	-17.817
5100	79.227	297.451	1984.327	-664.621	429.894	-18.421
5200	79.237	298.989	1987.031	-664.441	452.106	-19.001
5300	79.246	300.499	1989.719	-664.262	474.345	-19.559
5400	79.255	301.980	1992.392	-664.084	496.518	-20.094
5500	79.263	303.434	1995.049	-663.907	518.625	-20.611
5600	79.271	304.865	1997.692	-663.731	540.662	-21.107
5700	79.279	306.266	1999.321	-663.556	562.634	-21.586
5800	79.286	307.645	2000.936	-663.381	584.546	-22.048
5900	79.293	309.000	2002.536	-663.206	606.395	-22.493
6000	79.300	310.333	2004.121	-663.031	628.184	-22.923

Dec. 31, 1962; Dec. 31, 1965

DIPHOSPHORUS PENTOXIDE, DIMERIC ((P₂O₅)₂) (IDEAL GAS)

MOL. WT. = 283.8892

Point group T_d
ΔH_f⁰ = -671.0 ± 2.1 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -677.4 ± 2.1 kcal. mole⁻¹
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies					
ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
424 (1)	650 (2)	{ 750 } (3)	764 (3)		
721 (1)	952 (2)	257 (3)	1015 (3)		
1437 (1)	{ 170 } (3)	329 (3)	1390 (3)		
278 (2)	{ 470 } (3)	573 (3)			

Bond Distances: P-O_{apical} = 1.40 ± 0.03 Å P-O = 1.60 ± 0.01 Å P-P = 2.83 ± 0.03 Å
Bond Angle: O_{apical}-P-O = 117 ± 1° O-P-O = 101 ± 1° P-O-P = 124°30' ± 1° σ = 12
Product of the Moments of Inertia: I_AI_BI_C = 2.93798 × 10⁻¹¹¹ g.³ cm.⁶

Heat of Formation.

The value of ΔH_f⁰ 298.15 (P₄O₁₀/g) was calculated from the heats of formation and sublimation for P₄O₁₀ (hex., c). The heat of sublimation (ΔH_s⁰ 298.15) was derived from vapor pressure data by the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K	Second Law Value	Third Law Value	Drift, e.u.
Hoeftake and Schaffer ¹	260 -401	25.42±0.07	25.33	-0.39±0.13
Southern and Nelson ²	216.2-300.4	25.59±0.06	25.35	-0.18±0.14
	283.6-389.3	25.45±0.07	25.35	-0.10±0.07

1. J. W. A. Hoeftake and P. E. C. Schaffer, Rec. trav. chim. 45, 191 (1926).

2. J. C. Southern and R. A. Nelson, J. Am. Chem. Soc. 59, 911 (1937).

The value of ΔH_f⁰ 298.15 adopted was 25.34 ± 0.08 kcal. mole⁻¹. There are many vapor pressure measurements reported but only the above two over P₄O₁₀ (hex., c).

It has been shown that P₄O₁₀ has three solid phases and two liquid phases. The three solid phases are hexagonal, orthorhombic and tetragonal. As temperature increases, the thermal stability of P₄O₁₀ follows the same order. The metastable liquid, according to data of Hoeftake and Schaffer, loc. cit., is from hexagonal form. The stable liquid is from tetragonal form. W. L. Hill, O. T. Faust and S. B. Hendricks, J. Am. Chem. Soc. 65, 794 (1943) reported that molecules of P₄O₁₀ having the same structure as in the vapor are present in the hexagonal form of the solid. The vapor pressures of P₄O₁₀ over different condensed phases have been measured by many investigators and reviewed by T. D. Farr, "Phosphorus, Properties of the Elements and Some of Its Compounds", Tennessee Valley Authority, Wilson Dam, Alabama, 1950. The complexity of the solid state of P₄O₁₀ has also been discussed by A. Seits and A. J. Rutgers, J. Chem. Soc. 125, 2573 (1924); A. Seits, Z. physik. Chem. A149, 337 (1930); A. Seits, J. A. A. Keteleer and J. L. Meyer, ibid., B11, 87 (1938); and A. Seits, ibid., B45, 43 (1940).

Heat Capacity and Entropy.

The molecular structure and constants were obtained from P. A. Akishin, N. O. Rambidi and E. Z. Zesarin, Kristallografiya, 3, 360 (1959). The molecular structure of P₄O₁₀(g) has also been studied by the electron diffraction method by L. R. Maxwell, S. B. Hendricks and L. S. Deming, J. Chem. Phys. 5, 626 (1937), and O. C. Hampson and A. J. Stoeck, J. Am. Chem. Soc. 50, 1814 (1928). The model of the P₄O₁₀ molecule was later confirmed by the x-ray method reported by H. C. J. Decker and C. H. MacGillivray, Rec. trav. chim. 50, 153 (1941); and spectroscopic studies reported by H. Gerding and H. C. J. Decker, Rec. trav. chim. 64, 191 (1945), and T. A. Sidorov and N. N. Sobolav, Opt. Spectr. (USSR) 2, 717 (1957). All vibrational frequencies were obtained from E. P. Egan, Jr., private communication, Feb. 23, 1960, except nine frequencies, i.e. 170 (3), 470 (3), and 750 (3) cm⁻¹ which were estimated in order to make the second and third law values of ΔH_f⁰ 298.15 agree. The three principal moments of inertia are: I_A = I_B = 1.4322 × 10⁻³⁷ g. cm.² The heat capacities (549-1098°K. or 822-1371°K.) of P₄O₁₀(g) have been determined by M. Prandeaen, J. Res. Natl. Bur. Std. 10, 35 (1933). His results are in fair agreement with the calculated ones.

OPW = 927.3928

(IDEAL GAS)

TUNGSTEN TRIOXIDE, TETRAMERIC (WO₃)₄

Tungsten Trioxide, Tetrameric (WO₃)₄

(Ideal Gas) GFW = 927.3928

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	Log Kp
0	∞	∞	∞	∞	∞	∞
100	37.142	81.799	202.183	-13.719	-666.713	INFINITE
200	63.224	117.169	151.101	-12.038	-669.820	1425.479
298	73.894	144.635	144.635	-6.786	-670.664	693.007
300	74.038	145.093	144.637	-6.786	-670.664	693.007
400	79.917	167.276	147.621	-7.862	-670.664	693.007
500	83.380	185.513	153.431	-16.041	-667.693	253.751
600	85.538	200.920	160.095	-24.495	-666.213	563.239
700	86.821	215.597	167.559	-32.449	-663.309	1045.159
800	88.021	229.597	174.871	-40.181	-661.933	124.500
900	89.118	242.658	182.072	-47.587	-660.623	108.440
1000	89.500	254.171	191.881	-54.518	-659.382	95.329
1100	90.026	265.168	202.649	-61.449	-658.189	82.206
1200	90.212	275.847	207.642	-68.475	-657.099	70.203
1300	90.363	282.076	212.399	-75.517	-656.058	67.323
1400	90.487	287.012	216.938	-82.559	-655.087	64.699
1500	90.598	291.582	221.228	-89.601	-654.183	62.231
1600	90.678	295.862	225.228	-96.643	-653.344	59.908
1700	90.732	300.000	229.000	-103.685	-652.566	57.623
1800	90.775	304.000	232.500	-110.727	-651.849	55.376
1900	90.815	308.141	235.830	-117.769	-651.189	53.166
2000	90.851	312.426	239.000	-124.811	-650.582	50.991
2100	90.877	316.856	242.000	-131.853	-650.027	48.851
2200	90.895	321.431	245.000	-138.895	-649.522	46.746
2300	90.905	326.151	248.000	-145.937	-649.067	44.671
2400	90.909	331.016	251.000	-152.979	-648.662	42.626
2500	91.028	336.036	254.000	-160.021	-648.307	40.611
2600	91.056	341.211	257.000	-167.063	-647.992	38.626
2700	91.082	346.541	260.000	-174.105	-647.717	36.671
2800	91.105	352.026	263.000	-181.147	-647.482	34.746
2900	91.125	357.666	266.000	-188.189	-647.287	32.851
3000	91.144	363.461	269.000	-195.231	-647.122	30.986
3100	91.160	369.411	272.000	-202.273	-646.987	29.151
3200	91.173	375.516	275.000	-209.315	-646.882	27.346
3300	91.183	381.776	278.000	-216.357	-646.807	25.571
3400	91.190	388.191	281.000	-223.400	-646.752	23.826
3500	91.214	394.761	284.000	-230.442	-646.717	22.111
3600	91.235	401.496	287.000	-237.484	-646.692	20.426
3700	91.253	408.396	290.000	-244.526	-646.677	18.771
3800	91.269	415.461	293.000	-251.568	-646.672	17.146
3900	91.282	422.691	296.000	-258.610	-646.677	15.551
4000	91.290	430.086	299.000	-265.652	-646.692	13.986
4100	91.297	437.641	302.000	-272.694	-646.717	12.461
4200	91.302	445.356	305.000	-279.736	-646.752	10.966
4300	91.305	453.231	308.000	-286.778	-646.797	9.501
4400	91.308	461.266	311.000	-293.820	-646.852	8.066
4500	91.310	469.461	314.000	-300.862	-646.917	6.661
4600	91.312	477.816	317.000	-307.904	-646.992	5.286
4700	91.314	486.331	320.000	-314.946	-647.077	3.941
4800	91.315	495.006	323.000	-321.988	-647.172	2.626
4900	91.316	503.841	326.000	-329.030	-647.277	1.341
5000	91.317	512.836	329.000	-336.072	-647.392	0.096
5100	91.317	521.991	332.000	-343.114	-647.517	-1.201
5200	91.317	531.306	335.000	-350.156	-647.652	-2.526
5300	91.317	540.781	338.000	-357.198	-647.797	-3.881
5400	91.317	550.416	341.000	-364.240	-647.952	-5.276
5500	91.317	560.211	344.000	-371.282	-648.117	-6.711
5600	91.317	570.166	347.000	-378.324	-648.292	-8.186
5700	91.317	580.281	350.000	-385.366	-648.477	-9.701
5800	91.317	590.556	353.000	-392.408	-648.672	-11.256
5900	91.317	600.991	356.000	-399.450	-648.877	-12.851
6000	91.317	611.586	359.000	-406.492	-649.092	-14.486

Mar. 31, 1963; Sept. 30, 1966

Point Group [D_{2h}]
S_{298.15} = [144.6] g/bb/mol
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[800] (8)	[240] (8)
[300] (8)	[200] (18)

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O = [109.47°], W-O₂-bridge-W = [160.53°]

Product of the Moments of Inertia: I_AI_BI_C = [3.854 × 10⁻¹⁰⁹] g³cm⁶

Heat of Formation.

The adopted value, ΔH_{f298} (W₄O₁₂, g) = -670.2 kcal/mol, was reduced from ΔH_{f1450} (W₄O₁₂, g) = -655.6 kcal/mol of R. J. Ackermann and E. G. Reuh, J. Phys. Chem. 67, 2596 (1963), who studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600°K by mass spectrometry, mass effusion and x-ray diffraction, and determined ΔH_f (W₄O₁₂, g) = -655.600 ± 160.29 T (cal/mol) from partial pressure measurements over the W-WO₃(c). They reviewed the previous determinations 1,2,3,4 of the thermodynamic properties of sublimation of WO₃, and also pointed out that it was not possible to make quantitative observations on stoichiometric WO₃ in vacuo, since it is a "bivalent" system and the ion current is not constant until the composition of the sample reaches WO_{2.98}. This is probably the cause of previous discrepancies in sublimation studies.

J. E. Battles, Ph. D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide", The Ohio State University, 1964, has also studied the partial pressure of W₄O₁₂(g) over W-WO₂(c) in the temperature range from 1449 to 1527°K. Third law calculation of the partial pressure data gives ΔH_{f298} = 172.0 kcal/mol for 6 WO₂(c) = W₄O₁₂(g) + 2 W(c), which yields ΔH_{f298} (W₄O₁₂, g) = -673.6 kcal/mol, using all JANAP functions.

- References 1. K. Ueno, J. Chem. Soc. Japan 62, 980 (1941).
2. J. Berkowitz, W. A. Chupke, and M. G. Inghram, J. Chem. Phys. 27, 65 (1957).
3. P. E. Blackburn, M. Hoch, and H. L. Johnston, J. Phys. Chem. 62, 769 (1958).
4. O. Meyer, J. P. Oosterom, and J. L. DeRoos, Rec. Trav. Chim. 78, 412 (1959).

Investigator	Chemical Reaction	Temperature (°K)	ΔH _{f298} (kcal/mol)	Drift (eu)	ΔH _{f298} (W ₄ O ₁₂ , g) (kcal/mol)
--------------	-------------------	------------------	-------------------------------	------------	--

Ackermann & Reuh	6 WO ₂ (c) = W ₄ O ₁₂ (g) + 2W(c)	1300 - 1600*	175.41	0.01	-670.2
Battles	6 WO ₂ (c) = W ₄ O ₁₂ (g) + 2W(c)	1449 - 1527*	178.16	-2.90 ± 0.39	-673.6

* Third law value adopted in calculation.

Heat Capacity and Entropy.

The heat capacity was approximated by seeking a tentative choice of the vibrational frequencies of 800 cm⁻¹(9), 300 cm⁻¹(8), 240 cm⁻¹(8), and 200 cm⁻¹(18) in order to give the entropy at 1450°K, S₁₄₅₀ = 278.9 eu, corresponding to ΔH_{f1450} = -160.29 eu, reported by Ackermann and Reuh. The adopted value, S₂₉₈ (W₄O₁₂, g) = 144.6 eu, was reduced from the entropy at 1450°K, using JANAP functions. Second law calculation of the partial pressure data of Battles gives ΔH_{f1487} = 82.3 eu for 8 WO₂(c) = W₄O₁₂(g) + 2W(c). This yields S₂₉₈ (W₄O₁₂, g) = 147.4 eu.

The molecular configuration for W₄O₁₂(g) is estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and that each tetrahedron shares two oxygen atoms to form a planar eight-member ring. The bond distance W-O is estimated as 1.81 Å and the bond angles O-W-O = 109.47° and W-O₂-bridge-W = 160.53°. The three principal moments of inertia are: I_A = I_B = 5.935 × 10⁻³⁷ g cm², and I_C = 1.094 × 10⁻³⁶ g cm².

Phosphorus (P)

(Reference State) At. Wt. = 30.975

T, °K.	C _p	$\int_{T_0}^T C_p dT$	$S^\circ - (F^\circ - H^\circ_{298})/T$	$\int_{T_0}^T \frac{C_p}{T^2} dT$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	0.000	0.000	10.000	0.000	0.000	0.000	0.000	0.000
100	4.074	1.000	9.662	0.000	0.000	0.000	0.000	0.000
200	4.074	3.619	9.653	0.000	0.000	0.000	0.000	0.000
298	5.064	5.450	9.450	0.000	0.000	0.000	0.000	0.000
300	5.079	5.481	9.450	0.000	0.000	0.000	0.000	0.000
400	5.540	7.011	9.655	0.000	0.000	0.000	0.000	0.000
500	5.857	8.283	9.657	0.000	0.000	0.000	0.000	0.000
600	6.165	9.377	9.521	1.714	0.000	0.000	0.000	0.000
700	6.500	10.352	9.337	2.347	0.000	0.000	0.000	0.000
800	6.845	11.224	9.037	2.830	0.000	0.000	0.000	0.000
900	7.190	12.000	8.650	3.180	0.000	0.000	0.000	0.000
1000	7.535	12.683	8.195	3.435	0.000	0.000	0.000	0.000
1100	7.880	13.283	7.683	3.600	0.000	0.000	0.000	0.000
1200	8.225	13.800	7.114	3.683	0.000	0.000	0.000	0.000
1300	8.570	14.233	6.500	3.683	0.000	0.000	0.000	0.000
1400	8.915	14.583	5.857	3.600	0.000	0.000	0.000	0.000
1500	9.260	14.850	5.165	3.435	0.000	0.000	0.000	0.000
1600	9.605	15.033	4.425	3.180	0.000	0.000	0.000	0.000
1700	9.950	15.133	3.650	2.830	0.000	0.000	0.000	0.000
1800	10.295	15.150	2.830	2.347	0.000	0.000	0.000	0.000
1900	10.640	15.083	1.914	1.714	0.000	0.000	0.000	0.000
2000	10.985	14.933	0.962	0.962	0.000	0.000	0.000	0.000
2100	11.330	14.700	0.000	0.000	0.000	0.000	0.000	0.000
2200	11.675	14.383	0.000	0.000	0.000	0.000	0.000	0.000
2300	12.020	13.983	0.000	0.000	0.000	0.000	0.000	0.000
2400	12.365	13.500	0.000	0.000	0.000	0.000	0.000	0.000
2500	12.710	12.933	0.000	0.000	0.000	0.000	0.000	0.000
2600	13.055	12.283	0.000	0.000	0.000	0.000	0.000	0.000
2700	13.400	11.550	0.000	0.000	0.000	0.000	0.000	0.000
2800	13.745	10.733	0.000	0.000	0.000	0.000	0.000	0.000
2900	14.090	9.833	0.000	0.000	0.000	0.000	0.000	0.000
3000	14.435	8.850	0.000	0.000	0.000	0.000	0.000	0.000
3100	14.780	7.783	0.000	0.000	0.000	0.000	0.000	0.000
3200	15.125	6.633	0.000	0.000	0.000	0.000	0.000	0.000
3300	15.470	5.400	0.000	0.000	0.000	0.000	0.000	0.000
3400	15.815	4.083	0.000	0.000	0.000	0.000	0.000	0.000
3500	16.160	2.683	0.000	0.000	0.000	0.000	0.000	0.000
3600	16.505	1.200	0.000	0.000	0.000	0.000	0.000	0.000
3700	16.850	0.000	0.000	0.000	0.000	0.000	0.000	0.000
3800	17.195	0.000	0.000	0.000	0.000	0.000	0.000	0.000
3900	17.540	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4000	17.885	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4100	18.230	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4200	18.575	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4300	18.920	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4400	19.265	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4500	19.610	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4600	19.955	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4700	20.300	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4800	20.645	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4900	20.990	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5000	21.335	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5100	21.680	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5200	22.025	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5300	22.370	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5400	22.715	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5500	23.060	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5600	23.405	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5700	23.750	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5800	24.095	0.000	0.000	0.000	0.000	0.000	0.000	0.000
5900	24.440	0.000	0.000	0.000	0.000	0.000	0.000	0.000
6000	24.785	0.000	0.000	0.000	0.000	0.000	0.000	0.000

June 30, 1961

PHOSPHORUS (P)

AT. WT. = 30.975

(REFERENCE STATE)

The selected reference states are:
 0 to 704°K. Solid Phosphorus (red, V)
 704 to 6000°K. Ideal Diatomic Gas

For details see Phosphorus (Red, V) and P₂ (Ideal Gas).

P

Phosphorus, Red, V. (P)
(Crystal) At. Wt. = 30.975

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ cal. mole ⁻¹	ΔH° _f cal. mole ⁻¹	ΔF° cal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞	INFINITE
100	2.075	3.419	771	.000	.000	.000
200	2.075	3.419	.453	.000	.000	.000
298	5.069	5.450	.000	.000	.000	.000
300	5.079	5.481	.000	.000	.000	.000
400	5.560	5.550	.592	.000	.000	.000
500	5.952	6.057	1.112	.000	.000	.000
600	6.165	6.521	1.713	.000	.000	.000
700	6.500	7.050	2.306	.000	.000	.000
800	6.840	7.645	2.885	.000	.000	.000
900	7.180	8.291	3.448	.000	.000	.000
1000	7.570	8.992	4.000	.000	.000	.000
1100	7.860	9.630	4.528	.000	.000	.000
1200	8.100	10.212	5.021	.000	.000	.000
1300	8.300	10.742	5.482	.000	.000	.000
1400	8.480	11.221	5.918	.000	.000	.000
1500	8.640	11.655	6.334	.000	.000	.000
1600	8.780	12.047	6.733	.000	.000	.000
1700	8.900	12.402	7.108	.000	.000	.000
1800	9.000	12.722	7.463	.000	.000	.000
1900	9.080	13.014	7.798	.000	.000	.000
2000	9.150	13.282	8.118	.000	.000	.000

AT. WT. = 30.975

(CRYSTAL)

PHOSPHORUS, RED, V. (P)

ΔH°_f 298.15 = 0 kcal. mole⁻¹
 ΔH°_f 298.15 = 7.69 ± 0.1 kcal. mole⁻¹
 T_m = 870°K
 ΔH°_f 298.15 = 0 kcal. mole⁻¹
 S°_{298.15} = 5.45 ± 0.02 cal. deg⁻¹ mole⁻¹
 ΔH°_m = 4.5 ± 0.2 kcal. mole⁻¹

Heat of Formation

Zero by definition below 704°K. See P₂(g) sheet for details above 704°K.

Heat Capacity and Extrapolation

The only reliable low temperature measurements, 15 to 305°K, are reported by R. L. Potter, Dissertation, Massachusetts Institute of Technology (1946). A value at 10°K was obtained by graphical extrapolation and a T³ function was assumed from 0 to 10°K. High temperature heat capacities were obtained from a smooth curve joining the measurements of O. Kubaschewski and G. Schrag, Z. Elektrochem. 46, 675 (1940), in the range 573 to 773°K and that of V. Regnault, Ann. chim. phys. 9, 322 (1843) at 331°K with those of Potter. Measurements of A. Wigand, Ann. Physik, 22, 64 (1907), are too high. The uncertainty in the high temperature heat capacity is about 2%.

Melting

The values of ΔH°_m and T_m were calculated from the functions of the solid and liquid. This may be compared with a reported triple point of 882.7°K by A. Smits and S. C. Bohoret, Akad. Wetenschap. 23, 930 (1914).

Heat of Sublimation

Vapor pressure measurements on the triclinic allotrope, T. V. A. designation V, are reported by T. D. Farr, Tennessee Valley Authority Chemical Engineering Report No. 8 (1950). These data lead to a sublimation point of 704°K and ΔH°_f 298.15 of 30.77 ± 0.4 kcal. mole⁻¹ of P₄. A. Smits and S. C. Bohoret, Z. phys. Chem. 91, 248 (1916), measured the vapor pressure of a sample whose preparation indicates that it was probably P, V. These results lead to ΔH°_f 298.15 = 30.6 ± 1 kcal. An unpublished value of 30.84 kcal. mole⁻¹ of P₄ by C. C. Stephenson is quoted by J. S. Kane, Thesis Univ. of California (1955).

D. P. Stevenson and D. M. Yost, J. Chem. Phys. 9, 403 (1941), show that the vapor density measurements of A. Stock, O. E. Gibson and E. Stamm, Ber. 45, 3527 (1912) are best explained by a vapor essentially composed of only P₄(g) below 800°K. This conclusion is supported by recent mass spectrometer measurements of J. S. Kane and J. H. Reynolds, J. Chem. Phys. 25, 342 (1956).

(Crystal) At. Wt. = 30.975

T, °K.	C _p	S°	$-(F^{\circ}-H_{298}^{\circ})/T$	ΔH_f°	Log K _f
0	5.000	0.000	INFINITE	3.754	INFINITE
100	5.051	9.278	10.378	3.754	3.754
200	5.096	9.818	9.818	3.754	3.754
298	5.100	9.818	9.818	3.754	3.754
300	5.705	9.853	9.818	4.175	2.085
400	6.050	11.553	10.066	4.230	2.417
500	6.330	12.925	10.458	4.276	1.958
600	6.330	14.079	10.993	4.310	1.489
700	6.330	15.054	11.505	4.310	1.019
800	6.330	15.900	12.003	4.310	0.542
900	6.330	16.645	12.478	4.310	0.065
1000	6.330	17.312	12.929	4.310	-0.429
1100	6.330	17.914	13.355	4.310	-0.929
1200	6.330	18.466	13.759	4.310	-1.429
1300	6.330	18.973	14.140	4.310	-1.929
1400	6.330	19.442	14.503	4.310	-2.429
1500	6.330	19.874	14.847	4.310	-2.929

PHOSPHORUS, WHITE (P)

(CRYSTAL)

AT. WT. = 30.975

$$\Delta H_f^{\circ} = 3.75 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^{\circ} = 3.52 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\Delta H_t^{\circ} = 124.62 \pm 0.2 \text{ cal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 157.43 \pm 0.5 \text{ cal. mole}^{-1}$$

Heat Capacity and Extrapolation

Low temperature measurements, 15-315°K, were made by R. T. Maples, Dissertation, Massachusetts Institute of Technology (1949). A Debye θ temperature of 124 was used to extrapolate to 0°K. P. E. Young and J. H. Hildenbrand, J. Am. Chem. Soc. **64**, 859 (1942), obtained heat capacities from enthalpy measurements that are 4% higher than those from the low temperature calorimeter which are preferred because of the proximity to the melting point.

Transition

Observed by Maples.

Melting

The selected heat of fusion is that observed by Maples. Young and Hildenbrand obtain 125 cal. mole⁻¹ for the same quantity. Maples' value is consistent with vapor pressures and other thermochemical data; see P(11q) and P₄(g) sheets.

Heat of Sublimation

The vapor pressure measurements of F. S. Dainton and H. M. Kimberly, Trans. Faraday Soc. **46**, 912 (1950), are the most precise and lead to $\Delta H_g^{\circ} = 14.08 \pm 0.2 \text{ kcal. mole}^{-1}$ of P₄. Measurements of A. Jollibois, Compt. rend. **249**, 287 (1909), A. Smits and S. C. Bokhorst, Z. Phys. Chem. **91**, 249 (1916), and M. Centzner, Z. Phys. Chem. **85**, 99 (1913) lead to values that agree within the assigned uncertainty.

Heat of Formation

The heat of formation is obtained from the heats of sublimation represented by reaction I and II at 298.15°K.

See P, V sheet for details.



Of the calorimetric determinations only those of H. Givan, Ann. Chim. Phys. **30**, 203 (1903) result in a reliable value for the heat of formation, $4.4 \pm 0.4 \text{ kcal. mole}^{-1}$. A comprehensive review is given by H. J. Rode-wald, Helv. Chim. Acta **43**, 878 (1960).

June 30, 1961

Phosphorus (P)

(Liquid) At. Wt. = 30.975

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
100							
200							
298	6.292	10.249	10.249	.000	4.322	2.891	2.119
300	6.292	10.248	10.249	.012	4.325	2.893	2.100
400	6.292	12.098	10.496	.641	4.421	2.386	1.304
500	6.292	13.592	10.962	1.270	4.479	1.870	.817
600	6.292	14.849	11.484	1.899	4.507	1.344	.489
700	6.292	15.619	12.007	2.528	4.503	.816	.255
800	6.292	16.140	12.493	3.157	4.479	.286	.087
900	6.292	17.200	12.995	3.787	4.433	-.248	-.100
1000	6.292	17.863	13.447	4.416	4.370	-.781	-.309
1100	6.292	18.463	13.846	5.045	4.289	-.1.016	-.420
1200	6.292	19.010	14.282	5.674	4.193	-.1.281	-.551
1300	6.292	19.500	14.656	6.293	4.083	-.1.582	-.692
1400	6.292	19.940	15.025	6.933	3.959	-.1.912	-.842
1500	6.292	20.414	15.373	7.562	3.822	-.2.267	-.995
1600	6.292	20.821	15.701	8.191	3.673	-.2.646	-.1.148
1700	6.292	21.202	16.014	8.820	3.511	-.3.040	-.1.303
1800	6.292	21.556	16.313	9.449	3.337	-.3.450	-.1.458
1900	6.292	21.902	16.597	10.079	3.151	-.3.875	-.1.613
2000	6.292	22.225	16.871	10.708	2.954	-.4.315	-.1.768
2100	6.292	22.532	17.133	11.337	2.747	-.4.769	-.1.923
2200	6.292	22.824	17.385	11.966	2.530	-.5.237	-.2.078
2300	6.292	23.101	17.629	12.595	2.294	-.5.719	-.2.233
2400	6.292	23.372	17.861	13.225	2.039	-.6.215	-.2.388
2500	6.292	23.629	18.087	13.854	1.765	-.6.726	-.2.543
2600	6.292	23.875	18.305	14.483	1.481	-.7.251	-.2.698
2700	6.292	24.113	18.516	15.112	1.187	-.7.790	-.2.853
2800	6.292	24.342	18.721	15.741	.884	-.8.342	-.3.008
2900	6.292	24.562	18.919	16.371	.571	-.8.907	-.3.163
3000	6.292	24.776	19.109	17.000	.249	-.9.486	-.3.318

PHOSPHORUS (P)

(LIQUID)

At. Wt. = 30.975

$$\Delta H_{f, 298.15}^{\circ} = 5.2 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{\circ} = 10.25 \pm 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 317.30 \pm 0.05^{\circ}\text{K}, P_{\alpha} \rightarrow P(\text{liq})$$

$$T_m = 870^{\circ}\text{K}, P_{\gamma} \rightarrow P(\text{liq})$$

$$T_b = 550 \pm 3^{\circ}\text{K}$$

$$T_c = 935.8^{\circ}\text{K}$$

$$\Delta H_{f, 298.15}^{\circ} = 4.32 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\Delta H_{m, 298.15}^{\circ} = 157.43 \pm 0.5 \text{ cal. mole}^{-1}$$

$$\Delta H_{m, P_{\gamma}} \rightarrow P(\text{liq}) = 4.5 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\Delta H_{v, 298.15}^{\circ} = 3.37 \pm 0.03 \text{ kcal. mole}^{-1}$$

$$P_c = [93.3] \text{ atm.}$$

Heat of Formation

Derived from the ΔH_m by the following cycle:

$$(I) \quad P \quad 317.30 = P(\text{liq}) \quad 0.157 \text{ kcal.}$$

$$(II) \quad P_{\alpha} \quad 298.15 = P_{\alpha} \quad 317.30 \quad 0.113$$

$$(III) \quad P(\text{liq}) \quad 317.30 = P(\text{liq})_{298.15} \quad -0.121$$

$$(IV) \quad P_{\gamma} \quad 298.15 = P_{\alpha} \quad 298.15 \quad 4.08$$

The ΔH_f° 289.15 obtained from vapor pressure measurements on P_{γ} and on the liquid is 4.32 kcal. mole⁻¹ in agreement with that derived from the melting point.

Heat Capacity

P. E. Young and J. H. Hildenbrand, J. Am. Chem. Soc. **64**, 839 (1942), obtained an equation from enthalpy measurements which decreased with temperature. However, a better fit to the thermochemical data results if a constant heat capacity is assumed.

Entropy

Derived from low temperature measurements on P_{γ} White. See P, White sheet for details.

Vaporization Phenomena

D. MacRae and C. G. Van Voorhis, J. Am. Chem. Soc. **43**, 547 (1921), determinations of the vapor pressure, 44 to 150°C, are the most precise and lead to a $\Delta H_{v, 298.15}$ of 13.504 ± 0.1 kcal. mole⁻¹ of P_{α} . A vapor pressure equation derived by T. D. Farr, Tennessee Valley Authority Chemical Engineering Report No. 8 (1950) to fit the measurements reported in the literature leads to a value of 13.6 ± 0.1 kcal. mole⁻¹ of P_{α} . The boiling point is calculated from the functions of $P(\text{liq})$ and $P_{\alpha}(g)$, and may be compared with the values of 552.7 and 553.7 resulting from Farr's equation and observations of A. Smits and S. C. Bokhorst, Proc. Akad. Wetenschap. **16**, 106 (1915) respectively.

Critical Phenomena

T_c determined and P_c estimated by W. Marchwald and R. Helmholz, Z. anorg. Chem. **124**, 81 (1922).

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	(F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	Log K _p
0	4.000	INFINITE	1.481	79.176	INFINITE	79.176	INFINITE
100	4.948	33.552	4.337	98.84	79.582	76.376	-166.911
200	4.948	36.996	39.434	4.888	79.760	73.065	-79.860
298	4.948	38.980	40.000	4.000	79.795	69.795	-51.161
300	4.948	39.011	38.980	.009	79.795	69.736	-50.800
400	4.948	40.440	39.175	5.06	79.759	66.388	-36.271
500	4.948	41.548	39.563	1.003	79.685	63.052	-27.559
600	4.948	42.454	39.955	1.500	79.581	59.734	-21.757
700	4.948	43.183	40.347	2.093	79.447	56.416	-16.955
800	4.948	43.683	40.737	2.689	79.285	53.100	-12.152
900	4.948	44.069	41.126	3.289	79.097	49.784	-7.349
1000	4.948	44.352	41.505	3.887	78.885	46.467	-2.546
1100	4.948	44.544	41.884	3.984	78.653	43.150	2.253
1200	4.948	44.698	42.264	4.081	78.400	39.832	6.945
1300	4.971	44.826	42.647	4.178	78.127	36.515	11.638
1400	4.974	44.934	42.954	4.275	77.835	33.200	16.331
1500	4.979	45.008	43.026	4.372	77.522	29.885	21.024
1600	4.987	45.052	43.085	4.471	77.199	26.569	25.717
1700	4.999	45.077	43.128	4.570	76.866	23.252	30.410
1800	5.016	45.084	43.156	4.670	76.514	19.935	35.103
1900	5.036	45.073	43.169	4.773	76.144	16.617	39.796
2000	5.062	45.048	43.167	4.878	75.757	13.300	44.489
2100	5.094	44.999	43.152	4.986	75.355	9.982	49.182
2200	5.132	44.927	43.117	5.100	74.938	6.665	53.875
2300	5.175	44.824	43.064	5.220	74.506	3.348	58.568
2400	5.225	44.693	42.994	5.356	74.059	0.031	63.261
2500	5.279	44.537	42.909	5.517	73.597	-3.286	67.954
2600	5.339	44.359	42.811	5.704	73.120	-6.599	72.647
2700	5.407	44.159	42.699	5.918	72.629	-9.912	77.340
2800	5.482	43.938	42.574	6.161	72.124	-13.225	82.033
2900	5.562	43.697	42.437	6.434	71.605	-16.538	86.726
3000	5.647	43.437	42.290	6.737	71.072	-19.851	91.419
3100	5.737	43.159	42.132	7.070	70.525	-23.164	96.112
3200	5.832	42.864	41.964	7.434	69.964	-26.477	100.805
3300	5.931	42.554	41.786	7.829	69.389	-29.790	105.498
3400	6.034	42.230	41.599	8.256	68.800	-33.103	110.191
3500	6.141	41.892	41.404	8.714	68.197	-36.416	114.884
3600	6.254	41.539	41.201	9.203	67.580	-39.729	119.577
3700	6.382	41.174	40.990	9.724	66.949	-43.042	124.270
3800	6.525	40.798	40.764	10.277	66.304	-46.355	128.963
3900	6.682	40.412	40.517	10.862	65.645	-49.668	133.656
4000	6.853	40.016	40.257	11.479	64.972	-52.981	138.349
4100	7.038	39.611	40.000	12.128	64.285	-56.294	143.042
4200	7.237	39.196	39.747	12.809	63.584	-59.607	147.735
4300	7.450	38.772	39.500	13.522	62.878	-62.920	152.428
4400	7.677	38.339	39.257	14.267	62.158	-66.233	157.121
4500	7.919	37.897	39.016	15.044	61.424	-69.546	161.814
4600	8.176	37.446	38.779	15.853	60.677	-72.859	166.507
4700	8.448	36.986	38.546	16.695	60.000	-76.172	171.200
4800	8.734	36.517	38.317	17.570	59.303	-79.485	175.893
4900	9.034	36.039	38.092	18.478	58.586	-82.798	180.586
5000	9.348	35.552	37.871	19.419	57.850	-86.111	185.279
5100	9.677	35.057	37.654	20.393	57.095	-89.424	189.972
5200	10.020	34.552	37.441	21.399	56.321	-92.737	194.665
5300	10.377	34.037	37.231	22.437	55.538	-96.050	199.358
5400	10.748	33.512	37.024	23.507	54.745	-99.363	204.051
5500	11.134	32.977	36.821	24.609	53.942	-102.676	208.744
5600	11.534	32.432	36.631	25.743	53.130	-105.989	213.437
5700	11.948	31.877	36.444	26.909	52.308	-109.302	218.130
5800	12.376	31.312	36.260	28.107	51.467	-112.615	222.823
5900	12.818	30.737	36.079	29.337	50.616	-115.928	227.516
6000	13.274	30.152	35.900	30.600	49.755	-119.241	232.209

June 30, 1962

PHOSPHORUS (P)

(IDEAL GAS)

MOL. WT. = 30.975

$\Delta H_f^o = 79.18 \pm 0.05$ kcal. mole⁻¹
 Ground State Configuration $4s^2 4p^2$

$\Delta H_f^o = 79.18 \pm 0.05$ kcal. mole⁻¹
 $S_{298.15}^o = 38.98$ cal. mole⁻¹ deg.⁻¹

Electronic Levels and Multiplicities

ϵ_f , cm. ⁻¹	g_f	ϵ_f , cm. ⁻¹	g_f
0	4	59,643	12
11,370	10	65,984	58
18,740	6	69,696	102
56,190	12	75,380	180
59,075	6	78,762	162
		80,835	202

Heat of Formation.

The ΔH_f^o 298.15 was derived by the following cycle:

- (1) $4 P_{red}(v) [298.15^\circ] = P_4(g) [298.15^\circ]$ $\Delta H_f^o = 30.77$ kcal. mole⁻¹ of P_4 See $P_{red}(v)$ sheet under Heat of Sublimation.
- (2) $P_4(g) [298.15^\circ] = 2P_2(g) [298.15^\circ]$ $\Delta H_f^o = 54.59$ kcal. mole⁻¹ of P_4 See $P_2(g)$ sheet under Heat of Formation.
- (3) $2P_2(g) [298.15^\circ] = 2P_2(g) [0^\circ]$ $\Delta H_f^o = 2(-2.128)$ kcal. mole⁻¹ of P_4 See $P_2(g)$ table.
- (4) $2P_2(g) [0^\circ] = 4P(g) [0^\circ]$ $\Delta H_f^o = 2(116.075)$ kcal. mole⁻¹ of P_4 A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, 1953.
- (5) $4 P(g) [0^\circ] = 4 P(g) [298.15^\circ]$ $\Delta H_f^o = 4(1.481)$ kcal. mole⁻¹ of P_4 See $P(g)$ table.

D_0^o for reaction (4) was given by A. G. Gaydon (loc. cit.). He reported a predissociation limit at 51.958 ± 9 cm.⁻¹. He considered the dissociation to be $P_2 \rightarrow P(^4S) + P(^2D)$. From the predissociation limit and the energy level of the excited $P(^2D)$ state [11,360.8 cm.⁻¹] Gaydon (loc. cit.) obtained a $D_0^o = 5.033$ e.v. or 116.075 kcal. mole⁻¹. As a check, a graphical Birge-Sponer extrapolation by Gaydon (loc. cit.) [$\sum_{j=1}^{\infty} (v_j - 4.32)$] agrees with a $D_0^o = 5.0$ e.v.

The vapor equilibrium data of G. Freuner and I. Brockmoller, Z. physik. Chem. **81**, 129 (1913) gave a ΔH_f^o for reaction (4) which was much lower than the spectroscopic value i.e. 31.5(1073°K) vs. 116(0°) kcal. mole⁻¹ of P_2 . D. P. Stevenson and D. M. Yost, J. Chem. Phys. **9**, 403 (1941) reported that the vapor equilibrium measurements of G. Freuner and I. Brockmoller (loc. cit.) were doubtful while the measurements of A. Stock, G. E. Gibson, and E. Stamm Ber **45**, 3527 (1913) were correct. Stock et al. (loc. cit.) have shown that the reaction $P_2(g) \rightarrow 2P(g)$ is extremely slight even at 1473°K which is the highest temperature of the vapor equilibrium studies.

Heat Capacity and Entropy.

The thermodynamic functions were calculated from the electronic levels which were evaluated by averaging the spectroscopic values of W. C. Martin, J. Opt. Soc. Am. **49**, 1071, (1959).

Monophosphorus Monosulfide (PS)
(Ideal Gas) GFW = 63.0378

PS

MONOPHOSPHORUS MONOSULFIDE (PS) (IDEAL GAS) GFW = 63.0378

Ground State Configuration $2^1\Pi$ $\Delta H_f^\circ = 36.9 \pm 10 \text{ kcal/mol}$

$S_{298.15}^\circ = 56 \pm 0.2 \text{ gibbs/mol}$ $\Delta H_f^\circ = 37.3 \pm 10 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i	$g_i/\Sigma g_i$
0	0	0
324	324	0.20000
22000	4	0.00004
34594	2	0.00003

$\omega_e = 743.5 \pm 3.8 \text{ cm}^{-1}$ $\omega_e X_e = 3.8 \pm 0.9 \text{ cm}^{-1}$ $\sigma = 1$

$B_e = [0.29] \text{ cm}^{-1}$ $\alpha_e = [0.0016] \text{ cm}^{-1}$ $r_e = [1.92] \text{ \AA}$

Heat of Formation

The dissociation energy (D_0°) of PS(g) is estimated to be $140 \pm 25 \text{ kcal/mol}$ by comparison with the corresponding quantity for PO(g) and from a linear Birge-Sponer extrapolation of the third excited ($C^2\Sigma$) electronic state potential function. It is assumed that the $C^2\Sigma$ state dissociates to S(g) in its ground (3P) state and P(g) in its first excited (3D) state. The fundamental vibrational frequency in the $C^2\Sigma$ state (ω_e) is $531.8 \pm 2.5 \text{ cm}^{-1}$ and the corresponding anharmonic term ($\omega_e X_e$) is $2.6 \pm 0.5 \text{ cm}^{-1}$. These constants are calculated from a reanalysis of the spectral data of Dressler (1). The corresponding heat of formation of PS(g) is $37.3 \pm 25 \text{ kcal/mol}$. The excited state ($C^2\Sigma$) data are used to calculate D_0° instead of the ground state(X $^1\Pi$) data because the vibrational constants of the upper level are known more accurately and because the extrapolation is 50 kcal/mol smaller for this level.

Heat Capacity and Entropy

The spectra of PS(g) have been studied by Dressler (1) in the near UV and visible regions. He reported the above electronic levels which correspond to the doublet pi ground state and two of the excited levels ($^3\Pi$, $C^2\Sigma$). The level of the first excited electronic state ($A^2\Sigma$) is estimated by analogy with NO(g).

Dressler (1) estimated the value of the rotational constant B_e . The value of α_e is calculated from the Morse potential function. The bond distance is calculated from B_e . The fundamental vibrational frequency ω_e and the anharmonic vibrational term $\omega_e X_e$ are calculated from a reanalysis of the spectral data reported by Dressler (1).

References

1. K. Dressler, Helv. Phys. Acta 28, 563 (1955).

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	-2.297	36.918	INFINITE	INFINITE
100	7.302	47.280	6.205	-1.597	37.387	72.307	72.307
200	8.114	52.654	5.720	-0.813	37.436	28.753	31.420
298	8.423	55.958	5.558	-0.000	37.300	24.516	17.971
300	8.427	56.010	5.558	-0.016	37.297	24.437	17.803
400	8.506	58.461	5.111	1.968	36.537	20.207	11.543
500	8.718	60.395	56.925	1.735	35.075	16.293	7.082
600	8.793	61.991	57.640	2.610	35.292	12.324	4.889
700	8.865	63.351	58.361	3.492	34.781	9.563	2.673
800	8.983	64.534	59.061	4.379	34.000	7.178	1.469
900	9.113	65.582	59.728	5.269	32.983	5.183	0.718
1000	9.237	66.523	60.361	6.161	31.788	3.531	0.509
1100	8.956	67.376	60.961	7.056	30.325	2.641	0.525
1200	8.973	68.156	61.528	7.953	28.769	2.950	0.537
1300	8.988	68.874	62.066	8.851	27.178	3.258	0.548
1400	9.001	69.541	62.577	9.750	25.559	3.569	0.557
1500	9.013	70.162	63.062	10.651	23.922	3.881	0.565
1600	9.025	70.744	63.524	11.553	22.279	4.192	0.573
1700	9.035	71.292	63.965	12.455	20.635	4.504	0.579
1800	9.045	71.809	64.387	13.340	18.991	4.818	0.585
1900	9.055	72.298	64.790	14.225	17.348	5.128	0.590
2000	9.064	72.763	65.177	15.111	15.698	5.444	0.595
2100	9.073	73.205	65.549	16.077	14.052	5.757	0.599
2200	9.082	73.627	65.907	16.985	12.408	6.068	0.603
2300	9.091	74.031	66.251	17.894	10.765	6.384	0.607
2400	9.100	74.418	66.584	18.803	9.123	6.698	0.610
2500	9.109	74.790	66.904	19.714	7.487	7.011	0.613
2600	9.118	75.147	67.215	20.625	5.851	7.326	0.616
2700	9.128	75.492	67.515	21.537	4.215	7.643	0.619
2800	9.137	75.824	67.805	22.451	2.579	7.959	0.621
2900	9.146	76.145	68.084	23.365	0.944	8.273	0.623
3000	9.158	76.455	68.352	24.280	-0.693	8.586	0.625
3100	9.170	76.755	68.628	25.197	-2.327	8.900	0.627
3200	9.182	77.047	68.894	26.114	-3.956	9.219	0.630
3300	9.195	77.330	69.158	27.033	-5.586	9.536	0.632
3400	9.208	77.604	69.413	27.953	-7.215	9.854	0.633
3500	9.223	77.871	69.661	28.875	-8.844	10.167	0.635
3600	9.238	78.131	69.904	29.798	-10.473	10.484	0.636
3700	9.254	78.385	70.141	30.722	-12.082	10.802	0.638
3800	9.271	78.632	70.303	31.649	-13.691	11.119	0.639
3900	9.289	78.873	70.460	32.577	-15.299	11.436	0.641
4000	9.309	79.108	70.732	33.507	-16.908	11.751	0.642
4100	9.329	79.338	70.939	34.438	-18.517	12.070	0.643
4200	9.350	79.563	71.141	35.372	-20.126	12.385	0.644
4300	9.372	79.784	71.340	36.308	-21.735	12.711	0.646
4400	9.395	79.999	71.538	37.248	-23.344	13.025	0.647
4500	9.418	80.211	71.725	38.187	-24.953	13.340	0.648
4600	9.443	80.418	71.911	39.130	-26.562	13.657	0.649
4700	9.469	80.621	72.095	40.076	-28.171	13.988	0.650
4800	9.495	80.821	72.274	41.024	-29.780	14.312	0.652
4900	9.522	81.017	72.451	41.975	-31.389	14.639	0.654
5000	9.550	81.210	72.624	42.929	-33.000	14.965	0.654
5100	9.578	81.399	72.794	43.885	-34.611	15.297	0.655
5200	9.607	81.585	72.961	44.844	-36.222	15.630	0.656
5300	9.637	81.769	73.126	45.804	-37.833	15.962	0.657
5400	9.667	81.959	73.288	46.772	-39.444	16.295	0.658
5500	9.698	82.127	73.447	47.740	-41.055	16.627	0.659
5600	9.729	82.302	73.603	48.711	-42.666	16.960	0.660
5700	9.760	82.474	73.757	49.686	-44.277	17.293	0.661
5800	9.792	82.644	73.909	50.663	-45.888	17.626	0.662
5900	9.823	82.812	74.059	51.644	-47.499	17.959	0.663
6000	9.856	82.977	74.205	52.625	-49.110	18.292	0.664

Dec. 31, 1960; June 30, 1961; June 30, 1967

PS

Phosphorus, Diatomic (P₂)
(Ideal Gas) Mol. Wt. = 61.950

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈)/T	H ^o - H ₂₉₈	ΔH _f ^o	Log K _p
0	0.000	INFINITE	0.000	42.276	INFINITE
100	0.000	48.419	0.000	42.276	38.676
200	7.195	52.795	0.000	42.657	37.670
298	7.657	52.110	0.000	42.680	30.393
300	7.665	52.110	0.04	42.676	30.318
400	6.950	54.418	0.401	42.397	22.085
500	6.111	56.744	1.620	45.074	26.239
600	5.485	57.776	2.660	41.712	22.235
700	5.004	59.021	3.315	41.301	16.299
800	4.630	60.248	3.552	40.829	11.429
900	4.342	61.475	3.752	40.301	8.665
1000	4.100	62.600	3.930	40.000	6.665
1100	3.886	63.641	4.082	39.612	5.000
1200	3.688	64.611	4.217	39.156	3.665
1300	3.503	65.522	4.336	38.636	2.556
1400	3.331	66.382	4.443	38.064	1.654
1500	3.173	67.197	4.540	37.444	0.952
1600	3.029	67.967	4.628	36.783	0.452
1700	2.898	68.691	4.707	36.089	0.000
1800	2.778	69.369	4.778	35.361	0.000
1900	2.667	70.000	4.842	34.598	0.000
2000	2.564	70.584	4.899	33.800	0.000
2100	2.468	71.122	4.949	32.968	0.000
2200	2.378	71.614	4.993	32.102	0.000
2300	2.293	72.061	5.031	31.202	0.000
2400	2.213	72.464	5.063	30.268	0.000
2500	2.138	72.822	5.090	29.300	0.000
2600	2.067	73.146	5.112	28.300	0.000
2700	2.000	73.436	5.129	27.268	0.000
2800	1.937	73.692	5.142	26.211	0.000
2900	1.878	73.915	5.151	25.121	0.000
3000	1.823	74.104	5.156	24.000	0.000
3100	1.771	74.268	5.158	22.857	0.000
3200	1.721	74.408	5.158	21.692	0.000
3300	1.673	74.524	5.156	20.507	0.000
3400	1.627	74.617	5.153	19.302	0.000
3500	1.583	74.688	5.149	18.078	0.000
3600	1.541	74.736	5.143	16.835	0.000
3700	1.500	74.762	5.136	15.573	0.000
3800	1.460	74.767	5.128	14.292	0.000
3900	1.421	74.752	5.118	13.000	0.000
4000	1.383	74.718	5.107	11.698	0.000
4100	1.346	74.665	5.094	10.385	0.000
4200	1.310	74.594	5.079	9.060	0.000
4300	1.275	74.507	5.062	7.725	0.000
4400	1.241	74.404	5.043	6.380	0.000
4500	1.208	74.286	5.022	5.025	0.000
4600	1.176	74.153	5.000	3.650	0.000
4700	1.144	74.006	4.976	2.265	0.000
4800	1.113	73.846	4.950	0.870	0.000
4900	1.082	73.672	4.922	0.000	0.000
5000	1.051	73.486	4.892	0.000	0.000
5100	1.020	73.288	4.860	0.000	0.000
5200	0.990	73.078	4.826	0.000	0.000
5300	0.960	72.856	4.790	0.000	0.000
5400	0.930	72.622	4.751	0.000	0.000
5500	0.900	72.376	4.709	0.000	0.000
5600	0.870	72.118	4.664	0.000	0.000
5700	0.840	71.849	4.616	0.000	0.000
5800	0.810	71.569	4.565	0.000	0.000
5900	0.780	71.278	4.511	0.000	0.000
6000	0.750	70.976	4.454	0.000	0.000

June 30, 1961

PHOSPHORUS, DIATOMIC (P₂) (IDEAL GAS)

MOL. WT. = 61.950

D^o = 116 ± 1 kcal. mole⁻¹ ΔH_f^o 298.15 = 42.68 ± 0.5 kcal. mole⁻¹

Ground State Configuration 1Σ⁺ S₂₉₈^o = 52.11 ± 0.1 cal. deg.⁻¹ mole⁻¹

ω_ex_e = 760.43 cm.⁻¹ D_e = 0.21 × 10⁻⁶ cm.⁻¹

ω_e = 0.30327 cm.⁻¹ r_e = 1.8943 Å

Heat of Formation

D. P. Stevenson and D. M. Yost, J. Chem. Phys. 9, 403 (1941), have shown that the vapor density measurements of A. Stock, O. E. Gibson and E. Stamm, Ber. 45, 3527 (1912), best fit a vapor composed of P₂ and P₄ molecular species. From these data T. D. Parr, Tennessee Valley Authority, Chemical Engineering Report No. 8, calculated the equilibrium constants which lead to e ΔH_f^o of P₂ for I. From which ΔH_f^o of P₂ is obtained based upon a ΔH_f^o 298.15 of 30.77 kcal. mole⁻¹ of P₄(g).

(I) P₄(g) 298.15 = P₂(g) 298.15 ΔH_r^o = 54.59 ± 0.1 kcal. mole⁻¹

Heat Capacity and Entropy

Molecular end spectroscopic constants are those listed by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co. Inc., New York, 1945. More recent measurements of K. Dressler, Helv. Phys. Acta 28, 563 (1955) are in agreement with the values selected by Herzberg.

The dissociation energy is given by A. G. Oaydon, "Dissociation Energies", Chapman and Hall, Ltd., London, 1953.

Phosphorus, Tetratomic (P₄)
(Ideal Gas) Mol. Wt. = 123.90

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0	3.000	INFINITE	3.378	30.881	30.881	INFINITE	
100	5.000	61.010	1.425	31.128	31.128	12.506	
200	13.294	61.610	1.425	31.128	31.128	12.506	
298	16.493	66.893	1.000	30.771	17.337	12.700	
300	16.494	66.892	0.999	30.765	17.244	12.562	
400	17.440	67.440	0.717	29.829	16.478	12.506	
500	18.241	67.835	0.510	29.278	15.950	12.506	
600	18.735	68.212	0.343	28.635	15.425	12.506	
700	19.022	68.573	0.222	28.035	14.950	12.506	
800	19.214	68.824	0.134	27.476	14.525	12.506	
900	19.346	69.000	0.077	26.956	14.150	12.506	
1000	19.445	69.111	0.043	26.476	13.825	12.506	
1100	19.518	69.168	0.029	26.036	13.550	12.506	
1200	19.574	69.188	0.018	25.636	13.325	12.506	
1300	19.617	69.178	0.010	25.276	13.150	12.506	
1400	19.652	69.140	0.005	24.956	13.025	12.506	
1500	19.680	69.080	0.002	24.676	12.950	12.506	
1600	19.703	69.000	0.000	24.436	12.925	12.506	
1700	19.722	68.900	0.000	24.236	12.950	12.506	
1800	19.736	68.788	0.000	24.076	12.975	12.506	
1900	19.746	68.664	0.000	23.956	13.000	12.506	
2000	19.752	68.530	0.000	23.876	13.025	12.506	
2100	19.774	68.388	0.000	23.836	13.050	12.506	
2200	19.783	68.240	0.000	23.836	13.075	12.506	
2300	19.780	68.088	0.000	23.876	13.100	12.506	
2400	19.768	67.936	0.000	23.956	13.125	12.506	
2500	19.743	67.784	0.000	24.076	13.150	12.506	
2600	19.708	67.632	0.000	24.236	13.175	12.506	
2700	19.664	67.480	0.000	24.436	13.200	12.506	
2800	19.613	67.328	0.000	24.676	13.225	12.506	
2900	19.557	67.176	0.000	24.956	13.250	12.506	
3000	19.500	67.024	0.000	25.276	13.275	12.506	
3100	19.437	66.872	0.000	25.636	13.300	12.506	
3200	19.370	66.720	0.000	26.036	13.325	12.506	
3300	19.300	66.568	0.000	26.476	13.350	12.506	
3400	19.228	66.416	0.000	26.956	13.375	12.506	
3500	19.157	66.264	0.000	27.476	13.400	12.506	
3600	19.087	66.112	0.000	28.036	13.425	12.506	
3700	19.017	65.960	0.000	28.636	13.450	12.506	
3800	18.947	65.808	0.000	29.276	13.475	12.506	
3900	18.877	65.656	0.000	29.956	13.500	12.506	
4000	18.807	65.504	0.000	30.676	13.525	12.506	
4100	18.737	65.352	0.000	31.436	13.550	12.506	
4200	18.667	65.200	0.000	32.236	13.575	12.506	
4300	18.597	65.048	0.000	33.076	13.600	12.506	
4400	18.527	64.896	0.000	33.956	13.625	12.506	
4500	18.457	64.744	0.000	34.876	13.650	12.506	
4600	18.387	64.592	0.000	35.836	13.675	12.506	
4700	18.317	64.440	0.000	36.836	13.700	12.506	
4800	18.247	64.288	0.000	37.876	13.725	12.506	
4900	18.177	64.136	0.000	38.956	13.750	12.506	
5000	18.107	63.984	0.000	40.076	13.775	12.506	
5100	18.037	63.832	0.000	41.236	13.800	12.506	
5200	17.967	63.680	0.000	42.436	13.825	12.506	
5300	17.897	63.528	0.000	43.676	13.850	12.506	
5400	17.827	63.376	0.000	44.956	13.875	12.506	
5500	17.757	63.224	0.000	46.276	13.900	12.506	
5600	17.687	63.072	0.000	47.636	13.925	12.506	
5700	17.617	62.920	0.000	49.036	13.950	12.506	
5800	17.547	62.768	0.000	50.476	13.975	12.506	
5900	17.477	62.616	0.000	51.956	14.000	12.506	
6000	17.407	62.464	0.000	53.476	14.025	12.506	

June 30, 1961

PHOSPHORUS, TETRATOMIC (P₄) (IDEAL GAS) MOL. WT. = 123.90

ΔH_f[°] 298.15 = 30.84 ± 0.5 kcal. mole⁻¹
ΔH_f[°] 298.15 = 30.77 ± 0.5 kcal. mole⁻¹
S_{298.15} = 86.89 ± 0.1 cal. deg.⁻¹ mole⁻¹

Point Group T_d

Vibrational Levels and Multiplicities

(ω), cm.⁻¹

606 (1)
363 (2)
464.5 (3)

Bond Lengths and Angles P-P = 2.21 ± 0.2 Å
P-P-P = 109°.28
Moments of Inertia I_A = I_B = I_C = 25.1 X 10⁻³⁹ g. cm.² ϕ = 12

Heat of Formation

Taken as the heat of sublimation of P (red, v).

Heat Capacity and Entropy

The frequency and multiplicities are those assigned by H. S. Gutowsky and G. S. Hoffman, J. Am. Chem. Soc. 72, 5751 (1950). Molecular parameters of the gas were determined from electron diffraction measurements by L. R. Maxwell, S. B. Hendricks and V. M. Moseley, J. Chem. Phys. 23, 899 (1955). C. D. Thomas and N. S. Gingrich, J. Chem. Phys. 23, 659 (1955) obtained a P-P distance of 2.25 Å from x-ray studies on the liquid. On the basis of the selected values for P, White (see sheet) a third law entropy of 66.89 cal. deg.⁻¹ mole⁻¹ is derived for P₄(g) at 298.15°K.

Tetraphosphorus Trisulfide (P_4S_3)
(Solid) Mol. Wt. = 220.098

INTERIM TABLE

T, °K.	C_p	$S^\circ - (F^\circ - H^\circ_{298})/T$	ΔH°_f	ΔF°_f	Log K _p
0					
100					
200					
298	35.000	44.000	0.000	37.986	27.843
300	35.000	44.001	0.045	37.991	27.845
400	35.000	48.285	3.565	39.218	29.880
500	35.000	51.966	7.065	37.858	16.587
600	35.000	54.869	10.565	42.003	13.544
700	35.000	57.779	14.065	43.435	11.301
800	35.000	60.546	17.565	46.402	10.203
900	35.000	63.281	21.065	49.868	9.245
1000	35.000	65.791	24.565	53.833	8.453
1100	35.000	68.178	28.065	58.296	7.815
1200	35.000	70.433	31.565	63.259	7.310
1300	35.000	72.565	35.065	68.722	6.950
1400	35.000	74.588	38.565	74.685	6.717
1500	35.000	76.508	42.065	81.148	6.587
1600	35.000	78.328	45.565	88.111	6.553
1700	35.000	80.066	49.065	95.574	6.620
1800	35.000	81.735	52.565	103.537	6.786
1900	35.000	83.343	56.065	112.000	7.050
2000	35.000	84.898	59.565	120.963	7.414

December 31, 1960.

TETRAPHOSPHORUS TRISULFIDE (P_4S_3) (solid)

Mol. Wt. = 220.098
 $\Delta H^\circ_f 298.15 = [-37] \text{ kcal. mole}^{-1}$
 $S^\circ_{298.15} = [48] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 440^\circ\text{K.}$
 $\Delta H_m = [2.2] \text{ kcal. mole}^{-1}$

$\Delta H^\circ_f 298.15$ estimated from vapor density reported by D. M. Yost and H. Russell, "Systematic Inorganic Chemistry of the Fifth- and Sixth- Group Nonmetallic Elements", Prentice-Hall, New York (1944).
 T_m from Yost and Russell, loc. cit. Other data estimated.

Tetraphosphorus Trisulfide (P_4S_3)
(Liquid) Mol. Wt. = 220.098 **INTERIM TABLE**

T, °K.	C_p	$S^\circ - (F^\circ - H^\circ_{298})/T$	ΔH°_f	ΔF°_f	Log K_p
0					
100					
200					
250	44.000	49.510	.000	- 36.077	- 37.513
300	44.000	49.782	.081	- 36.062	- 37.521
350	44.000	49.850	.123	- 36.047	- 37.528
400	44.000	49.890	.140	- 36.032	- 37.534
450	44.000	49.910	.146	- 36.027	- 37.539
500	44.000	49.920	.150	- 36.023	- 37.543
600	44.000	49.930	.153	- 36.019	- 37.547
700	44.000	49.940	.155	- 36.016	- 37.550
800	44.000	49.950	.157	- 36.013	- 37.553
900	44.000	49.960	.158	- 36.011	- 37.555
1000	44.000	49.970	.159	- 36.009	- 37.557
1100	44.000	49.980	.160	- 36.007	- 37.559
1200	44.000	49.990	.161	- 36.005	- 37.561
1300	44.000	49.995	.162	- 36.004	- 37.562
1400	44.000	49.998	.163	- 36.003	- 37.563
1500	44.000	49.999	.164	- 36.002	- 37.564
1600	44.000	49.999	.165	- 36.001	- 37.565
1700	44.000	49.999	.166	- 36.000	- 37.566
1800	44.000	49.999	.167	- 36.000	- 37.567
1900	44.000	49.999	.168	- 36.000	- 37.568
2000	44.000	49.999	.169	- 36.000	- 37.569
2100	44.000	49.999	.170	- 36.000	- 37.570
2200	44.000	49.999	.171	- 36.000	- 37.571
2300	44.000	49.999	.172	- 36.000	- 37.572
2400	44.000	49.999	.173	- 36.000	- 37.573
2500	44.000	49.999	.174	- 36.000	- 37.574
2600	44.000	49.999	.175	- 36.000	- 37.575
2700	44.000	49.999	.176	- 36.000	- 37.576
2800	44.000	49.999	.177	- 36.000	- 37.577
2900	44.000	49.999	.178	- 36.000	- 37.578
3000	44.000	49.999	.179	- 36.000	- 37.579

TETRAPHOSPHORUS TRISULFIDE (P_4S_3) (Liquid)

Mol. Wt. = 220.098
 $\Delta H^\circ_f 298.15 = [-36.077] \text{ kcal. mole}^{-1}$
 $S^\circ_{298.15} = [49.510] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 440^\circ\text{K.}$
 $\Delta H_m = [2.2] \text{ kcal. mole}^{-1}$
 $T_b = 680^\circ\text{K.}$
 $\Delta H_v 680 = [14.3] \text{ kcal. mole}^{-1}$

T_m and T_b from D. M. Yost and H. Russell, "Systematic Inorganic Chemistry of the Fifth- and Sixth- Group Nonmetallic Elements", Prentice-Hall, New York (1944). Other data estimated.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH°	ΔF°	Log K _p
0						
100	37.000	76.280	.000	- 19.408	- 20.826	21.129
200	37.000	76.280	.000	- 19.408	- 20.826	21.129
300	37.000	76.280	.000	- 19.408	- 20.826	21.129
400	37.000	76.280	.000	- 19.408	- 20.826	21.129
500	37.000	76.280	.000	- 19.408	- 20.826	21.129
600	37.000	76.280	.000	- 19.408	- 20.826	21.129
700	37.000	76.280	.000	- 19.408	- 20.826	21.129
800	37.000	76.280	.000	- 19.408	- 20.826	21.129
900	37.000	76.280	.000	- 19.408	- 20.826	21.129
1000	37.000	76.280	.000	- 19.408	- 20.826	21.129
1100	37.000	76.280	.000	- 19.408	- 20.826	21.129
1200	37.000	76.280	.000	- 19.408	- 20.826	21.129
1300	37.000	76.280	.000	- 19.408	- 20.826	21.129
1400	37.000	76.280	.000	- 19.408	- 20.826	21.129
1500	37.000	76.280	.000	- 19.408	- 20.826	21.129
1600	37.000	76.280	.000	- 19.408	- 20.826	21.129
1700	37.000	76.280	.000	- 19.408	- 20.826	21.129
1800	37.000	76.280	.000	- 19.408	- 20.826	21.129
1900	37.000	76.280	.000	- 19.408	- 20.826	21.129
2000	37.000	76.280	.000	- 19.408	- 20.826	21.129
2100	37.000	76.280	.000	- 19.408	- 20.826	21.129
2200	37.000	76.280	.000	- 19.408	- 20.826	21.129
2300	37.000	76.280	.000	- 19.408	- 20.826	21.129
2400	37.000	76.280	.000	- 19.408	- 20.826	21.129
2500	37.000	76.280	.000	- 19.408	- 20.826	21.129
2600	37.000	76.280	.000	- 19.408	- 20.826	21.129
2700	37.000	76.280	.000	- 19.408	- 20.826	21.129
2800	37.000	76.280	.000	- 19.408	- 20.826	21.129
2900	37.000	76.280	.000	- 19.408	- 20.826	21.129
3000	37.000	76.280	.000	- 19.408	- 20.826	21.129
3100	37.000	76.280	.000	- 19.408	- 20.826	21.129
3200	37.000	76.280	.000	- 19.408	- 20.826	21.129
3300	37.000	76.280	.000	- 19.408	- 20.826	21.129
3400	37.000	76.280	.000	- 19.408	- 20.826	21.129
3500	37.000	76.280	.000	- 19.408	- 20.826	21.129
3600	37.000	76.280	.000	- 19.408	- 20.826	21.129
3700	37.000	76.280	.000	- 19.408	- 20.826	21.129
3800	37.000	76.280	.000	- 19.408	- 20.826	21.129
3900	37.000	76.280	.000	- 19.408	- 20.826	21.129
4000	37.000	76.280	.000	- 19.408	- 20.826	21.129
4100	37.000	76.280	.000	- 19.408	- 20.826	21.129
4200	37.000	76.280	.000	- 19.408	- 20.826	21.129
4300	37.000	76.280	.000	- 19.408	- 20.826	21.129
4400	37.000	76.280	.000	- 19.408	- 20.826	21.129
4500	37.000	76.280	.000	- 19.408	- 20.826	21.129
4600	37.000	76.280	.000	- 19.408	- 20.826	21.129
4700	37.000	76.280	.000	- 19.408	- 20.826	21.129
4800	37.000	76.280	.000	- 19.408	- 20.826	21.129
4900	37.000	76.280	.000	- 19.408	- 20.826	21.129
5000	37.000	76.280	.000	- 19.408	- 20.826	21.129
5100	37.000	76.280	.000	- 19.408	- 20.826	21.129
5200	37.000	76.280	.000	- 19.408	- 20.826	21.129
5300	37.000	76.280	.000	- 19.408	- 20.826	21.129
5400	37.000	76.280	.000	- 19.408	- 20.826	21.129
5500	37.000	76.280	.000	- 19.408	- 20.826	21.129
5600	37.000	76.280	.000	- 19.408	- 20.826	21.129
5700	37.000	76.280	.000	- 19.408	- 20.826	21.129
5800	37.000	76.280	.000	- 19.408	- 20.826	21.129
5900	37.000	76.280	.000	- 19.408	- 20.826	21.129
6000	37.000	76.280	.000	- 19.408	- 20.826	21.129

December 31, 1950.

TETRAPHOSPHORUS TRISULFIDE (P₄S₃) (Ideal Gas)

Mol. Wt. = 220.098

ΔH°_f 298.15 = [-19.408] kcal. mole⁻¹S°_{298.15} = [76.280] cal. deg.⁻¹ mole⁻¹C_p = [37] cal. deg.⁻¹ mole⁻¹

All data estimated.

Lead (Pb)

(Reference State) At. Wt. = 207.21

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔF°	Log K _p
0	.000	INFINITE	1.644	.000	.000
100	5.436	21.013	.000	.000	.000
200	12.972	14.062	.618	.000	.000
298	6.414	15.484	.000	.000	.000
300	6.418	15.524	.012	.000	.000
400	6.626	17.399	.664	.000	.000
500	6.823	18.898	1.337	.000	.000
600	7.026	20.157	2.007	.000	.000
700	7.240	21.143	2.687	.000	.000
800	7.474	21.843	3.371	.000	.000
900	7.698	22.484	4.060	.000	.000
1000	7.926	23.128	4.760	.000	.000
1100	8.153	23.784	5.473	.000	.000
1200	8.380	24.452	6.200	.000	.000
1300	8.608	25.132	6.941	.000	.000
1400	8.841	25.825	7.707	.000	.000
1500	9.083	26.532	8.498	.000	.000
1600	9.334	27.254	9.315	.000	.000
1700	9.597	28.000	10.158	.000	.000
1800	9.872	28.772	11.028	.000	.000
1900	10.159	29.579	11.934	.000	.000
2000	10.459	30.422	12.878	.000	.000
2100	10.772	31.302	13.861	.000	.000
2200	11.099	32.217	14.884	.000	.000
2300	11.440	33.168	15.948	.000	.000
2400	11.796	34.156	17.053	.000	.000
2500	12.168	35.182	18.200	.000	.000
2600	12.556	36.247	19.390	.000	.000
2700	12.960	37.352	20.624	.000	.000
2800	13.381	38.498	21.904	.000	.000
2900	13.819	39.686	23.230	.000	.000
3000	14.274	40.917	24.604	.000	.000
3100	14.746	42.192	26.028	.000	.000
3200	15.235	43.513	27.503	.000	.000
3300	15.741	44.881	29.030	.000	.000
3400	16.264	46.297	30.610	.000	.000
3500	16.805	47.763	32.244	.000	.000
3600	17.364	49.280	33.934	.000	.000
3700	17.941	50.849	35.681	.000	.000
3800	18.536	52.472	37.486	.000	.000
3900	19.150	54.150	39.350	.000	.000
4000	19.783	55.884	41.274	.000	.000
4100	20.436	57.675	43.259	.000	.000
4200	21.109	59.524	45.306	.000	.000
4300	21.802	61.433	47.416	.000	.000
4400	22.516	63.404	49.590	.000	.000
4500	23.251	65.438	51.830	.000	.000
4600	24.008	67.537	54.137	.000	.000
4700	24.788	69.703	56.513	.000	.000
4800	25.592	71.938	58.960	.000	.000
4900	26.421	74.244	61.480	.000	.000
5000	27.276	76.623	64.074	.000	.000
5100	28.158	79.077	66.744	.000	.000
5200	29.068	81.608	69.491	.000	.000
5300	29.997	84.218	72.317	.000	.000
5400	30.947	86.908	75.224	.000	.000
5500	31.919	89.681	78.214	.000	.000
5600	32.914	92.539	81.288	.000	.000
5700	33.934	95.486	84.448	.000	.000
5800	34.979	98.524	87.695	.000	.000
5900	36.050	101.655	91.031	.000	.000
6000	37.148	104.881	94.458	.000	.000

See crystal, liquid, and ideal monatomic gas for details.

(REFERENCE STATE)

LEAD (Pb)

0° to 600.58°K
600.58° to 2026°K
2026° to 5000°K

Crystal
Liquid
Ideal Monatomic Gas

AT. WT. = 207.21

Pb

March 31, 1962

Pb

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	(C _p - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100	5.000	8.000	INFINITE	-	1.664	.000	.000	INFINITE
200	6.985	12.972	16.062	-	.618	.000	.000	.000
298	6.418	15.484	15.484	.000	.000	.000	.000	.000
300	6.418	15.524	15.484	.012	.000	.000	.000	.000
400	6.624	17.399	15.738	.664	.000	.000	.000	.000
500	6.821	18.898	16.725	1.337	.000	.000	.000	.000
600	7.028	20.151	16.718	2.027	.000	.000	.000	.000
700	7.235	21.257	17.341	2.741	1.156	.190	.190	.059
800	7.491	22.242	17.893	3.479	1.139	.382	.382	.104
900	7.723	23.137	18.427	4.239	1.093	.569	.569	.138
1000	7.956	23.963	18.940	5.023	1.015	.750	.750	.164
1100	8.189	24.732	19.432	5.831	.906	.921	.921	.183
1200	8.422	25.455	19.904	6.661	.767	1.083	1.083	.197
1300	8.654	26.138	20.357	7.515	.599	1.230	1.230	.207
1400	8.887	26.788	20.794	8.392	.407	1.363	1.363	.213
1500	9.120	27.409	21.214	9.292	.191	1.483	1.483	.216

March 31, 1962

LEAD (Pb)

(CRYSTAL)

AT. WT. = 207.21

$$\Delta H_{f0}^0 = 0$$

$$\Delta H_{f298.15}^0 = 0$$

$$\Delta H_g^0 298.15 = 46.75 \pm 0.13 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 15.484 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^0 = 1.141 \text{ kcal. mole}^{-1}$$

$$T_m = 800.58 \pm 0.00^\circ \text{K}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Heat capacity measurements have been reported by M. Horowitz, A. A. Silvini, S. P. Malaker and J. O. Daunt, (1° to 4°, 14° to 21°, and 84° to 77°K.), Phys. Rev. **89**, 1182 (1952); P. P. Maada, W. R. Foraythe and W. P. Olaque, (15° to 300°K.), J. Am. Chem. Soc. **83**, 1902 (1961); T. B. Douglas and J. L. Dever, (298.16° to 1200°K.), J. Am. Chem. Soc. **76**, 4824 (1954), and many others whose work is listed by K. K. Kelley, U. S. Bur. Mines Bull. **584** (1960).

Heat capacities from 15° to 300° and 1° to 4°K. (in superconducting state) were taken from Neada, Foraythe, and Oiaque, and Horowitz, Silvini, Malaker, and Daunt, respectively. The missing data below the melting point were obtained by graphical extrapolation and joined smoothly to data of Douglas and Dever on approaching the melting point.

Melting.

The melting point of pure Pb(c) was found by E. H. McLaren and E. G. Mardock, Can. J. Phys. **38**, 577 (1960) to be $327.426 \pm 0.002^\circ \text{C}$. ΔH_m given by Douglas and Dever, loc. cit.

Heat of Sublimation.

$\Delta H_g^0 298.15$ was derived from third law analysis of the vapor pressure data of W. H. Rodebush and A. L. Dixon, J. Am. Chem. Soc. **47**, 1036 (1925) and Phys. Rev. **28**, 851 (1925); A. C. O. Egerton, Proc. Roy. Soc. (London) **A103**, 469 (1923); P. Hartack, Z. physik. Chem. **134**, 1 (1928); A. T. Aldeed and J. N. Pratt, Trans. Faraday Soc. **57**, 611 (1961); E. Baur and R. Brunner, Helv. Chim. Acta. **17**, 958 (1934), and J. Fischer, Z. anorg. Chem. **219**, 1, 367 (1934), which are in good agreement. Most weight was given to the results of Rodebush and Dixon. Older vapor pressure data of lower accuracy have not been used.

Lead (Pb)

(Liquid) At. Wt. = 207.21

T, °K.	C_p^o	$S^o - (F^o - H_{298}^o)/T$	$H^o - H_{298}^o$	ΔH_f^o	ΔF_f^o	Log K_f
0						
100						
200						
298	6.414	17.141	.000	1.025	.531	.389
300						
400	6.418	17.181	.012	1.025	.528	.385
500	7.470	19.056	.664	1.025	.362	.198
600	7.396	20.715	1.407	1.095	.187	.082
700	7.322	22.056	1.588	1.161	.002	.001
800	7.250	23.169	1.951	.000	.000	.000
900	7.198	24.082	2.098	.000	.000	.000
1000	7.026	25.126	2.714	.000	.000	.000
1100	6.953	26.393	3.201	.000	.000	.000
1200	6.880	27.584	3.569	.000	.000	.000
1300	6.807	28.700	3.832	.000	.000	.000
1400	6.733	29.741	4.000	.000	.000	.000
1500	6.659	30.718	4.078	.000	.000	.000
1600	6.585	31.632	4.078	.000	.000	.000
1700	6.511	32.484	4.000	.000	.000	.000
1800	6.437	33.280	3.932	.000	.000	.000
1900	6.363	34.021	3.875	.000	.000	.000
2000	6.289	34.708	3.828	.000	.000	.000
2100	6.215	35.341	3.791	.000	.000	.000
2200	6.141	35.919	3.764	.000	.000	.000
2300	6.067	36.442	3.746	.000	.000	.000
2400	5.993	36.910	3.736	.000	.000	.000
2500	5.919	37.323	3.734	.000	.000	.000
2600	5.845	37.681	3.739	.000	.000	.000
2700	5.771	38.084	3.750	.000	.000	.000
2800	5.697	38.432	3.764	.000	.000	.000
2900	5.623	38.725	3.781	.000	.000	.000
3000	5.549	38.962	3.800	.000	.000	.000

LEAD (Pb)

(LIQUID)

AT. WT. = 207.21

$$\Delta H_f^o 298.15 = [1.025] \text{ kcal. mole}^{-1}$$

$$T_m = 600.58 \pm 0.00^\circ \text{K}$$

$$T_b = 2026^\circ \text{K}$$

$$S_{298.15}^o = [17.141] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^o = 1.141 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^o = 42.53 \pm 0.13 \text{ kcal. mole}^{-1}$$

Heat of Formation.

Obtained from ΔH_m^o .

Heat Capacity and Extrapolation.

Heat capacity from T_m to 1200°K taken from T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76, 4824 (1954). C_p values below T_m and above 1200°K were extrapolated, a glass transition being assumed at 400°K.

Entropy.

Calculated from that of crystal.

Vaporization Phenomena.

T_b and ΔH_v^o calculated from $\Delta H_f^o 298.15$ and functions for condensed and gaseous states.

From the vapor pressure, the free energy functions of Pb(g) and Pb₂(g), and the dissociation energy of Pb₂(g), it appears that below the boiling point the amount of Pb₂(g) in the vapor is negligible.

AT. WT. = 207.21

(IDEAL GAS)

LEAD (Pb)

T, °K.	C_p	S°	$-(F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	INFINITE	INFINITE	46,910	46,910	INFINITE
100	36.327	42.335	4.488	46,910	45,337	45.337
200	4,998	42.335	4.488	46,910	45,337	45.337
298	4,998	41.890	4.488	46,910	45,337	45.337
300	4,998	41.890	4.488	46,910	45,337	45.337
400	4,998	41.890	4.488	46,910	45,337	45.337
500	4,998	41.890	4.488	46,910	45,337	45.337
600	4,998	41.890	4.488	46,910	45,337	45.337
700	4,998	41.890	4.488	46,910	45,337	45.337
800	4,998	41.890	4.488	46,910	45,337	45.337
900	4,998	41.890	4.488	46,910	45,337	45.337
1000	4,998	41.890	4.488	46,910	45,337	45.337
1100	4,998	41.890	4.488	46,910	45,337	45.337
1200	4,998	41.890	4.488	46,910	45,337	45.337
1300	4,998	41.890	4.488	46,910	45,337	45.337
1400	4,998	41.890	4.488	46,910	45,337	45.337
1500	4,998	41.890	4.488	46,910	45,337	45.337
1600	4,998	41.890	4.488	46,910	45,337	45.337
1700	4,998	41.890	4.488	46,910	45,337	45.337
1800	4,998	41.890	4.488	46,910	45,337	45.337
1900	4,998	41.890	4.488	46,910	45,337	45.337
2000	4,998	41.890	4.488	46,910	45,337	45.337
2100	4,998	41.890	4.488	46,910	45,337	45.337
2200	4,998	41.890	4.488	46,910	45,337	45.337
2300	4,998	41.890	4.488	46,910	45,337	45.337
2400	4,998	41.890	4.488	46,910	45,337	45.337
2500	4,998	41.890	4.488	46,910	45,337	45.337
2600	4,998	41.890	4.488	46,910	45,337	45.337
2700	4,998	41.890	4.488	46,910	45,337	45.337
2800	4,998	41.890	4.488	46,910	45,337	45.337
2900	4,998	41.890	4.488	46,910	45,337	45.337
3000	4,998	41.890	4.488	46,910	45,337	45.337
3100	4,998	41.890	4.488	46,910	45,337	45.337
3200	4,998	41.890	4.488	46,910	45,337	45.337
3300	4,998	41.890	4.488	46,910	45,337	45.337
3400	4,998	41.890	4.488	46,910	45,337	45.337
3500	4,998	41.890	4.488	46,910	45,337	45.337
3600	4,998	41.890	4.488	46,910	45,337	45.337
3700	4,998	41.890	4.488	46,910	45,337	45.337
3800	4,998	41.890	4.488	46,910	45,337	45.337
3900	4,998	41.890	4.488	46,910	45,337	45.337
4000	4,998	41.890	4.488	46,910	45,337	45.337
4100	4,998	41.890	4.488	46,910	45,337	45.337
4200	4,998	41.890	4.488	46,910	45,337	45.337
4300	4,998	41.890	4.488	46,910	45,337	45.337
4400	4,998	41.890	4.488	46,910	45,337	45.337
4500	4,998	41.890	4.488	46,910	45,337	45.337
4600	4,998	41.890	4.488	46,910	45,337	45.337
4700	4,998	41.890	4.488	46,910	45,337	45.337
4800	4,998	41.890	4.488	46,910	45,337	45.337
4900	4,998	41.890	4.488	46,910	45,337	45.337
5000	4,998	41.890	4.488	46,910	45,337	45.337
5100	4,998	41.890	4.488	46,910	45,337	45.337
5200	4,998	41.890	4.488	46,910	45,337	45.337
5300	4,998	41.890	4.488	46,910	45,337	45.337
5400	4,998	41.890	4.488	46,910	45,337	45.337
5500	4,998	41.890	4.488	46,910	45,337	45.337
5600	4,998	41.890	4.488	46,910	45,337	45.337
5700	4,998	41.890	4.488	46,910	45,337	45.337
5800	4,998	41.890	4.488	46,910	45,337	45.337
5900	4,998	41.890	4.488	46,910	45,337	45.337
6000	4,998	41.890	4.488	46,910	45,337	45.337

March 31, 1962

$\Delta H_f^\circ = 46.91 \pm 0.13 \text{ kcal. mole}^{-1}$
 $\Delta F_f^\circ = 46.91 \pm 0.13 \text{ kcal. mole}^{-1}$
 $\Delta G_f^\circ = 46.91 \pm 0.13 \text{ kcal. mole}^{-1}$
 $\Delta S_f^\circ = 46.91 \pm 0.13 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Configuration $3P_0$

Electronic Levels and Multiplicities

E_1	E_1	E_1	E_1
0.00	1	46,152.76	15
7,819.35	3	48,760.32	12
10,650.47	5	51,741.79	12
21,457.90	5	52,505.53	48
29,468.61	1	53,493.33	4
34,959.30	1	54,895.15	4
35,287.24	3	55,343.74	80
42,918.68	3	56,716.24	52
44,400.92	1	57,520.36	68
44,875.00	3	58,403.73	139
44,809.41	5	59,321.54	51
45,443.26	5		

Heat of Formation.

The same as ΔH_f° 298.15

Heat Capacity and Entropy.

Electronic levels and multiplicities from C. E. Moore, Natl. Bur. Standards (U. S.) Circ. 467, Vol. III (1959).

Lead, Diatomic (Pb₂)

(Ideal Gas) Mol. Wt. = 414.42

Pb₂

LEAD, DIATOMIC (Pb₂) (IDEAL GAS) MOL. WT. = 414.42

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.000	INFINITE	2.391	80.397	80.397	INFINITE
100	7.712	58.087	1.675	80.267	76.219	-166.568
200	8.545	63.744	0.816	79.882	72.026	-79.026
298	8.825	67.216	0.000	79.500	68.693	-50.351
300	8.828	67.270	0.016	79.492	68.626	-49.991
400	8.928	71.840	1.807	78.633	61.611	-26.929
500	9.050	73.496	2.716	78.162	58.252	-21.217
600	9.115	74.905	3.630	75.336	55.354	-17.282
700	9.219	76.133	4.549	74.813	52.536	-14.351
800	9.349	77.200	5.472	74.416	49.800	-11.400
900	9.490	78.200	6.402	73.820	47.082	-8.402
1000	9.631	79.089	7.335	73.361	44.430	-5.432
1100	9.773	79.905	8.273	72.917	41.821	-2.461
1200	9.915	80.658	9.214	72.486	39.247	0.508
1300	10.056	81.344	10.159	72.061	36.707	3.477
1400	10.195	81.973	11.109	71.643	34.197	6.446
1500	10.332	82.554	12.063	71.223	31.713	9.415
1600	10.468	83.090	13.020	70.802	29.258	12.384
1700	10.603	83.583	13.982	70.376	26.824	15.353
1800	10.737	84.035	14.947	69.945	24.415	18.322
1900	10.870	84.447	15.915	69.508	22.031	21.291
2000	11.002	84.819	16.886	69.066	19.672	24.260
2100	11.134	85.151	17.860	68.619	17.336	27.229
2200	11.265	85.443	18.836	68.167	15.014	30.198
2300	11.396	85.695	19.814	67.710	12.704	33.167
2400	11.526	85.907	20.794	67.248	10.404	36.136
2500	11.656	86.079	21.775	66.781	8.114	39.105
2600	11.785	86.211	22.757	66.309	5.834	42.074
2700	11.914	86.303	23.740	65.832	3.564	45.043
2800	12.043	86.355	24.724	65.351	1.304	48.012
2900	12.171	86.377	25.709	64.865	-0.956	50.981
3000	12.299	86.369	26.694	64.374	-3.226	53.950
3100	12.426	86.331	27.679	63.878	-5.506	56.919
3200	12.553	86.263	28.664	63.377	-7.791	59.888
3300	12.679	86.165	29.649	62.871	-10.076	62.857
3400	12.805	86.037	30.634	62.360	-12.361	65.826
3500	12.930	85.879	31.619	61.844	-14.646	68.795
3600	13.055	85.691	32.604	61.323	-16.931	71.764
3700	13.179	85.473	33.589	60.797	-19.216	74.733
3800	13.303	85.225	34.574	60.266	-21.501	77.702
3900	13.426	84.947	35.559	59.730	-23.786	80.671
4000	13.549	84.639	36.544	59.189	-26.071	83.640
4100	13.672	84.301	37.529	58.643	-28.356	86.609
4200	13.795	83.933	38.514	58.092	-30.641	89.578
4300	13.918	83.535	39.499	57.536	-32.926	92.547
4400	14.040	83.107	40.484	56.975	-35.211	95.516
4500	14.163	82.649	41.469	56.409	-37.496	98.485
4600	14.285	82.161	42.454	55.838	-39.781	101.454
4700	14.408	81.643	43.439	55.262	-42.066	104.423
4800	14.530	81.095	44.424	54.681	-44.351	107.392
4900	14.653	80.517	45.409	54.095	-46.636	110.361
5000	14.775	79.909	46.394	53.504	-48.921	113.330
5100	14.898	79.271	47.379	52.908	-51.206	116.300
5200	15.020	78.603	48.364	52.307	-53.491	119.269
5300	15.143	77.905	49.349	51.701	-55.776	122.238
5400	15.265	77.177	50.334	51.090	-58.061	125.207
5500	15.388	76.419	51.319	50.474	-60.346	128.176
5600	15.510	75.631	52.304	49.853	-62.631	131.145
5700	15.633	74.813	53.289	49.227	-64.916	134.114
5800	15.755	73.965	54.274	48.596	-67.201	137.083
5900	15.878	73.087	55.259	47.961	-69.486	140.052
6000	15.999	72.179	56.244	47.321	-71.771	143.021

Mar. 31, 1952; June 30, 1953; Sept. 30, 1953.

Ground State Configuration [3Σ_g⁻]
 $\Delta H_f^{\circ} = 80.4 \pm 4.6 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} = [62.216] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{\circ} = 298.15 = 79.5 \pm 4.6 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{\epsilon_i}{\epsilon_1} = \frac{g_i}{g_1}$$

$\omega_e x_e = 2.98 \text{ cm.}^{-1}$
 $\omega_e = [0.01727] \text{ cm.}^{-1}$
 $B_e = 0.01727 \text{ cm.}^{-1}$
 $\sigma = 2$
 $r_g = [3.08] \text{ \AA}$

Heat of Formation.

Heat of formation was calculated from the dissociation energy of Pb₂(g) reported by A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.

Heat Capacity and Entropy.

The values of ω_e and $\omega_e x_e$ were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950. Those for B_e and σ were estimated according to the method suggested by G. Herzberg, loc. cit. The bond distance (r_g) was calculated from the moment of inertia, $I = 1650 \times 10^{-40} \text{ g. cm.}^2$, estimated by K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592, 1961. The ground state configuration was assumed to be 3Σ_g by comparison to that for Si₂(g) reported by A. E. Douglas, Can. J. Phys. 33, 801 (1955).

Pb₂

Sulfur (S)

(Reference State) At. Wt. = 32.064

SULFUR (S)

(REFERENCE STATE)

AT. WT. = 32.064

0° to 368.54°K. Crystal, Rhombic
 368.54° to 388.36°K. Crystal, Monoclinic
 388.36° to 717.75°K. Liquid
 717.75° to 6000°K. Ideal Gas, Diatomic

See crystal, liquid and diatomic gas for details.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔF°	Log K _p
0	.000	INFINITE	- 1.053	.000	.000	.000
100	3.050	11.855	.889	.000	.000	.000
200	4.422	6.822	.683	.000	.000	.000
298	5.401	7.631	.631	.000	.000	.000
300	5.412	7.665	.632	.010	.000	.000
400	7.734	10.674	.780	.000	.000	.000
500	9.081	12.768	.863	.000	.000	.000
600	8.200	14.333	.9432	.000	.000	.000
700	7.799	15.601	1.0309	.000	.000	.000
800	4.368	31.363	9.4452	17.529	.000	.000
900	4.366	31.879	11.616	17.967	.000	.000
1000	4.418	32.344	13.636	18.408	.000	.000
1100	4.435	32.765	15.628	18.851	.000	.000
1200	4.450	33.152	17.073	19.295	.000	.000
1300	4.461	33.509	18.324	19.740	.000	.000
1400	4.471	33.840	19.420	20.187	.000	.000
1500	4.480	34.148	20.392	20.635	.000	.000
1600	4.488	34.438	21.261	21.083	.000	.000
1700	4.495	34.710	22.044	21.532	.000	.000
1800	4.501	34.967	22.755	21.982	.000	.000
1900	4.507	35.211	23.404	22.432	.000	.000
2000	4.513	35.442	24.000	22.883	.000	.000
2100	4.518	35.662	24.550	23.335	.000	.000
2200	4.523	35.873	25.060	23.787	.000	.000
2300	4.528	36.074	25.535	24.240	.000	.000
2400	4.532	36.267	25.978	24.693	.000	.000
2500	4.537	36.452	26.393	25.146	.000	.000
2600	4.541	36.630	26.784	25.600	.000	.000
2700	4.545	36.801	27.151	26.054	.000	.000
2800	4.549	36.966	27.499	26.509	.000	.000
2900	4.553	37.126	27.828	26.964	.000	.000
3000	4.557	37.281	28.141	27.420	.000	.000
3100	4.561	37.430	28.438	27.875	.000	.000
3200	4.565	37.575	28.721	28.332	.000	.000
3300	4.568	37.715	28.992	28.788	.000	.000
3400	4.572	37.852	29.250	29.245	.000	.000
3500	4.575	37.984	29.498	29.703	.000	.000
3600	4.579	38.113	29.735	30.160	.000	.000
3700	4.583	38.239	29.964	30.619	.000	.000
3800	4.586	38.361	30.183	31.077	.000	.000
3900	4.590	38.480	30.394	31.536	.000	.000
4000	4.593	38.597	30.598	31.995	.000	.000
4100	4.596	38.710	30.794	32.454	.000	.000
4200	4.600	38.821	30.984	32.914	.000	.000
4300	4.603	38.929	31.168	33.374	.000	.000
4400	4.607	39.035	31.345	33.835	.000	.000
4500	4.610	39.139	31.517	34.296	.000	.000
4600	4.613	39.240	31.684	34.757	.000	.000
4700	4.617	39.339	31.846	35.218	.000	.000
4800	4.620	39.436	32.003	35.680	.000	.000
4900	4.624	39.532	32.156	36.142	.000	.000
5000	4.627	39.625	32.304	36.605	.000	.000
5100	4.630	39.717	32.449	37.068	.000	.000
5200	4.633	39.807	32.589	37.531	.000	.000
5300	4.637	39.895	32.726	37.994	.000	.000
5400	4.640	39.982	32.860	38.458	.000	.000
5500	4.643	40.067	32.990	38.922	.000	.000
5600	4.647	40.151	33.117	39.387	.000	.000
5700	4.650	40.233	33.241	39.852	.000	.000
5800	4.653	40.314	33.363	40.317	.000	.000
5900	4.656	40.393	33.481	40.782	.000	.000
6000	4.660	40.472	33.597	41.248	.000	.000

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965

Sulfur (S)

(Crystal) At. Wt. = 32.064

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	.000	INFINITE	1.053	.000	.000	.000
100	3.050	2.965	11.855	.889	.000	.000	.000
200	4.639	5.622	8.104	.469	.000	.000	.000
298	5.401	7.631	7.631	.000	.000	.000	.000
300	5.412	7.665	7.432	.010	.000	.000	.000
400	6.133	9.571	6.871	.680	.000	.000	.000
500	6.819	11.013	6.358	1.327	.720	.158	.069
600	7.504	12.317	6.011	2.044	.860	.349	.127
700	8.190	13.525	5.842	2.868	.966	.488	.180
800	8.876	14.652	5.762	3.692	1.046	.583	.227
900	9.561	15.709	5.769	4.603	1.107	.648	.269
1000	10.247	16.792	5.792	5.594	1.154	.688	.308
1100	10.933	17.800	5.832	6.653	1.198	.723	.347
1200	11.619	18.781	5.881	7.781	1.235	.753	.385
1300	12.305	19.738	5.938	8.970	1.266	.778	.422
1400	12.990	20.675	6.000	10.241	1.292	.800	.458
1500	13.676	21.595	6.067	11.575	1.315	.819	.493
1600	14.361	22.499	6.138	12.976	1.335	.836	.527
1700	15.047	23.390	6.212	14.447	1.352	.851	.561
1800	15.732	24.269	6.288	15.989	1.367	.865	.594
1900	16.418	25.139	6.366	17.593	1.380	.878	.627
2000	17.104	25.998	6.444	19.270	1.391	.890	.659

SULFUR (S)

(CRYSTAL)

AT. WT. = 32.064

$$\Delta H_f^0 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 298.15 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_{f,1}^0 = 96.01 \pm 0.5 \text{ cal. mole}^{-1}$$

$$\Delta H_{f,2}^0 = 0.38 \pm 0.2 \text{ cal. mole}^{-1}$$

$$\Delta H_m^0 = 410.52 \pm 0.5 \text{ cal. mole}^{-1}$$

$$\Delta H_g^0 298.15 = 66.68 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 7.63 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_{f,1} = 368.54^\circ \text{K.}$$

$$T_{f,2} = 374^\circ \text{K.}$$

$$T_m = 368.36^\circ \text{K.}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

E. D. Eastman and W. C. McDevock, J. Am. Chem. Soc. 59, 145 (1937), have measured the low temperature heat capacities of sulfur from 15° to 375°K. E. D. West, J. Am. Chem. Soc. 81, 29 (1959), has measured the high temperature heat capacities from 298° to 678°K. These two sets of data were joined smoothly at 298.15 K. by a graphical method.

The values of entropy at 110°C and above in E. D. West's paper (table VIII) have been lowered by 0.5841 joule. deg.⁻¹ mole⁻¹ because of a calculational error which was pointed out by J. P. McCullough and D. W. Scott, private communication, Sept. 27, 1960.

The entropy of rhombic sulfur at 298.15°K. was taken from E. D. Eastman and W. C. McDevock, loc. cit., based on an extrapolation of $S_{15}^0 = 0.12 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Transition Data.

The enthalpies of transition at 368.54°K. and 374°K. were obtained from E. D. West, loc. cit. The first transition at 368.54°K. was the known rhombic-monoclinic transition, but the second one near 374°K. was a previously unreported transition.

Melting Data.

The heat of melting and the temperature were obtained from E. D. West, loc. cit.

Heat of Sublimation.

The heat of sublimation of sulfur (c) is the heat of formation of monatomic sulfur (g). See S(g) table for details. Since S_8 and lower polymers are major vapor species at room temperature, the heat of sublimation to the equilibrium gas is much smaller. See $S_8(g)$ table for details.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0						
100	7.579	8.444	0.000	+0.336	+0.093	-0.068
200	7.579	8.444	0.000	+0.336	+0.093	-0.068
298	7.579	8.444	0.000	+0.336	+0.093	-0.068
300	7.579	8.444	0.000	+0.336	+0.093	-0.068
400	7.579	8.444	0.000	+0.336	+0.093	-0.068
500	7.579	8.444	0.000	+0.336	+0.093	-0.068
600	8.200	10.053	2.568	+0.000	+0.000	+0.000
700	7.799	10.790	2.369	+0.000	+0.000	+0.000
800	7.694	11.457	2.170	+0.000	+0.000	+0.000
900	7.694	12.124	1.971	+0.000	+0.000	+0.000
1000	7.694	12.791	1.772	+0.000	+0.000	+0.000
1100	7.694	13.458	1.573	+0.000	+0.000	+0.000
1200	7.694	14.125	1.374	+0.000	+0.000	+0.000
1300	7.694	14.792	1.175	+0.000	+0.000	+0.000
1400	7.694	15.459	0.976	+0.000	+0.000	+0.000
1500	7.694	16.126	0.777	+0.000	+0.000	+0.000
1600	7.694	16.793	0.578	+0.000	+0.000	+0.000
1700	7.694	17.460	0.379	+0.000	+0.000	+0.000
1800	7.694	18.127	0.180	+0.000	+0.000	+0.000
1900	7.694	18.794	0.081	+0.000	+0.000	+0.000
2000	7.694	19.461	0.000	+0.000	+0.000	+0.000

Dec. 31, 1960; Dec. 31, 1965

$$S_{298.15}^{\circ} = 8.44 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 388.36^{\circ}\text{K.}$$

$$T_b = 717.75^{\circ}\text{K.}$$

$$\Delta H_f^{\circ} 298.15 = 0.34 \pm 0.01 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 410.52 \pm 0.5 \text{ cal. mole}^{-1}$$

$$\Delta H_v^{\circ} = [2.30] \text{ kcal. mole}^{-1}$$

Heat of Formation.

The $\Delta H_f^{\circ} 298.15$ (S, l) was obtained from that of the crystal by adding ΔH_m° and the difference between $H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase was obtained from E. D. West, J. Am. Chem. Soc. **81**, 29 (1959). No simple equation fits the curve of C_p against T which shows a peak.

The value of $S_{298.15}^{\circ}$ (S, l) was obtained in a manner analogous to that of the heat of formation. The heat capacity of sulfur (liquid) below the melting point was assumed to be constant as $7.579 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, and above the boiling point, it was assumed as $7.694 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

The heat of melting and the temperature were obtained from E. D. West, loc. cit.

Vaporization Data.

According to the international practical temperature scale, the boiling point is 717.75°K. The heat of vaporization to the equilibrium vapor mixture was estimated by D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D.C., 1956. The equilibrium vapor involves monomeric and several polymeric species; S₂ and S₃ predominate above 1000°K. while S₈, S₆ and possible S₄ and S₃ are favored at lower temperatures.

Sulfur, Monatomic (S)

(Ideal Gas) At. Wt. = 32.064

T, °K.	C _p	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	Log K _p
0	∞	∞	∞	∞	∞
100	5.103	34.127	1.591	66.142	INFINITE
200	5.589	37.831	4.546	66.477	-138.468
298	5.659	40.804	1.092	66.621	-65.758
			∞	66.680	57.004
300	5.658	40.121	40.086	66.680	-61.481
400	5.524	41.736	40.707	66.113	-63.718
500	5.436	42.962	40.720	65.754	-63.141
600	5.340	43.944	41.178	65.435	-62.669
700	5.266	44.762	41.634	65.166	-62.272
800	5.205	45.450	42.099	64.932	-61.932
900	5.153	46.042	42.568	64.724	-61.642
1000	5.112	46.551	42.968	64.540	-61.400
1100	5.078	47.000	43.311	64.380	-61.199
1200	5.053	47.397	43.572	64.241	-61.028
1300	5.033	47.750	43.766	64.120	-60.880
1400	5.016	48.071	43.898	64.016	-60.751
1500	5.002	48.368	43.968	63.926	-60.638
1600	4.990	48.641	43.978	63.848	-60.540
1700	4.979	48.889	43.917	63.781	-60.456
1800	4.970	49.114	43.787	63.724	-60.384
1900	4.962	49.316	43.588	63.676	-60.322
2000	4.955	49.495	43.321	63.636	-60.269
2100	4.949	49.652	42.990	63.602	-60.224
2200	4.944	49.788	42.604	63.573	-60.186
2300	4.940	49.905	42.174	63.549	-60.154
2400	4.936	50.005	41.704	63.529	-60.126
2500	4.933	50.091	41.194	63.512	-60.101
2600	4.930	50.163	40.644	63.497	-60.077
2700	4.927	50.222	40.054	63.484	-60.054
2800	4.925	50.269	39.424	63.472	-60.032
2900	4.923	50.305	38.754	63.461	-60.011
3000	4.921	50.331	38.044	63.451	-59.991
3100	4.919	50.348	37.294	63.441	-59.971
3200	4.917	50.356	36.504	63.432	-59.952
3300	4.915	50.355	35.674	63.423	-59.933
3400	4.913	50.345	34.804	63.414	-59.914
3500	4.911	50.326	33.894	63.405	-59.895
3600	4.909	50.298	32.944	63.396	-59.876
3700	4.907	50.261	31.954	63.387	-59.857
3800	4.905	50.215	30.924	63.378	-59.838
3900	4.903	50.161	29.854	63.369	-59.819
4000	4.901	50.099	28.744	63.360	-59.800
4100	4.899	50.030	27.594	63.351	-59.781
4200	4.897	49.954	26.404	63.342	-59.762
4300	4.895	49.871	25.174	63.333	-59.743
4400	4.893	49.780	23.904	63.324	-59.724
4500	4.891	49.681	22.594	63.315	-59.705
4600	4.889	49.574	21.244	63.306	-59.686
4700	4.887	49.460	19.854	63.297	-59.667
4800	4.885	49.339	18.424	63.288	-59.648
4900	4.883	49.211	16.954	63.279	-59.629
5000	4.881	49.077	15.444	63.270	-59.610
5100	4.879	48.937	13.894	63.261	-59.591
5200	4.877	48.791	12.304	63.252	-59.572
5300	4.875	48.639	10.674	63.243	-59.553
5400	4.873	48.482	9.004	63.234	-59.534
5500	4.871	48.320	7.294	63.225	-59.515
5600	4.869	48.153	5.544	63.216	-59.496
5700	4.867	47.981	3.754	63.207	-59.477
5800	4.865	47.804	1.924	63.198	-59.458
5900	4.863	47.622	0.054	63.189	-59.439
6000	4.861	47.435	-1.844	63.180	-59.420

Dec. 31, 1960; June 30, 1961; Dec. 31, 1965

AT. WT. = 32.064

(IDEAL GAS)

SULFUR, MONATOMIC (S)

 $\Delta H_f^\circ 0 = 66.14 \pm 0.5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = 66.68 \pm 0.5 \text{ kcal. mole}^{-1}$

Ground State Configuration $3p_2^2$
 $S^\circ_{298.15} = 40.1 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Electronic Levels and Quantum Weight

ϵ_1 , cm ⁻¹	ϵ_2 , cm ⁻¹	ϵ_3 , cm ⁻¹	ϵ_4 , cm ⁻¹	ϵ_5 , cm ⁻¹	ϵ_6 , cm ⁻¹
0.0	5	67,878.03	9	73,921.14	7
396.8	3	67,890.45	7	74,269.2	5
573.6	1	67,888.25	5	74,270.28	3
9,239.0	5	67,885.97	3	74,272.32	1
22,181.4	1	67,884.67	1	75,342.02	40
52,623.68	5	69,238.7	5	76,706.70	73
55,331.15	3	70,165.9	3	77,986.31	39
63,446.36	3	70,166.8	5	78,338.35	54
63,457.33	5	70,170.7	7	79,014.3	83
63,475.26	7	[70,706.0]	5	79,782.1	52
64,891.71	1	71,352.5	3	80,158.61	24
64,899.23	3	72,025.5	5	80,634.	89
64,892.89	5	72,382.5	3	81,089.9	29
67,815.87	3	72,572.4	1	81,405.23	84
67,825.72	5	73,911.53	3	81,864.6	101
67,843.38	7	73,915.16	5	82,353.3	25

Heat of Formation.

L. Brewer, J. Chem. Phys. **31**, 1143 (1959), has reviewed the three possible values of $D_0^\circ(S_2)$, i.e. 4.4 e.v., 3.6 e.v. and 3.3 e.v., which were due to the ambiguity of defining the excitation state of the atomic products resulting from predissociation in the spectroscopic measurements. The value of 4.4 e.v. (101.5 kcal. mole⁻¹) was shown to be the most probable one. Since this review, further support for his value have been given by the following investigators. J. R. Marquart, Dissertation Abstract 24, 5027 (1964), has found that the value of $D_0^\circ(S_2)$ to be consistent with the value of 4.4 e.v. in mass spectrometric studies. R. Coln, P. Goldfinger and M. Jeunhomme, Trans. Faraday Soc. **60**, 306 (1964), have found $D_0^\circ(S_2) = 97 \pm 5 \text{ kcal. mole}^{-1}$ in their mass-spectrometric studies of the vaporization of CS_2 , CS_2 and CS_2 , but they reported a revised value, i.e. $D_0^\circ(S_2) = 101 \pm 1 \text{ kcal. mole}^{-1}$, which was given in the note in proof. A. N. Singh and D. K. Rai, J. Chem. Phys. **43**, 2151 (1965), have selected the best value of $D_0^\circ(S_2) = 4.4 \text{ e.v.}$ in theoretical comparisons of the potential-energy curve. As pointed out by L. Brewer, loc. cit., and A. O. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., 2nd. Ed., London, 1953, the old vapor pressure measurements which are not consistent with $D_0(S_2) = 4.4 \text{ e.v.}$ (101.5 kcal. mole⁻¹) are probably not reliable.

The value $D_0(S_2, g) = 4.4 \text{ e.v.}$ (101.5 kcal. mole⁻¹) was selected as the dissociation energy of diatomic sulfur, and combination of this value with heat of formation of monatomic sulfur gives the heat of formation of monatomic sulfur, $\Delta H_f^\circ 298(S, g) = 66.68 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The ground state configuration, electronic levels and quantum weight were obtained from C. E. Moore, "Atomic Energy Levels", Vol. 1, National Bureau of Standards Circular 467, June, 1949.

Silicon Monosulfide (SiS)

INTERIM TABLE

Mol. Wt. = 60.156

(Ideal Gas)

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	6.000	∞	∞	∞	16.600	∞	∞
100	6.942	55.567	17.439	17.439	16.600	16.600	∞
200	7.231	50.449	17.106	17.106	16.600	16.600	∞
298	7.711	53.427	16.926	16.926	16.600	16.600	∞
300	7.720	53.474	16.921	16.921	16.600	16.600	∞
400	8.106	55.751	16.806	16.806	16.600	16.600	∞
500	8.359	57.587	16.730	16.730	16.600	16.600	∞
600	8.516	59.126	16.684	16.684	16.600	16.600	∞
700	8.712	61.603	16.637	16.637	16.600	16.600	∞
800	8.771	62.636	16.608	16.608	16.600	16.600	∞
900	8.771	63.562	16.593	16.593	16.600	16.600	∞
1000	8.752	64.405	16.587	16.587	16.600	16.600	∞
1100	8.725	65.169	16.587	16.587	16.600	16.600	∞
1200	8.691	65.888	16.593	16.593	16.600	16.600	∞
1300	8.650	66.569	16.604	16.604	16.600	16.600	∞
1400	8.605	67.215	16.623	16.623	16.600	16.600	∞
1500	8.557	67.833	16.645	16.645	16.600	16.600	∞
1600	8.506	68.422	16.670	16.670	16.600	16.600	∞
1700	8.453	68.989	16.697	16.697	16.600	16.600	∞
1800	8.398	69.535	16.726	16.726	16.600	16.600	∞
1900	8.342	70.061	16.757	16.757	16.600	16.600	∞
2000	8.285	70.568	16.790	16.790	16.600	16.600	∞
2100	8.227	71.057	16.824	16.824	16.600	16.600	∞
2200	8.168	71.528	16.860	16.860	16.600	16.600	∞
2300	8.108	71.982	16.897	16.897	16.600	16.600	∞
2400	8.047	72.419	16.936	16.936	16.600	16.600	∞
2500	7.985	72.839	16.977	16.977	16.600	16.600	∞
2600	7.922	73.243	17.020	17.020	16.600	16.600	∞
2700	7.858	73.632	17.065	17.065	16.600	16.600	∞
2800	7.793	74.007	17.112	17.112	16.600	16.600	∞
2900	7.727	74.369	17.161	17.161	16.600	16.600	∞
3000	7.660	74.719	17.212	17.212	16.600	16.600	∞
3100	7.592	75.057	17.265	17.265	16.600	16.600	∞
3200	7.523	75.383	17.320	17.320	16.600	16.600	∞
3300	7.453	75.697	17.377	17.377	16.600	16.600	∞
3400	7.382	76.000	17.436	17.436	16.600	16.600	∞
3500	7.310	76.292	17.497	17.497	16.600	16.600	∞
3600	7.237	76.573	17.560	17.560	16.600	16.600	∞
3700	7.163	76.844	17.625	17.625	16.600	16.600	∞
3800	7.088	77.107	17.692	17.692	16.600	16.600	∞
3900	7.012	77.362	17.761	17.761	16.600	16.600	∞
4000	6.935	77.609	17.832	17.832	16.600	16.600	∞
4100	6.857	77.848	17.905	17.905	16.600	16.600	∞
4200	6.778	78.079	17.980	17.980	16.600	16.600	∞
4300	6.698	78.302	18.057	18.057	16.600	16.600	∞
4400	6.617	78.517	18.136	18.136	16.600	16.600	∞
4500	6.535	78.724	18.217	18.217	16.600	16.600	∞
4600	6.452	78.923	18.299	18.299	16.600	16.600	∞
4700	6.368	79.114	18.383	18.383	16.600	16.600	∞
4800	6.283	79.297	18.469	18.469	16.600	16.600	∞
4900	6.197	79.473	18.557	18.557	16.600	16.600	∞
5000	6.110	79.642	18.647	18.647	16.600	16.600	∞
5100	6.022	79.804	18.739	18.739	16.600	16.600	∞
5200	5.933	79.959	18.833	18.833	16.600	16.600	∞
5300	5.843	80.107	18.929	18.929	16.600	16.600	∞
5400	5.752	80.248	19.027	19.027	16.600	16.600	∞
5500	5.660	80.383	19.127	19.127	16.600	16.600	∞
5600	5.567	80.512	19.229	19.229	16.600	16.600	∞
5700	5.473	80.635	19.333	19.333	16.600	16.600	∞
5800	5.378	80.752	19.439	19.439	16.600	16.600	∞
5900	5.282	80.863	19.547	19.547	16.600	16.600	∞
6000	5.185	80.968	19.657	19.657	16.600	16.600	∞

December 31, 1980.

Silicon Monosulfide (SiS)

Mol. Wt. = 60.156

ΔH°_f 298.15 = 16.926 kcal. mole⁻¹

S°_{298.15} = 53.427 cal. deg. mole⁻¹

Ground State Configuration 1Σ⁺

Electronic Level and Multiplicity

$$\frac{\epsilon \text{ cm.}^{-1}}{0} = \frac{g_i}{1}$$

ω_e = 743.5 cm.⁻¹

ω_ex_e = 2.56 cm.⁻¹

B_e = 0.30363 cm.⁻¹

ζ = 1

r_e = 1.9288 Å

Heat of Formation. ΔH°_f 298.15 was found in J. S. Gordon, Thiokol Chemical Corp., Reaction Motors Division, Denville, N. J., "Thermodynamic Data for Combustion Products", January, 1960.

Heat Capacity and Entropy. Molecular constants were taken from J. S. Gordon, op. cit.

Sulfur, Diatomic (S_2)
(Ideal Gas) Mol. wt. = 64.128

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH° _f	Log K _p
0	.000	INFINITE	INFINITE	0.000	30.805	INFINITE
100	6.964	46.623	31.075	1.445	27.104	-59.232
200	7.265	51.515	31.075	.738	23.040	-25.176
298	7.759	54.510	30.840	.000	19.138	-14.028
300	7.768	54.528	30.834	.014	19.066	-13.889
400	8.144	56.848	29.433	.811	15.233	-8.323
500	8.389	58.693	28.385	1.639	11.806	-5.160
600	8.549	60.238	27.518	2.466	8.575	-3.123
700	8.738	61.726	26.717	3.293	5.346	-1.180
800	8.935	63.175	25.975	4.120	2.117	.000
900	9.142	64.687	25.293	4.947	.000	.000
1000	9.360	66.266	24.660	5.775	.000	.000
1100	9.590	67.917	24.075	6.600	.000	.000
1200	9.832	69.640	23.540	7.425	.000	.000
1300	10.086	71.435	23.045	8.250	.000	.000
1400	10.352	73.300	22.590	9.075	.000	.000
1500	10.630	75.235	22.175	9.900	.000	.000
1600	10.918	77.240	21.800	10.725	.000	.000
1700	11.216	79.315	21.465	11.550	.000	.000
1800	11.524	81.460	21.170	12.375	.000	.000
1900	11.842	83.675	20.915	13.200	.000	.000
2000	12.170	85.960	20.690	14.025	.000	.000
2100	12.508	88.315	20.495	14.850	.000	.000
2200	12.856	90.740	20.330	15.675	.000	.000
2300	13.214	93.235	20.195	16.500	.000	.000
2400	13.582	95.800	20.090	17.325	.000	.000
2500	13.960	98.435	20.015	18.150	.000	.000
2600	14.348	101.140	20.000	18.975	.000	.000
2700	14.746	103.915	20.000	19.800	.000	.000
2800	15.154	106.760	20.000	20.625	.000	.000
2900	15.572	109.675	20.000	21.450	.000	.000
3000	16.000	112.660	20.000	22.275	.000	.000
3100	16.438	115.715	20.000	23.100	.000	.000
3200	16.886	118.840	20.000	23.925	.000	.000
3300	17.344	122.035	20.000	24.750	.000	.000
3400	17.812	125.300	20.000	25.575	.000	.000
3500	18.290	128.635	20.000	26.400	.000	.000
3600	18.778	132.040	20.000	27.225	.000	.000
3700	19.276	135.515	20.000	28.050	.000	.000
3800	19.784	139.060	20.000	28.875	.000	.000
3900	20.302	142.675	20.000	29.700	.000	.000
4000	20.830	146.360	20.000	30.525	.000	.000
4100	21.368	150.115	20.000	31.350	.000	.000
4200	21.926	153.940	20.000	32.175	.000	.000
4300	22.494	157.835	20.000	33.000	.000	.000
4400	23.072	161.800	20.000	33.825	.000	.000
4500	23.660	165.835	20.000	34.650	.000	.000
4600	24.258	169.940	20.000	35.475	.000	.000
4700	24.866	174.115	20.000	36.300	.000	.000
4800	25.484	178.360	20.000	37.125	.000	.000
4900	26.112	182.675	20.000	37.950	.000	.000
5000	26.750	187.060	20.000	38.775	.000	.000
5100	27.398	191.515	20.000	39.600	.000	.000
5200	28.056	196.040	20.000	40.425	.000	.000
5300	28.724	200.635	20.000	41.250	.000	.000
5400	29.402	205.300	20.000	42.075	.000	.000
5500	30.090	210.035	20.000	42.900	.000	.000
5600	30.788	214.840	20.000	43.725	.000	.000
5700	31.496	219.715	20.000	44.550	.000	.000
5800	32.214	224.660	20.000	45.375	.000	.000
5900	32.942	229.675	20.000	46.200	.000	.000
6000	33.680	234.760	20.000	47.025	.000	.000

Dec. 31, 1960 Dec. 31, 1965

MOL. WT. = 64.128

(IDEAL GAS)

SULFUR, DIATOMIC (S_2)

Ground State Configuration $\sum g$
 $S_{298.15}^0 = 54.51$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^0 = 30.80 \pm 0.2$ kcal. mole⁻¹
 $\Delta H_f^0 = 30.84 \pm 0.2$ kcal. mole⁻¹
 $S_{298.15}^0 = 54.51$ cal. deg.⁻¹ mole⁻¹
Electronic Levels and Quantum Weight
 $\epsilon, \text{ cm.}^{-1}$ g_i
 $\epsilon = 0$ $g_i = 3$
 $\omega_e = 724.66$ cm.⁻¹
 $\alpha_e = 0.0016$ cm.⁻¹
 $\sigma = 2$
 $r_e = 1.889 \text{ \AA}$

Heat of Formation.

The standard enthalpy of formation of gaseous diatomic sulfur, $\Delta H_f^0 = 30.84$ kcal. mole⁻¹, was calculated from $\Delta H_f^0 = -20.30$ kcal. mole⁻¹ for the reaction $H_2(g) + 0.5 S_2(g) \rightarrow H_2S(g)$ with JANAP value $\Delta H_f^0 = -4.88 \pm 0.15$ kcal. mole⁻¹. The ΔH_f^0 was obtained by the second and third law analyses of equilibrium constants which have been determined by G. Preuner and W. Schupp (ref. 1) and M. Randall and P. R. Bichowsky (ref. 2). The results obtained are presented as follows:

Ref.	Temp. Range	Pointa	2nd law ΔH_f^0 298 kcal. mole ⁻¹	3rd law ΔH_f^0 298 kcal. mole ⁻¹	Drift
1	1023-1405°K	5	-19.92 ± 0.13	-20.295	-0.282 ± 0.097
2	1362-1667°K	4	-20.74 ± 0.40	-20.307	+0.281 ± 0.269
3	1023-1667°K	9	-20.13 ± 0.12	-20.300	-0.066 ± 0.093

References

1. G. Preuner and W. Schupp, Z. physik. Chem., 68, 157 (1910).
2. M. Randall and P. R. Bichowsky, J. Am. Chem. Soc., 40, 368 (1918).
3. Combination of above references.

The third law value of the combination set was selected to calculate the heat of formation of diatomic sulfur.

The dissociation energy of gaseous diatomic sulfur, $D_0^0(S_2) = 101.5$ kcal. mole⁻¹, was chosen. For discussions see JANAP monatomic sulfur (g) and sulfur monoxide (g) tables.

Heat Capacity and Entropy.

The molecular constants which were taken from G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., D. Van Nostrand Company, New York, have been modified for the natural isotopic abundances reported by D. Strominger, J. M. Hollander and G. T. Saaborg, Rev. Mod. Phys. 30, 585 (1958).

Silicon Disulfide (SiS₂)
(Solid) Mol. Wt. = 92.222

INTERIM TABLE

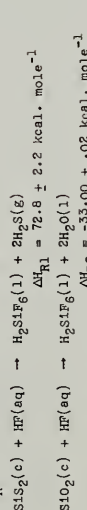
T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100	14.990	16.000	.000	- 43.000	- 41.899	30.711
200						
298						
300	15.000	16.000	.028	- 43.001	- 41.892	30.517
400	15.700	16.500	1.560	- 44.176	- 41.867	22.656
500	16.400	17.000	3.165	- 44.996	- 40.693	17.786
600	17.100	17.500	4.840	- 45.608	- 39.772	14.486
700	17.800	18.000	6.595	- 46.053	- 38.714	12.087
800	18.500	18.500	8.400	- 46.360	- 37.460	10.761
900	19.200	19.000	10.240	- 46.540	- 36.032	9.511
1000	19.900	19.500	12.240	- 46.600	- 34.467	8.321
1100	20.600	20.000	14.265	- 46.540	- 32.784	7.197
1200	21.300	20.500	16.360	- 46.371	- 30.990	6.127
1300	22.000	21.000	18.525	- 46.083	- 29.086	5.107
1400	22.700	21.500	20.760	- 45.683	- 27.076	4.233
1500	23.400	22.000	23.065	- 45.183	- 24.966	3.503
1600	24.100	22.500	25.440	- 44.583	- 22.756	2.919
1700	24.800	23.000	27.885	- 43.883	- 20.546	2.419
1800	25.500	23.500	30.390	- 43.083	- 18.336	1.973
1900	26.200	24.000	32.945	- 42.183	- 16.126	1.573
2000	26.900	24.500	35.550	- 41.183	- 13.916	1.213

December 31, 1960.

Silicon Disulfide (SiS₂) (Crystall)

Mol. Wt. = 92.222
 $\Delta H_f^{298.15} = -50.7$ kcal. mole⁻¹
 $S_{298.15}^{298.15} = [16.0]$ cal. deg.⁻¹ mole⁻¹
 $T_m = 1363^\circ K.$
 $\Delta H_m = [5.0]$ kcal. mole⁻¹

Heat of Formation. $\Delta H_f^{298.15}$ was calculated from the measured ΔH_f^0 's of the following reactions:



ΔH_{R1} was taken from R. Rocquet, M. T. Ancey-Maret, Bull. Soc. Chim. France 1954, 1039 (1954); ΔH_{R2} was from D. Torgeson and Th. G. Semak, J. Am. Chem. Soc. 70, 2156 (1948). $\Delta H_f^{298.15}$ of SiS₂ was recalculated using the corrected value for $\Delta H_f^{298.15}$ of SiO₂.

Heat Capacity and Entropy. C_p and $S_{298.15}$ values are estimated.

Melting Data. T_m was from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties", 1952. ΔH_m was estimated.

Silicon Disulfide (SiS₂)
(Liquid) Mol. Wt. = 92.222

INTERIM TABLE

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹ -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ^o	cal. mole ⁻¹ ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100	11.040	21.421	21.621	0.000	37.303	37.878	27.764
200	11.070	21.590	21.622	0.070	37.312	37.881	27.595
300	12.700	25.096	25.065	3.496	36.830	37.942	20.740
400	14.300	28.109	25.066	2.561	39.903	37.617	16.442
500	15.600	30.435	24.071	4.059	40.692	37.081	13.506
600	16.900	33.339	25.218	5.605	41.256	36.186	10.438
700	18.100	35.675	26.381	7.445	41.784	35.194	8.383
800	19.200	37.641	27.575	9.431	67.382	34.521	6.752
900	20.200	39.247	28.875	11.272	66.918	30.894	5.928
1000	21.200	41.920	29.790	13.343	66.365	27.320	5.218
1100	22.150	43.605	30.880	15.510	65.624	23.790	4.618
1200	23.000	45.611	31.885	17.703	64.768	20.300	4.068
1300	23.800	47.986	33.995	22.485	63.366	13.580	1.979
1400	24.000	50.437	34.981	24.689	62.509	10.265	1.405
1500	24.000	51.992	35.939	27.289	73.765	6.435	0.995
1600	24.000	53.164	36.970	29.689	71.491	3.822	0.506
1700	24.000	54.661	38.446	34.459	71.106	4.632	0.506
1800	24.000	55.692					

S₂Si

Silicon Disulfide (SiS₂) (liquid)

Mol. Wt. = 92.222
 $\Delta H_f^o 298.15 = [45.0] \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = [21.621] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1363^\circ\text{K.}$
 $\Delta H_m^o = [5.0] \text{ kcal. mole}^{-1}$
 Heat of Formation. $\Delta H_f^o 298.15$ was calculated from the $\Delta H_f^o 298.15$ of the crystal and the heat of melting.
 Heat Capacity and Entropy. C_p and $S_{298.15}^o$ were estimated.
 Melting Data. T_m was from National Bureau of Standards Circ. 500, 1952. ΔH_m^o was estimated.

S₂Si

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f kcal. mole ⁻¹	ΔF° _f	Log K _p
0	∞	∞	∞	∞	∞	∞
100	20.831	70.514	132.035	7.487	25.137	INFINITE
200	32.066	88.909	106.090	6.142	20.481	44.758
298	37.296	102.823	102.823	3.437	15.944	17.422
300	37.361	103.054	102.824	∞	11.745	8.609
400	39.641	114.183	104.324	0.69	11.469	8.500
500	41.137	123.227	107.429	3.944	19.272	4.237
600	41.887	130.799	110.544	7.969	15.823	2.508
700	42.355	137.293	113.912	12.153	3.440	1.253
800	42.682	142.818	116.587	16.367	10.935	2.695
900	42.882	146.909	120.346	20.897	2.681	4.008
1000	43.038	152.536	123.342	24.807	12.346	2.698
1100	43.154	156.643	126.186	33.503	22.919	4.553
1200	43.244	160.402	128.883	37.923	92.337	6.000
1300	43.309	163.857	131.375	42.481	8.250	8.350
1400	43.369	167.072	133.618	46.881	5.288	9.414
1500	43.414	170.072	135.563	51.024	6.612	9.414
1600	43.450	172.875	138.395	55.168	74.910	10.232
1700	43.481	175.510	140.502	59.514	85.147	10.946
1800	43.508	177.918	142.846	64.062	95.147	11.585
1900	43.528	180.149	144.446	68.216	87.040	12.135
2000	43.547	182.582	146.298	72.569	81.566	12.633
2100	43.563	184.707	148.077	76.925	85.555	13.079
2200	43.577	186.734	149.786	81.282	89.814	13.483
2300	43.589	188.682	151.432	85.640	94.360	13.858
2400	43.599	190.527	153.027	90.000	99.117	14.209
2500	43.609	192.337	154.563	94.360	104.082	14.538
2600	43.617	194.018	156.048	98.721	109.250	14.848
2700	43.625	195.564	157.485	103.083	114.617	15.135
2800	43.631	197.078	158.878	107.350	120.184	15.401
2900	43.637	198.561	160.227	111.810	125.947	15.648
3000	43.643	200.021	161.537	116.174	131.904	15.876
3100	43.648	201.462	162.809	120.538	138.000	16.083
3200	43.652	202.882	164.046	124.803	144.235	16.272
3300	43.656	204.282	165.242	129.068	150.608	16.448
3400	43.659	205.662	166.420	133.634	157.126	16.603
3500	43.663	206.990	167.582	138.000	163.882	16.743
3600	43.666	208.220	168.674	142.367	170.873	16.868
3700	43.669	209.417	169.759	146.734	178.094	16.978
3800	43.672	210.581	170.818	151.101	185.545	17.075
3900	43.674	211.711	171.851	155.468	193.226	17.160
4000	43.676	212.822	172.863	159.836	201.139	17.235
4100	43.678	213.900	173.851	164.203	209.281	17.300
4200	43.680	214.953	174.817	168.571	217.654	17.358
4300	43.682	215.981	175.762	172.939	226.261	17.409
4400	43.684	216.984	176.688	177.306	235.097	17.456
4500	43.685	217.966	177.594	181.676	244.163	17.499
4600	43.687	218.927	178.482	186.045	253.461	17.538
4700	43.688	219.866	179.353	190.413	262.991	17.572
4800	43.690	220.783	180.206	194.782	272.754	17.602
4900	43.691	221.678	181.043	199.152	282.751	17.628
5000	43.692	222.570	181.865	203.521	292.983	17.651
5100	43.693	223.435	182.672	207.890	303.454	17.671
5200	43.694	224.283	183.464	212.259	314.167	17.688
5300	43.695	225.113	184.241	216.628	325.122	17.702
5400	43.696	225.936	185.007	220.998	336.327	17.716
5500	43.697	226.734	185.758	225.368	347.782	17.728
5600	43.698	227.521	186.497	229.737	359.487	17.738
5700	43.698	228.295	187.223	234.107	371.442	17.746
5800	43.699	229.055	187.938	238.477	383.657	17.752
5900	43.700	229.803	188.647	242.847	396.132	17.757
6000	43.700	230.536	189.334	247.217	408.867	17.761

Dec. 31, 1960; June 30, 1964

Point group D_{4d}

$$\Delta H_f^0 = 25.14 \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 102.823 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 24.20 \pm 0.15 \text{ kcal. mole}^{-1}$$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies			
(ν), cm. ⁻¹	(ν), cm. ⁻¹	(ν), cm. ⁻¹	(ν), cm. ⁻¹
475 (1)	475 (2)	475 (2)	243 (1)
218 (1)	152 (2)	437 (2)	
471 (2)	58 (2)	248 (2)	
191 (2)	411 (1)		

Bond Distance: S-S = 2.059 ± 0.002 Å

Bond Angle: S-S-S = 107.9 ± 0.6°

Product of the Moments of Inertia: I_AI_BI_C = 3.90326 × 10⁻¹¹¹ g.³ cm.⁶

σ = 8

Heat of Formation.

The vapor pressure of S(c) has been measured by many investigators. Using the seven more recent vapor pressure data, the respective heat of sublimation (ΔH_g^0 298.15°) was calculated by both the third and second law methods. The values obtained are tabulated as follows:

Investigator	Temperature Range, °K.	Third Law Value	Second Law Value
West-Menzies 1	376.8 - 448.8	24.29	21.29
Neumann 2	332.6 - 362.1	24.35	26.47
Fourtner 3	304.1 - 351.6	24.36	24.10
Tallade 4	303.6 - 352.5	24.29	24.87
Bradley 5	288.3 - 305.7	24.29	23.80
Magee 6	331.9 - 368.0	24.11	24.44
Brake 7	352.7 - 367.4	24.12	23.88
	275.2 - 313.2	24.28	24.00

1 W. A. West and A. W. Menzies, J. Phys. Chem. **53**, 1880 (1949).2 K. Neumann, Z. physik. Chem. **117**, 416 (1944).3 O. Fourtner, Compt. rend. **218**, 194 (1944).4 M. Tallade, Compt. rend. **218**, 838 (1944).5 R. S. Bradley, Proc. Roy. Soc. (London) **A 205**, 553 (1951).

6 D. W. Magee, Ph. D. Thesis, The Ohio State University, 1955.

7 C. Brake, N. H. Hartshorne and D. R. Stranks, J. Chem. Soc. (London), 1200 (1960).

Due to the presence of S₂(g) in S₈(g), the measured total pressures were corrected to give the partial pressures of S₈(g) for the first five sets of vapor pressure data, according to D. W. Scott, U. S. Bureau of Mines, Bartlesville, Oklahoma, private communication, May 22, 1964. However, the magnitude of the correction is only 0.1 - 0.2 kcal. mole⁻¹. The adopted value is the weighted average of both the third and second law values.

Heat Capacity and Entropy.

The vibrational frequencies were taken from D. W. Scott, J. P. McCullough and P. H. Kruse, "Vibrational Assignment and Force Constants of S₈ (condensed states) from a Normal-Coordinate Treatment", Prepublication Report 64, U. S. Bureau of Mines, May 20, 1963. Four of the eighteen frequencies, i.e. 86(2) and 218(2) cm.⁻¹ were changed to 56(2) and 248(2) cm.⁻¹, respectively, suggested by D. W. Scott, loc. cit., private communication, April 23, 1964. The molecular structure and bond distance and angle were reported by J. Donohue, A. Caron and E. Goldfarb, J. Am. Chem. Soc. **85**, 3748 (1961). The three principle moments of inertia are: I_A = I_B = 1.28594 × 10⁻³⁷ and I_C = 2.36042 × 10⁻³⁷ g. cm.².

Silicon (Si)

(Reference State) GFW = 28.086

SILICON (Si)

(REFERENCE STATE)

0 to 1685°K Crystal

1685 to 3513.8°K Liquid

3513.8 to 6000°K Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

T, °K	Cp ^b	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	1.000	.000	INF	0.000	.000	.000	.000
100	1.700	.000	1.700	.769	.000	.000	.000
200	3.737	.000	3.737	1.538	.000	.000	.000
298	4.780	.000	4.780	2.286	.000	.000	.000
300	4.782	.000	4.782	.009	.000	.000	.000
400	5.292	.000	5.292	.516	.000	.000	.000
500	5.576	.000	5.576	1.006	.000	.000	.000
600	5.773	.000	5.773	1.478	.000	.000	.000
700	5.928	.000	5.928	1.931	.000	.000	.000
800	6.061	.000	6.061	2.365	.000	.000	.000
900	6.184	.000	6.184	2.780	.000	.000	.000
1000	6.295	.000	6.295	3.176	.000	.000	.000
1100	6.400	.000	6.400	3.554	.000	.000	.000
1200	6.500	.000	6.500	3.915	.000	.000	.000
1300	6.600	.000	6.600	4.260	.000	.000	.000
1400	6.700	.000	6.700	4.590	.000	.000	.000
1500	6.800	.000	6.800	4.906	.000	.000	.000
1600	6.900	.000	6.900	5.209	.000	.000	.000
1700	7.000	.000	7.000	5.500	.000	.000	.000
1800	7.100	.000	7.100	5.779	.000	.000	.000
1900	7.200	.000	7.200	6.046	.000	.000	.000
2000	7.300	.000	7.300	6.301	.000	.000	.000
2100	7.400	.000	7.400	6.544	.000	.000	.000
2200	7.500	.000	7.500	6.776	.000	.000	.000
2300	7.600	.000	7.600	6.997	.000	.000	.000
2400	7.700	.000	7.700	7.207	.000	.000	.000
2500	7.800	.000	7.800	7.406	.000	.000	.000
2600	7.900	.000	7.900	7.594	.000	.000	.000
2700	8.000	.000	8.000	7.771	.000	.000	.000
2800	8.100	.000	8.100	7.937	.000	.000	.000
2900	8.200	.000	8.200	8.092	.000	.000	.000
3000	8.300	.000	8.300	8.237	.000	.000	.000
3100	8.400	.000	8.400	8.372	.000	.000	.000
3200	8.500	.000	8.500	8.497	.000	.000	.000
3300	8.600	.000	8.600	8.612	.000	.000	.000
3400	8.700	.000	8.700	8.717	.000	.000	.000
3500	8.800	.000	8.800	8.812	.000	.000	.000
3600	8.900	.000	8.900	8.897	.000	.000	.000
3700	9.000	.000	9.000	8.972	.000	.000	.000
3800	9.100	.000	9.100	9.037	.000	.000	.000
3900	9.200	.000	9.200	9.092	.000	.000	.000
4000	9.300	.000	9.300	9.137	.000	.000	.000
4100	9.400	.000	9.400	9.172	.000	.000	.000
4200	9.500	.000	9.500	9.197	.000	.000	.000
4300	9.600	.000	9.600	9.212	.000	.000	.000
4400	9.700	.000	9.700	9.217	.000	.000	.000
4500	9.800	.000	9.800	9.212	.000	.000	.000
4600	9.900	.000	9.900	9.197	.000	.000	.000
4700	10.000	.000	10.000	9.172	.000	.000	.000
4800	10.100	.000	10.100	9.137	.000	.000	.000
4900	10.200	.000	10.200	9.092	.000	.000	.000
5000	10.300	.000	10.300	9.037	.000	.000	.000
5100	10.400	.000	10.400	8.972	.000	.000	.000
5200	10.500	.000	10.500	8.897	.000	.000	.000
5300	10.600	.000	10.600	8.812	.000	.000	.000
5400	10.700	.000	10.700	8.717	.000	.000	.000
5500	10.800	.000	10.800	8.612	.000	.000	.000
5600	10.900	.000	10.900	8.497	.000	.000	.000
5700	11.000	.000	11.000	8.372	.000	.000	.000
5800	11.100	.000	11.100	8.237	.000	.000	.000
5900	11.200	.000	11.200	8.092	.000	.000	.000
6000	11.300	.000	11.300	7.937	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966; Mar. 31, 1967

QFW = 28.086

(CRYSTAL)

SILICON (Si)

GFW = 28.086

Silicon (Si)
(Crystal)

T, °K	Cp°	S° -(C°-H° ₂₉₈)/T	gibbs/mol	H°-H° ₂₉₈	ΔHf° kcal/mol	ΔGf°	Log Kp
0	0.000	INFINITE	-	0.000	0.000	0.000	INFINITE
100	1.737	9.16	-	0.000	0.000	0.000	0.000
200	3.737	2.788	4.908	0.000	0.000	0.000	0.000
298	4.780	4.498	0.000	0.000	0.000	0.000	0.000
300	4.792	4.528	0.000	0.000	0.000	0.000	0.000
400	5.292	5.985	0.000	0.000	0.000	0.000	0.000
500	5.576	7.197	0.000	0.000	0.000	0.000	0.000
600	5.773	8.231	5.518	1.628	0.000	0.000	0.000
700	5.928	9.133	5.071	2.213	0.000	0.000	0.000
800	6.054	9.853	4.440	3.251	0.000	0.000	0.000
900	6.164	10.453	3.653	4.640	0.000	0.000	0.000
1000	6.295	11.312	2.263	4.049	0.000	0.000	0.000
1100	6.400	11.917	7.659	4.684	0.000	0.000	0.000
1200	6.500	12.478	5.359	5.359	0.000	0.000	0.000
1300	6.600	13.000	6.246	6.246	0.000	0.000	0.000
1400	6.700	13.495	6.246	6.246	0.000	0.000	0.000
1500	6.800	13.961	9.078	7.324	0.000	0.000	0.000
1600	6.900	14.403	9.397	8.009	0.000	0.000	0.000
1700	7.000	14.824	10.704	8.704	0.000	0.000	0.000
1800	7.100	15.224	10.960	10.124	0.000	0.000	0.000
1900	7.200	15.614	10.980	10.124	0.000	0.000	0.000
2000	7.300	15.985	10.561	10.849	0.000	0.000	0.000
2100	7.400	16.344	10.828	11.584	0.000	0.000	0.000
2200	7.500	16.691	11.086	12.329	0.000	0.000	0.000
2300	7.600	17.024	11.331	13.084	0.000	0.000	0.000
2400	7.700	17.352	11.581	13.849	0.000	0.000	0.000
2500	7.800	17.668	11.818	14.624	0.000	0.000	0.000

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966

$\Delta H_f^\circ = 0$ kcal/mol
 $\Delta H_f^{298.15} = 0$ kcal/mol
 $\Delta H_m^\circ = 12.0 \pm 0.1$ kcal/mol
 $\Delta H_f^{298.15} = 107.7 \pm 1$ kcal/mol

Heat of Formation.
 Zero by definition.

Heat Capacity and Entropy.
 Low temperature heat capacities are based on the precise data (8-300°K) of Flubacher, Leadbetter and Morrison. The entropy is obtained from the heat capacity using $S_0^\circ = 0.0003$ eu. The selected values are consistent with recent data of Keesom and Seidel (1.2 - 4.2°K) and Kalishevich et al. (60-300°K). Earlier data have been reviewed by R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1955.

High temperature studies are summarized below, along with the pertinent low temperature studies. The selected heat capacities above 300°K are obtained from a Shomate plot of the adopted low temperature heat capacities and the enthalpies reported or derived from the work of Dennison (1953), Kantor et al. (1960), Olette (1956), Serebrennikov and Gel'd (1952), and Magnus (1923). Discrepancies are apparent in the enthalpy data, particularly in the range of 370 to 1100°K, where only the recent study of Dennison made use of a high purity sample. Enthalpies from Dennison join most smoothly with the low temperature Cp but deviate increasingly at higher temperatures, being 1-2% lower than the other measurements above 1000°K. The selected functions agree with Dennison below 600°K, with Magnus from 600 to 1200°K, and with Kantor et al. above 1200°K. The resulting heat capacities are slightly different from those selected by Hultgren et al., loc. cit.; the latter are 0.07 gibbs/mol higher at 800°K and 0.21 gibbs/mol lower at the melting point.

Investigators	Method	Quantity Reported	T Range, °K	Sample
1. Flubacher et al. (1959)	Calorimetry	Cp°	7.7 - 300	Single crystal, annealed, resistance (300°K) 10.0 ohm cm, Carrier Concentration $\leq 10^{15}$ cm ⁻³
2. Keesom et al. (1959)	Calorimetry	Specific Heat	1.2 - 4.2	
3. Kalishevich et al. (1965)	Calorimetry	Cp°	60 - 300	99.99%
4. Oerlich et al. (1965)	Temperature Modulation	Cp°	300 - 900	Resistance (300°K) = 0.027 ohm cm, Carrier Concentration = 10^{19} cm ⁻³
5. Dennison (1953)	Drop Calorimetry	Specific Heat	275 - 1375	Resistance (300°K) = 107 ohm cm
6. Kantor et al. (1960)	Drop Calorimetry	Enthalpy Equation	1148 - 1685	"Highly purified"
7. Olette (1956)	Drop Calorimetry	Specific Enthalpy	1467 - 1685	99.9%
8. Serebrennikov et al.	Drop Calorimetry	Specific Enthalpy	302 - 1556	99.3%
9. Magnus (1923)	Drop Calorimetry	Specific Enthalpy	372 - 1175	99.2%

Reference:

1. P. Flubacher, A. J. Leadbetter and J. A. Morrison, Phil. Mag. **4**, 273 (1959).
2. P. H. Keesom and O. Seidel, Phys. Rev. **113**, 33 (1959).
3. O. I. Kalishevich, P. V. Oel'd. and R. P. Krentsis, Russ. J. Phys. Chem. **39**, 1602 (1965).
4. D. Gerlich, B. Abeles and R. E. Miller, J. Appl. Phys. **35**, 76 (1965).
5. D. H. Dennison quoted by H. R. Shanks et al., Phys. Rev. **130**, 1743 (1963).
6. P. B. Kantor, A. M. Kisil and E. M. Fomichev, Ukrain. Fiz. Zhur. **5**, 358 (1960).
7. M. Olette, Phys. Chem. Steelmaking, Proc. Dedham, Mass. 1956, 18-26 (Pub. 1958).
8. N. N. Serebrennikov and P. V. Oel'd. Dokl. Akad. Nauk SSSR **87**, 1021 (1952).
9. A. Magnus, Ann. Physik **70**, 303 (1923).

Melting Data.

See the Si(1) table for details.

Heat of Sublimation.

 $\Delta H_f^{298.15}$ is calculated as the difference between $\Delta H_f^{298.15}$ for Si(g) and Si(c).

Silicon (Si)
(Liquid)

GF_W = 28.086

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈ ^o)/T	H ₂₉₈ ^o - H _T ^o	kcal/mol ΔH _f ^o	ΔG ^o	Log K _p
100						
200						
298	6.500	10.826	10.826	.000	9.758	- 7.153
300	6.500	10.866	10.826	.012	9.747	- 7.100
400	6.500	12.536	10.881	.662	9.110	- 4.977
500	6.500	13.987	11.363	1.312	8.442	- 3.690
600	6.500	15.172	11.902	1.942	7.758	- 2.825
700	6.500	16.142	12.442	2.542	7.055	- 2.203
800	6.500	17.042	12.966	3.242	6.337	- 1.734
900	6.500	17.807	13.460	3.912	5.635	- 1.368
1000	6.500	18.492	13.930	4.562	5.019	- 1.075
1100	6.500	19.112	14.373	5.212	4.499	- .838
1200	6.500	19.677	14.792	5.838	4.079	- .638
1300	6.500	20.197	15.186	6.512	3.740	- .464
1400	6.500	20.679	15.563	7.162	3.400	- .319
1500	6.500	21.128	15.920	7.812	3.132	- .193
1600	6.500	21.547	16.256	8.462	2.908	- .083
1700	6.500	21.935	16.575	9.112	2.720	- .000
1800	6.500	22.313	16.889	9.762	2.568	- .000
1900	6.500	22.664	17.184	10.412	2.440	- .000
2000	6.500	22.997	17.466	11.062	2.332	- .000
2100	6.500	23.315	17.737	11.712	2.240	- .000
2200	6.500	23.617	17.998	12.362	2.162	- .000
2300	6.500	23.906	18.249	13.012	2.098	- .000
2400	6.500	24.183	18.490	13.662	2.048	- .000
2500	6.500	24.448	18.723	14.312	2.000	- .000
2600	6.500	24.703	18.948	14.962	1.962	- .000
2700	6.500	24.948	19.166	15.612	1.932	- .000
2800	6.500	25.185	19.377	16.262	1.908	- .000
2900	6.500	25.413	19.581	16.912	1.888	- .000
3000	6.500	25.633	19.779	17.562	1.870	- .000
3100	6.500	25.846	19.971	18.212	1.852	- .000
3200	6.500	26.055	20.157	18.862	1.838	- .000
3300	6.500	26.253	20.340	19.512	1.828	- .000
3400	6.500	26.447	20.517	20.162	1.820	- .000
3500	6.500	26.635	20.689	20.812	1.812	- .000
3600	6.500	26.816	20.854	21.462	1.804	- .137
3700	6.500	26.986	21.020	22.112	1.796	- .288
3800	6.500	27.170	21.180	22.762	1.788	- .431
3900	6.500	27.338	21.338	23.412	1.780	- .566
4000	6.500	27.503	21.487	24.062	1.772	- .694
4100	6.500	27.643	21.636	24.712	1.764	- .816
4200	6.500	27.820	21.782	25.362	1.756	- .932
4300	6.500	27.973	21.926	26.012	1.748	- 1.043
4400	6.500	28.122	22.063	26.662	1.740	- 1.148
4500	6.500	28.259	22.199	27.312	1.732	- 1.249

SILICON (Si) (LIQUID) GF_W = 28.086

S_{298.15}^o = 10.826 gibbs/mol
 T_m = 1685 ± 3°K
 T_b = [3513.8] °K (to monomer only)
 T_b = [3492] °K (to equilibrium mixture)

ΔH_f^o_{298.15} = 11.585 kcal/mol
 ΔH_m^o = 12.0 ± 0.1 kcal/mol
 ΔH_v^o = [92.047] kcal/mol
 ΔH_v^o = [85.8] kcal/mol

Heat of Formation.

The heat of formation is obtained from that of the crystal by adding ΔH_m^o and the difference between H_{298.15}^o - H_{298.15}^o for crystal and liquid.

Heat Capacity and Entropy.

Enthalpy data for high purity samples in quartz or vitreous silica capsules have been reported for the range 1698-1915°K by P.B. Kantor, A. M. Kisil and E. M. Fomichev, Ukrain. Fiz. Zhur. 5, 358 (1960), and for the range 1686-1825°K by M. Olette, Phys. Chem. Steelmaking, Proc. Dedham, Mass. 1955, 18-26 (pub. 1958). Due to the limited temperature range and the experimental uncertainty, the data do not appear to justify more than a constant heat capacity. A value of 6.5 gibbs/mol is selected, intermediate between the values of 6.75 and 6.15 obtained from the separate experiments. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data.

Modern determinations of the melting point range from 1683 ± 1 to 1690 ± 4°K, the former from the specific volume study of L. D. Lucas and G. Urbain, Compt. Rend. 255, 2414 (1962), and the latter from the enthalpy study of Kantor et al. The selected value of T_m = 1685°K is taken from R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1965, who have reviewed the melting data. The heat of melting is calculated from the selected enthalpy of the crystal and the liquid enthalpy measurements of Kantor et al. and Olette, who reported comparable values of ΔH_m^o = 11.95 ± 0.18 and 12.095 ± 0.1 kcal/mol, respectively.

Vaporization Data.

T_b is calculated as the temperature for which the ΔG_r^o = 0 for Si(l) = Si(g). ΔH_v^o is calculated as the difference between ΔH_f^o(g) and ΔH_f^o(l) at T_b. The normal boiling for the equilibrium vapor is calculated as the temperature at which Si₁, Si₂ and Si₃ attain a total pressure of one atm. ΔH_v^o at this temperature is calculated as the enthalpy of vaporization of one GF_W of liquid to vapor containing 92.1, 7.0 and 0.9 mole percent of monomer, dimer and trimer, respectively. Tetramer and higher polymers, which are ignored in the equilibrium calculation, are probably negligible at this temperature.

T, °K	Cp°	S° —(G°—H° ₂₉₈)/T	—H°—H° ₂₉₈	—ΔH°	ΔG°	Log Kp
0	-0.00	INFINITE	-1.805	106.664	106.664	INFINITE
100	6.697	33.446	45.140	107.256	-227.254	-
200	5.687	37.931	40.617	107.587	-109.558	-227.254
298	5.318	40.121	40.121	107.700	-71.161	-71.161
300	5.318	40.154	40.121	107.701	97.013	-70.474
400	5.166	42.460	40.326	107.717	93.466	-51.057
500	5.095	42.804	40.713	107.685	89.882	-39.287
600	5.056	43.729	41.441	107.625	86.326	-31.444
700	5.033	44.506	41.568	107.547	82.783	-25.886
800	5.012	45.176	41.639	107.456	79.264	-21.390
900	5.000	45.756	41.674	107.356	75.734	-16.890
1000	5.011	46.296	42.734	107.213	72.229	-15.786
1100	5.016	46.774	43.080	107.000	68.737	-13.657
1200	5.027	47.211	43.566	106.937	65.287	-11.885
1300	5.043	47.618	44.105	106.792	61.790	-10.369
1400	5.067	48.000	44.702	106.458	58.182	-7.998
1500	5.087	48.338	45.284	106.458	54.682	-7.998
1600	5.113	48.668	45.848	106.283	51.459	-7.029
1700	5.142	48.978	46.399	106.108	48.145	-6.189
1800	5.170	49.270	46.930	105.933	44.815	-5.468
1900	5.202	49.543	47.440	105.758	42.753	-4.816
2000	5.232	49.821	47.931	105.583	40.667	-4.378
2100	5.261	50.077	48.403	105.408	38.588	-3.891
2200	5.289	50.322	48.858	105.233	37.375	-3.449
2300	5.316	50.558	49.305	105.058	36.162	-3.045
2400	5.343	50.784	49.746	104.883	34.949	-2.675
2500	5.364	51.003	50.179	104.708	33.736	-2.336
2600	5.386	51.214	50.607	104.533	32.523	-2.024
2700	5.406	51.418	51.030	104.358	31.310	-1.734
2800	5.426	51.619	51.446	104.183	30.097	-1.464
2900	5.445	51.819	51.857	104.008	28.884	-1.214
3000	5.454	51.990	52.264	103.833	27.671	-0.983
3100	5.466	52.169	52.667	103.658	26.458	-0.766
3200	5.478	52.343	53.067	103.483	25.245	-0.562
3300	5.489	52.511	53.464	103.308	24.032	-0.372
3400	5.500	52.679	53.859	103.133	22.819	-0.192
3500	5.502	52.835	54.254	102.958	21.606	-0.025
3600	5.508	52.990	54.649	102.783	20.393	-0.000
3700	5.513	53.141	55.044	102.608	19.180	-0.000
3800	5.519	53.286	55.439	102.433	17.967	-0.000
3900	5.521	53.427	55.834	102.258	16.754	-0.000
4000	5.521	53.571	56.229	102.083	15.541	-0.000
4100	5.523	53.707	56.624	101.908	14.328	-0.000
4200	5.524	53.840	57.019	101.733	13.115	-0.000
4300	5.524	53.971	57.414	101.558	11.902	-0.000
4400	5.524	54.102	57.809	101.383	10.689	-0.000
4500	5.524	54.222	58.204	101.208	9.476	-0.000
4600	5.523	54.343	58.599	101.033	8.263	-0.000
4700	5.522	54.462	58.994	100.858	7.050	-0.000
4800	5.522	54.581	59.389	100.683	5.837	-0.000
4900	5.520	54.699	59.784	100.508	4.624	-0.000
5000	5.519	54.803	60.179	100.333	3.411	-0.000
5100	5.519	54.913	60.574	100.158	2.198	-0.000
5200	5.518	55.020	60.969	99.983	0.985	-0.000
5300	5.519	55.125	61.364	99.808	-0.228	-0.000
5400	5.520	55.229	61.759	99.633	-1.441	-0.000
5500	5.520	55.329	62.154	99.458	-2.654	-0.000
5600	5.521	55.429	62.549	99.283	-3.867	-0.000
5700	5.524	55.527	62.944	99.108	-5.080	-0.000
5800	5.531	55.621	63.339	98.933	-6.293	-0.000
5900	5.531	55.717	63.734	98.758	-7.506	-0.000
6000	5.536	55.810	64.129	98.583	-8.719	-0.000

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1965; Mar. 31, 1967

Heat Capacity and Entropy.

Electronic levels and quantum weights are from L. J. Redziemski and K. L. Andrew, *J. Opt. Soc. Am.* **55**, 474 (1965), and V. Kaufman, L. J. Redziemski and K. L. Andrew, *ibid.* **55**, 911 (1966). An additional level with quantum weight of 200 is estimated above the observed levels and below the dissociation limit; however, the effect of this level on the entropy at 6000°K is negligible. Levels above 39000 cm⁻¹ are averaged.

T, °K	C _p ^a	S ^b	-(C _p ^a - H ^c)/T	H ^c - H ²⁹⁸	ΔG ^d	Log K _p
0	0.000	INFINITE	-	2.214	140.324	INFINITE
100	7.029	46.555	61.829	1.517	140.993	-298.124
200	7.592	51.715	55.632	0.783	131.937	-144.004
298	8.234	54.895	51.000	0.000	127.315	-93.325
300	8.242	54.946	50.995	0.015	127.230	-92.687
400	8.558	57.375	55.228	0.861	120.829	-67.021
500	9.079	59.352	55.857	1.747	118.148	-51.643
600	9.499	61.045	56.584	2.674	113.671	-41.004
700	9.844	62.537	57.330	3.645	109.219	-34.103
800	10.151	63.875	58.066	4.647	104.814	-28.634
900	10.343	65.082	58.779	5.672	100.482	-24.387
1000	10.453	66.178	59.465	6.713	139.615	-20.994
1100	10.502	67.177	60.122	7.761	139.393	-18.222
1200	10.501	68.091	60.768	8.812	139.154	-15.916
1300	10.485	68.932	61.348	9.861	138.893	-13.968
1400	10.447	69.707	61.916	10.908	138.610	-12.302
1500	10.401	70.427	62.460	11.951	138.303	-10.861
1600	10.354	71.094	62.970	12.989	137.970	-9.603
1700	10.309	71.723	63.456	14.022	137.628	-8.523
1800	10.268	72.311	63.950	15.050	137.286	-7.713
1900	10.232	72.865	64.404	16.075	136.951	-7.130
2000	10.200	73.389	64.841	17.097	136.630	-6.340
2100	10.174	73.884	65.260	18.114	136.322	-5.753
2200	10.153	74.359	65.663	19.132	136.028	-5.222
2300	10.135	74.810	66.050	20.144	135.746	-4.737
2400	10.122	75.241	66.425	21.159	135.475	-4.295
2500	10.112	75.654	66.785	22.171	135.217	-3.889
2600	10.104	76.050	67.130	23.182	134.988	-3.515
2700	10.100	76.432	67.472	24.192	134.788	-3.169
2800	10.099	76.799	67.798	25.202	134.608	-2.849
2900	10.099	77.153	68.115	26.212	134.448	-2.552
3000	10.100	77.496	68.422	27.222	134.299	-2.276
3100	10.103	77.827	68.720	28.232	134.160	-2.018
3200	10.107	78.148	69.009	29.242	134.038	-1.787
3300	10.111	78.459	69.291	30.253	133.930	-1.579
3400	10.117	78.761	69.565	31.265	133.833	-1.388
3500	10.124	79.054	69.832	32.277	133.750	-1.199
3600	10.131	79.339	70.092	33.289	133.680	-1.025
3700	10.139	79.617	70.346	34.303	133.625	-0.869
3800	10.147	79.887	70.594	35.317	133.583	-0.729
3900	10.156	80.151	70.835	36.332	133.550	-0.603
4000	10.165	80.408	71.071	37.349	133.526	-0.486
4100	10.175	80.640	71.302	38.365	133.510	-0.376
4200	10.185	80.905	71.528	39.383	133.500	-0.271
4300	10.195	81.145	71.749	40.402	133.496	-0.176
4400	10.206	81.379	71.965	41.422	133.496	-0.086
4500	10.218	81.609	72.177	42.444	133.499	-0.000
4600	10.229	81.833	72.384	43.466	133.506	0.084
4700	10.241	82.053	72.588	44.489	133.516	0.168
4800	10.254	82.269	72.787	45.514	133.529	0.237
4900	10.266	82.481	72.983	46.540	133.543	0.295
5000	10.279	82.688	73.175	47.567	133.556	0.343
5100	10.293	82.892	73.363	48.594	133.568	0.381
5200	10.306	83.092	73.548	49.626	133.578	0.409
5300	10.320	83.288	73.730	50.657	133.586	0.427
5400	10.335	83.481	73.909	51.690	133.592	0.435
5500	10.349	83.671	74.085	52.724	133.596	0.433
5600	10.364	83.859	74.258	53.760	133.598	0.421
5700	10.379	84.041	74.428	54.797	133.598	0.399
5800	10.395	84.222	74.595	55.836	133.596	0.367
5900	10.410	84.400	74.760	56.876	133.592	0.326
6000	10.426	84.575	74.929	57.919	133.586	0.276

Dec. 31, 1960; Dec. 31, 1962; Mar. 31, 1967

Ground State Configuration: $3\Sigma_g^-$
 $S_{298.15}^\circ = 54.895$ gibbs/mol
 $\Delta H_f^\circ = 140.3 \pm 3$ kcal/mol
 $\Delta H_f^\circ = 141 \pm 3$ kcal/mol

Electronic Levels and Quantum Weights					
State	ϵ_1 , cm ⁻¹	ϵ_2 , cm ⁻¹	ϵ_3 , cm ⁻¹	ϵ_4 , cm ⁻¹	ϵ_5 , cm ⁻¹
$3\Sigma_g^-$	0	3	$1\Sigma_g^+$	[10000]	6
$3\Pi_u$	[2000]	6	$1\Sigma_g^+$	[13000]	3
$1\Sigma_g^+$	[6000]	[1]	$3\Sigma_g^-$	[40000]	[2]
$1\Pi_u$	[8000]	[2]	$3\Sigma_g^-$	[45000]	[1]

$w_e = 510.98$ cm⁻¹
 $\omega_e x_e = 2.02$ cm⁻¹
 $\sigma = 2$
 $B_e = 0.2390$ cm⁻¹
 $\alpha_e = 0.0013$ cm⁻¹
 $r_e = 2.246$ Å

Heat of Formation.

The selected value is based on the spectroscopic and equilibrium data summarized below. Verma and Worsop¹ concluded from analysis of the absorption spectra that $D_0^\circ = 70 \pm 4$ kcal/mol. Predissociation of the H state suggested the upper limit $D_0^\circ \leq 74.0$, while linear Birge-Sponer extrapolations of the H and K states gave 78.4 and 68.9 kcal/mol for the ground state. By assuming that the true extrapolation would not reduce the linear extrapolation for the H state by more than half, i.e., from 26 to 13 kcal, the authors arrived at the lower limit of $D_0^\circ \geq 65.5$ for the ground state.

Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor equilibria over the systems SiC-graphite², SiC-silicon³, and boron-carbon-silicon⁴. Third law analysis of the partial pressures of Si₂ and Si over the three systems yields D_0° values of 73.3, 74.3 and 70.4 kcal/mol, which are in good agreement with the spectroscopic values. The selected value, $\Delta H_f^\circ = 141 \pm 3$ kcal/mol, corresponds to $D_0^\circ = 73.0$ kcal/mol.

Source	Method	Range, °K	No. of Points	ΔH_f° (kcal/mol)*	Drift (kcal/mol)
Verma (1963)	Prediss. of H state	-	-	2nd law	±140.0
	LEX of K state	-	-	3rd law	±140.0
	Extrap. of H state	-	-	70.3	145.1
Drowart (1958)	Mass Spec.	2149-2316	7	95.3±7.1	±148.5
Drowart (1960)	Mass Spec.	1703-2160	9	81.0±1.1	140.7
Verhaegen (1964)	Mass Spec.	2166-2344	4	69 ± 16	139.7
*For the reaction Si ₂ (g) = 2 Si(g)					143.6

Heat Capacity and Entropy.

Vibrational and rotational constants are those obtained by Verma and Worsop¹ through combination of their data for the H-X system with those of Douglas⁵. Observation of the same H-X system in matrix isolation by Welner and McLeod⁶ confirms that the lower state is the ground state. Comparison with the isoelectronic molecules C₂, BN, BeO and MgO (7,8,10) suggests that there are several possible low-lying excited states in Si₂. Tentative estimates for these levels are given above, based on this comparison and on the observed states (1,5). These estimates are relatively uncertain and probably yield an upper limit for the entropy at temperatures where Si₂ is significant. A probable lower limit may be obtained by increasing the two $3\Pi_u$ states by 8000 cm⁻¹ and omitting the other estimated levels. This would reduce the entropy by 1.7 eu at 2000°K, corresponding to a change of 3.4 kcal/mol in ΔH_f° values based on equilibrium data.

References.

1. R. D. Verma and P. A. Worsop, Can. J. Phys. **41**, 152 (1963).
2. J. Drowart and G. DeMaris, J. Chim. Phys. **29**, 1015 (1958).
3. J. Drowart and G. DeMaris, pp. 16-23 in Silicon Carbide, Edited by J. R. O'Connor and J. Smiltens, Pergamon Press, New York, 1960.
4. E. Starford and J. Drowart, J. Chem. Phys. **40**, 1622 (1964).
5. A. E. Douglas, Can. J. Phys. **33**, 801 (1955).
6. W. Welner, Jr., and D. McLeod, Jr., J. Chem. Phys. **41**, 235 (1964).
7. P. F. Fougere and R. K. Nesbet, J. Chem. Phys. **44**, 285 (1966).
8. R. S. Mulliken, Phys. Rev. **56**, 778 (1939).
9. O. Verneeg, W. O. Richards and C. M. Rogers, J. Chem. Phys. **46**, 160 (1967); **45**, 3226 (1966); **45**, 1828 (1966).
10. L. Brewer and S. Trajman, J. Chem. Phys. **30**, 1595 (1962).

Silicon, Triatomic (Si₃)

(Ideal Gas) GFW = 84.258

OPW = 84.258

SILICON, TRIATOMIC (Si₃) (IDEAL GAS)Point Group [D_{3h}]

$$\Delta H_f^\circ = 151.2 \pm 10 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = 152 \pm 10 \text{ kcal/mol}$$

$$S_{298.15}^\circ = [64.0] \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	g_1
0	3
[10000]	[6]
[18000]	[2]
21460	3

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	g_e
[360] (1)	
[200] (2)	
[630] (1)	

$$\text{Bond Distance: Si-Si} = [2.25] \text{ \AA}$$

$$\text{Bond Angle: Si-Si-Si} = [180]^\circ$$

$$\text{Rotational Constant: } B_0 = [0.05928] \text{ cm}^{-1}$$

Heat of Formation.

The selected value is an average based on the equilibrium data summarized below. Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor species over the systems SiC-graphite¹ and SiC-silicon². Third law analysis of the partial pressures of Si₃ and Si yields the values 154.0 and 149.9 kcal/mol. Both drifts suggest that the entropy may be lower than the tabulated values. It is unlikely that the entropy is in error by more than 5 eu so that most of the drift is inherent in the data. The adopted value of $\Delta H_f^\circ = 152 \pm 10$ kcal/mol includes allowance for an error of up to 5 eu.

Source	Method	Range, °K	No. of Points	ΔH_f° (kcal/mol)*	Drift (eu)	ΔH_f° (kcal/mol)
Drowart (1958)	Mass Spec.	2230-2316	2	209	169.1	154.0
Drowart (1960)	"	1703-1890	4	204±3	173.2	149.9

*For reaction Si₃(g) = 3 Si(g)

Heat Capacity and Entropy.

Wetner and McLeod³ observed an absorption band near 4660 Å in matrix isolation studies. Their tentative assignment of this band as the $3\Sigma_u^- \leftarrow 3\Sigma_g^-$ transition of Si₃ is adopted here. A $1W_u$ state is assumed at 18000 cm⁻¹, which is 7000 and 2000 cm⁻¹ below the analogous levels³ for C₃ and C₂Si. Also a $3W_u$ level is assumed at 10000 cm⁻¹, presumably arising from the same molecular orbital configuration as the $1W_u$ state. The molecule is assumed to be linear with a bond distance equal to that in Si₂. Vibrational frequencies are estimated from a valence bond calculation using $k_1 = 2.16 \times 10^5$ and $kd/1^2 = 0.11 \times 10^5$ dyn/cm. The stretching force constant is obtained from Si₂, while the bending force constant is based on C₂Si and the $1W_u$ excited state³ of C₃. The moment of inertia is 47.22×10^{-39} g cm².

References.

1. J. Drowart, G. DeMaria and M. U. Inghram, J. Chem. Phys. **29**, 1015 (1958).
2. J. Drowart and G. DeMaria, pp. 16-23 in "Silicon Carbide," Edited by J. R. O'Connor and J. Smilens, Pergamon Press, New York, 1960.
3. W. Wetner, Jr. and D. McLeod, Jr., J. Chem. Phys. **41**, 235 (1964); **40**, 1305 (1964); **45**, 3095 (1966).

Dec. 31, 1960; Dec. 31, 1961; Mar. 31, 1967

Titanium (Ti)

(Reference State) GFW = 47.90

T, °K	Cp ^a	S ^b - (C ^c - H ²⁹⁸)/T	H ^c - H ²⁹⁸	ΔH ^f	ΔG ^f	Log K _p
0	0.000	INFINITE	- 1.152	0.000	0.000	0.000
100	3.612	1.969	12.155	- 1.018	0.000	0.000
200	5.333	5.069	7.870	- 0.560	0.000	0.000
298	5.987	7.325	7.325	0.000	0.000	0.000
300	5.996	7.362	7.325	0.011	0.000	0.000
400	6.550	10.578	8.028	1.275	0.000	0.000
500	6.755	11.791	8.557	1.941	0.000	0.000
600	6.976	12.848	9.096	2.627	0.000	0.000
700	7.229	13.796	9.525	3.337	0.000	0.000
800	7.497	14.663	10.137	4.071	0.000	0.000
1000	7.767	15.867	10.631	4.857	0.000	0.000
1100	8.025	16.220	11.105	5.626	0.000	0.000
1200	8.268	16.741	11.592	6.378	0.000	0.000
1300	8.500	17.412	12.087	7.092	0.000	0.000
1400	8.727	18.302	12.581	7.767	0.000	0.000
1500	8.950	19.366	13.089	8.406	0.000	0.000
1600	9.169	20.333	13.603	9.000	0.000	0.000
1700	9.384	21.212	14.122	9.556	0.000	0.000
1800	9.595	22.012	14.642	10.075	0.000	0.000
1900	9.800	22.734	15.173	10.556	0.000	0.000
2000	10.000	23.377	15.712	11.000	0.000	0.000
2100	10.200	24.042	16.258	11.412	0.000	0.000
2200	10.400	24.727	16.812	11.797	0.000	0.000
2300	10.600	25.432	17.372	12.152	0.000	0.000
2400	10.800	26.157	17.937	12.687	0.000	0.000
2500	11.000	26.902	18.512	13.202	0.000	0.000
2600	11.200	27.667	19.097	13.697	0.000	0.000
2700	11.400	28.452	19.692	14.172	0.000	0.000
2800	11.600	29.257	20.297	14.627	0.000	0.000
2900	11.800	30.082	20.912	15.162	0.000	0.000
3000	12.000	30.927	21.537	15.677	0.000	0.000
3100	12.200	31.792	22.172	16.172	0.000	0.000
3200	12.400	32.677	22.817	16.647	0.000	0.000
3300	12.600	33.582	23.472	17.102	0.000	0.000
3400	12.800	34.507	24.137	17.537	0.000	0.000
3500	13.000	35.452	24.812	17.952	0.000	0.000
3600	13.200	36.417	25.497	18.347	0.000	0.000
3700	13.400	37.402	26.192	18.722	0.000	0.000
3800	13.600	38.407	26.897	19.077	0.000	0.000
3900	13.800	39.432	27.612	19.412	0.000	0.000
4000	14.000	40.477	28.337	19.727	0.000	0.000
4100	14.200	41.542	29.072	20.022	0.000	0.000
4200	14.400	42.627	29.817	20.297	0.000	0.000
4300	14.600	43.732	30.572	20.552	0.000	0.000
4400	14.800	44.857	31.337	20.787	0.000	0.000
4500	15.000	45.992	32.112	21.002	0.000	0.000
4600	15.200	47.147	32.897	21.197	0.000	0.000
4700	15.400	48.322	33.692	21.372	0.000	0.000
4800	15.600	49.517	34.497	21.527	0.000	0.000
4900	15.800	50.732	35.312	21.662	0.000	0.000
5000	16.000	51.967	36.137	21.777	0.000	0.000
5100	16.200	53.222	36.972	21.872	0.000	0.000
5200	16.400	54.497	37.817	21.947	0.000	0.000
5300	16.600	55.792	38.672	22.002	0.000	0.000
5400	16.800	57.107	39.537	22.037	0.000	0.000
5500	17.000	58.442	40.412	22.052	0.000	0.000
5600	17.200	59.797	41.297	22.047	0.000	0.000
5700	17.400	61.172	42.192	22.022	0.000	0.000
5800	17.600	62.567	43.097	21.977	0.000	0.000
5900	17.800	63.982	44.012	21.912	0.000	0.000
6000	18.000	65.417	44.937	21.827	0.000	0.000

Dec. 31, 1960; Sept. 30, 1965

TITANIUM (Ti)

GFW = 47.90

(REFERENCE STATE)

0 to 1155°K Crystal alpha
 1155 to 1933°K Crystal beta
 1933 to 3591°K Liquid
 3591 to 5000°K Ideal Monatomic Gas

See crystal, liquid and monatomic gas for details.

Ti

Ti

T, °K	Cp	S°	-(G°-H° _{298.15})/T	H°-H° _{298.15}	ΔH°	ΔG°	Log Kp
0	∞	∞	INFINITE	-1.152	∞	∞	∞
100	3.412	1.969	12.152	-1.018	∞	∞	∞
200	5.333	5.069	7.870	∞	∞	∞	∞
298	5.987	7.325	7.325	∞	∞	∞	∞
300	5.996	7.362	7.325	∞	∞	∞	∞
400	6.341	9.139	7.565	∞	∞	∞	∞
500	6.559	10.576	8.028	∞	∞	∞	∞
600	6.755	11.791	8.557	1.941	∞	∞	∞
800	7.229	13.798	9.096	2.537	∞	∞	∞
900	7.499	14.663	10.137	4.073	∞	∞	∞
1000	7.767	15.467	10.631	4.837	∞	∞	∞
1100	8.025	16.220	11.105	5.626	∞	∞	∞
1200	8.256	16.933	11.561	6.436	∞	∞	∞
1300	8.461	17.603	12.000	7.242	∞	∞	∞
1400	8.616	18.247	12.423	8.153	∞	∞	∞
1500	8.767	18.864	12.832	9.048	∞	∞	∞
1600	8.936	19.458	13.228	9.968	∞	∞	∞
1800	9.456	20.956	13.611	11.945	∞	∞	∞
1900	9.656	21.128	14.346	12.866	∞	∞	∞
2000	10.376	21.651	14.698	13.910	∞	∞	∞

Dec. 31, 1960; Sept. 30, 1966

$\Delta H^\circ_0 = 0$ kcal/mol
 $\Delta H^\circ_{298.15} = 7.325 \pm 0.02$ gibbs/mol
 $\Delta H^\circ = 0.99$ kcal/mol
 $\Delta H^\circ_{298.15} = 113.0 \pm 1.0$ kcal/mol

Heat of Formation.
Zero by definition.
Heat Capacity and Entropy.

The low temperature heat capacities, 1.1 - 305.5°K, have been measured by many investigators. Their measured temperature range, specimen purity and value of $S^\circ_{298.15}$ reported are listed in the following table. The Cp values, below 298°K, adopted were mainly derived from the data obtained from reference 3, 5 and 6, which are in good agreement with other sets of Cp data.

Investigator	Temperature, °K	Purity, %	$S^\circ_{298.15}$, eu
1. K. K. Kelley (1944)	53.5 - 295.1	98.75	7.24 ± 0.07
2. Estermann et al. (1952)	1.8 - 4.2	99	-
3. Kothan and Johnston (1953)	15.44 - 305.51	99.96	7.33 ± 0.02
4. Aven et al. (1956)	3.95 - 15.76	99.95	-
5. Wolcott (1957)	1.17 - 20.95	99.98	-
6. Clusius and Franzosini (1958)	13.72 - 271.92	99.88	-
7. Burk et al. (1959)	22.5 - 200.0	99	-
8. Kneip et al. (1963)	1.1 - 4.5	99.86	-
9. Hake and Cape (1964)	1.2 - 4.5	99.92	-
1. K. K. Kelley, Ind. Eng. Chem. 36, 665 (1944). $S^\circ_{50.12} = 0.401$ eu.			
2. I. Estermann, S. A. Friedberg and J. E. Goldman, Phys. Rev. 87, 582 (1952).			
3. C. W. Kothan and H. L. Johnston, J. Am. Chem. Soc. 75, 3101 (1953). $S^\circ_{15} = 0.013$ eu.			
4. M. H. Aven, R. S. Craig, T. R. Waite and W. E. Wallace, Phys. Rev. 102, 1263 (1956).			
5. N. M. Wolcott, Phil. Mag. 2, 1248 (1957).			
6. K. Clusius and P. Franzosini, Z. Physik. Chem. 16, 194 (1958).			
7. D. L. Burk, I. Estermann and S. A. Friedberg, Z. Physik. Chem. 16, 183 (1958).			
8. O. D. Kneip, Jr., J. O. Betterton, Jr. and J. O. Scarbrough, Phys. Rev. 130, 1687 (1963).			
9. R. P. Hake and J. A. Cape, Phys. Rev. 135, A1151 (1964).			

The high temperature heat capacities, 320-1856°K, have also been determined by many investigators. The values above 1155°K are not in good agreement. The measured temperature range, method used, and kind of data reported by these investigators are presented in the table below.

Investigator	Temperature, °K	Method	Property Measured
1. Jaeger et al. (1936)	492.9 - 1475.6	drop calorimetry	$H^\circ_T - H^\circ_{298.15}$
2. Kothan (1952)	1067.0 - 1856.0	drop calorimetry	$H^\circ_T - H^\circ_{298.15}$
3. Scott (1957)	333.2 - 1233.2	adiabatic calorimetry	Cp
4. Backhurst (1958)	873.2 - 1353.2	adiabatic calorimetry	Cp
5. Golutvin (1959)	398.0 - 1401.9	drop calorimetry	$H^\circ_T - H^\circ_{298.15}$
6. Holland (1963)	595.0 - 1345.0	resistance measurement	Cp
7. Kohlhaase et al. (1965)	320.0 - 1800.0	adiabatic calorimetry	Cp
1. F. M. Jaeger, E. Rosenbohm and R. Fonteyne, Rec. trav. chim. 55, 615 (1936).			
2. C. W. Kothan, Ph. D. Dissertation, The Ohio State University, 1952. Sample purity 99.96%.			
3. J. L. Scott, ORNL-2328, Oak Ridge National Laboratory, July 1957.			
4. I. Backhurst, J. Iron Steel Inst. (London) 169, 124 (1958).			
5. Y. M. Golutvin, Russ. J. Phys. Chem. 33, 164 (1959).			
6. L. R. Holland, J. Appl. Phys. 34, 2350 (1963).			
7. R. Kohlhaase, M. Braun and O. Vollmer, Z. Naturforsch. 20a, 1077 (1965). Sample purity 99.96%.			

The adopted Cp values, 298.15 - 1155°K, were mainly derived from the Cp data reported by reference 7. The low temperature and high temperature Cp data were joined smoothly at 298°K. The Cp values above 1155°K were estimated by graphical extrapolation. $S^\circ_{298.15}$ was derived from the adopted Cp, based on $S^\circ_{13} = 0.015$ eu.

Transition Data.

See the Ti (β, c) table for details.

Heat of Sublimation.

$\Delta H^\circ_{298.15}$ is calculated as the difference between $\Delta H^\circ_{298.15}$ for Ti(g) and Ti (α, c).

T, °K	Cp	$\frac{\text{gibbs/mol}}{S} - (G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log Kp
0						
100						
200						
298	6.205	8.691	8.691	0.000	1.026	- .752
300	6.206	8.729	8.691	0.011	1.023	- .746
400	6.280	10.525	8.636	1.440	.885	- .484
500	6.358	11.934	9.499	1.426	.748	- .327
600	6.439	13.101	9.922	1.399	.613	- .223
700	6.525	14.100	10.449	2.556	.485	- .151
800	6.618	14.977	10.661	1.309	.364	- .099
900	6.682	15.762	11.452	3.279	.250	- .061
1000	6.823	16.475	11.919	1.152	.144	- .032
1100	6.940	17.131	12.363	5.245	.050	- .010
1200	7.058	17.741	12.786	5.945	.000	.000
1300	7.210	18.312	13.190	6.659	.000	.000
1400	7.397	18.842	13.575	7.387	.000	.000
1500	7.590	19.336	13.944	8.133	.000	.000
1600	7.730	19.858	14.298	8.896	.000	.000
1700	7.840	20.333	14.639	9.679	.000	.000
1800	7.960	20.793	14.969	10.484	.000	.000
1900	8.090	21.240	15.291	11.211	.000	.000
2000	8.230	21.677	15.602	11.967	.019	.017
2100	8.860	22.103	15.895	13.037	.385	.040
2200	9.090	22.521	16.187	13.934	.611	.061
2300	9.312	22.930	16.471	14.855	.836	.079
2400	9.530	23.331	16.749	15.797	1.058	.096
2500	9.750	23.724	17.020	16.761	1.277	.112

Sept. 30, 1956

ΔH°_0 = Unknown
 $\Delta H^\circ_{298.15} = 1.433$ kcal/mol
 $\Delta H^\circ = 0.99$ kcal/mol
 $\Delta S^\circ = [4.45]$ kcal/mol
 $\Delta S^\circ_{298.15} = [111.57]$ kcal/mol

$\Delta^\circ_{298.15} = 8.691$ gibbs/mol
 $T = 1155 \pm 3^\circ\text{K}$
 $T_m = 1933 \pm 10^\circ\text{K}$

Heat of Formation.
The heat of formation ($\Delta H^\circ_{298.15}$) was obtained from $\Delta H^\circ_{298.15}(\alpha, c)$ by adding ΔH° and the difference $H^\circ_{\text{Ti}} - H^\circ_{\text{Ti}}(\alpha, c)$ and $T(\beta, c)$.

Heat Capacity and Entropy.

The heat capacities, 1155 - 1856°K, have been determined by many investigators. See the Ti (α, c) table for details. The selected Cp values were evaluated based on the data reported by C. W. Kothen, Ph. D. Dissertation, The Ohio State University, 1952, and R. Kohlhaas, M. Braun and O. Vollmer, Z. Naturforsch. 20A, 1077 (1965). The heat capacities below 1155°K and above 1800°K were estimated by graphical extrapolation. The entropy was obtained in a manner analogous to that of the heat of formation.

Transition Data.

Titanium has two crystal forms, i.e., the hexagonal close-packed low-temperature form and the body-centered cubic high-temperature form. The $\alpha \rightarrow \beta$ transition temperature has been determined and reported over a range of temperatures, 1154-1187°K, by many investigators. The value of Tt is affected by the impurities in the specimen or adsorbed by the specimen during the measurement and the method used for the determination. The following table indicates the values of Tt reported by different investigators. Also included are the heats of transition (ΔH°), purity of specimen and property measured. The value of Tt adopted is 1155 $\pm$ 3°K, and the value of ΔH° is selected as 0.99 kcal/mol.

Investigator	Tt, °K	ΔH° , kcal/mol	Purity, %	Method or Property Measured
1. Fast (1939)	1158 $\pm$ 10	-	Iodide	electrical resistance
2. Greiner and Ellis (1949)	1158 $\pm$ 2	-	99.9	electrical resistance
3. McQuillan (1950)	1155.7 $\pm$ 1	-	99.93	hydrogen solubility
4. Dwez (1951)	1155 $\pm$ 4	-	Iodide	cooling curve
5. Womer (1951)	1158 $\pm$ 2	-	99.93	thermoelectric power
6. Kothen (1952)	1154	0.943	99.96	dropping calorimetry
7. Edwards et al. (1953)	1157 $\pm$ 3.5	-	99.88	cooling curve
8. Schofield (1956)	1158	0.814	-	rate of heating
9. Scott (1957)	1156 $\pm$ 2	0.978 $\pm$ 0.025	Iodide	adiabatic calorimetry
10. Backhurst (1958)	-	0.880	Commercial	adiabatic calorimetry
11. Golutvin (1959)	1155	0.820 $\pm$ 0.020	Iodide	dropping calorimetry
12. Kohlhaas, et al. (1965)	1167	0.992	99.8	adiabatic calorimetry

1. J. D. Fast, Rec. trav. chim. 58, 973 (1939).
2. E. S. Greiner and W. C. Ellis, Trans. Am. Inst. Min. Met. Eng. 180, 657 (1949).
3. A. D. McQuillan, J. Inst. Metals, 78, 249 (1950).
4. P. Dwez, J. Metals, 3, 785 (1951).
5. H. W. Womer, Australian J. Sci. Res. 4, 62 (1951).
6. C. W. Kothen, Ph. D. Dissertation, The Ohio State University, 1952.
7. J. W. Edwards, H. L. Johnston and W. E. Dittmar, J. Am. Chem. Soc. 75, 2467 (1953).
8. T. H. Schofield, J. Inst. Metals, 85, 68 (1956).
9. J. L. Scott, ORNL - 2328, Oak Ridge National Laboratory, July 1957.
10. I. Backhurst, J. Iron Steel Inst. (London) 189, 124 (1956).
11. Y. M. Golutvin, Russ. J. Phys. Chem. 33, 164 (1959).
12. R. Kohlhaas, M. Braun and D. Vollmer, Z. Naturforsch. 20A, 1077 (1965).

Melting Data.

See the Ti(l) table for details.

Heat of Sublimation.

$\Delta H^\circ_{298.15}$ is calculated as the difference between $\Delta H^\circ_{298.15}$ for Ti(g) and Ti(β, c).

Titanium (Ti)

(Liquid) GFW = 47.90

T, °K	Cp°	$S^{\circ} - (C^{\circ} - H^{\circ})/T$	$H^{\circ} - H^{\circ}_{298}$	kcal/mol ΔH°	ΔG°	Log Kp
0						
100	6.205	10.695	0.000	5.433	4.428	-3.246
200						
300	6.206	10.733	0.011	5.433	4.422	-3.222
400	6.280	12.529	0.636	5.440	4.084	-2.231
500	6.358	13.938	1.268	5.426	3.746	-1.637
600	6.439	15.105	1.907	5.399	3.411	-1.242
700	6.525	16.104	2.556	5.362	3.082	-0.862
800	6.618	16.981	3.213	5.309	2.761	-0.594
900	6.718	17.766	3.879	5.239	2.447	-0.347
1000	6.825	18.479	4.556	5.152	2.140	-0.108
1100	6.940	19.135	5.245	5.045	1.845	-0.077
1200	7.068	19.745	5.945	4.900	1.555	-0.050
1300	7.200	20.316	6.659	4.700	1.270	-0.024
1400	7.338	20.846	7.389	4.450	0.990	-0.001
1500	7.480	21.332	8.135	4.150	0.715	0.000
1600	7.628	21.773	8.897	3.800	0.445	0.000
1700	7.780	22.170	9.675	3.400	0.180	0.000
1800	7.938	22.523	10.468	2.950	-0.080	0.000
1900	8.100	22.832	11.275	2.450	-0.340	0.000
2000	8.268	23.097	12.099	1.900	-0.600	0.000
2100	8.440	23.322	12.939	1.300	-0.860	0.000
2200	8.618	23.508	13.795	0.650	-1.120	0.000
2300	8.800	23.655	14.668	0.000	-1.380	0.000
2400	8.988	23.763	15.558	-0.650	-1.640	0.000
2500	9.180	23.832	16.465	-1.300	-1.900	0.000
2600	9.378	23.862	17.389	-1.950	-2.160	0.000
2700	9.580	23.853	18.338	-2.600	-2.420	0.000
2800	9.788	23.805	19.312	-3.250	-2.680	0.000
2900	9.998	23.718	20.312	-3.900	-2.940	0.000
3000	10.210	23.592	21.338	-4.550	-3.200	0.000
3100	10.425	23.427	22.391	-5.200	-3.460	0.000
3200	10.645	23.223	23.471	-5.850	-3.720	0.000
3300	10.870	22.980	24.588	-6.500	-3.980	0.000
3400	11.100	22.698	25.741	-7.150	-4.240	0.000
3500	11.335	22.377	26.930	-7.800	-4.500	0.000
3600	11.575	22.017	28.155	-8.450	-4.760	0.000
3700	11.820	21.618	29.417	-9.100	-5.020	0.000
3800	12.070	21.180	30.715	-9.750	-5.280	0.000
3900	12.325	20.703	32.049	-10.400	-5.540	0.000
4000	12.585	20.187	33.419	-11.050	-5.800	0.000
4100	12.850	19.632	34.825	-11.700	-6.060	0.000
4200	13.120	19.037	36.267	-12.350	-6.320	0.000
4300	13.395	18.402	37.745	-13.000	-6.580	0.000
4400	13.675	17.727	39.259	-13.650	-6.840	0.000
4500	13.960	17.012	40.809	-14.300	-7.100	0.000

Dec. 31, 1960; Sept. 30, 1966

TITANIUM (Ti)

(LIQUID)

OPW = 47.90

$$S^{\circ}_{298.15} = [10.695] \text{ gibbs/mol}$$

$$\Delta H^{\circ}_{f298.15} = [5.433] \text{ kcal/mol}$$

$$T_m = 1933 \pm 10^{\circ} \text{K}$$

$$\Delta H_m^{\circ} = [4.45] \text{ kcal/mol}$$

$$T_b = [3591]^{\circ} \text{K}$$

$$\Delta H_v^{\circ} = [101.65] \text{ kcal/mol}$$

Heat of Formation.

The heat of formation ($\Delta H^{\circ}_{f298.15}$) was obtained from $\Delta H^{\circ}_{f298.15}(\beta, c)$ by adding ΔH_m° and the difference between $H^{\circ}_{Tm} - H^{\circ}_{298.15}$ for Ti (β, c) and Ti(l).

Heat Capacity and Entropy.

A glass transition temperature at 1300°K was assumed. The heat capacities below 1300°K were obtained from those for Ti (β, c). The Cp value above 1300°K was estimated by comparison with those for the other transition elements and assumed to be constant in the temperature range 1300 - 4500°K. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

Because of the highly reactive nature of Ti(c), the accurate determination of the melting point is difficult. The results reported by different investigators show wide discrepancies. The T_m value adopted was determined by Schofield and Bacon (1953) and later confirmed by Mastrum and Peick (1963). The other values of T_m reported are presented in the table below. The heat of melting was calculated based on an estimated entropy of melting, $\Delta S_m^{\circ}_{1933} = 2.3 \text{ eu}$.

$T_m, ^{\circ} \text{K}$	Investigator
2068 ± 15	G. K. Burgess and R. O. Waltenberg, Z. anorg. Chem. 82 , 361 (1913).
1933	J. D. Fast, Rec. trav. chim. 58 , 975 (1939).
1933 ± 25	M. Hansen, H. D. Kessler and D. J. McPherson, Trans. Am. Soc. Metals, 44 , 518 (1952).
1973 ± 15	H. K. Adamstedt, J. R. Pequinot and J. M. Raymer, Trans. Am. Soc. Metals, 44 , 990 (1952).
1953 ± 10	D. J. Maykuth, H. R. Ogden and R. I. Jeffes, Trans. Am. Inst. Min. Met. Eng. 197 , 231 (1953).
1933 ± 10	T. H. Schofield and A. E. Bacon, J. Inst. Metals, 92 , 167 (1953).
1945 ± 4	R. A. Oriani and T. S. Jones, Rev. Sci. Instr. 25 , 248 (1954).
1941 ± 10	D. K. Deardorff and E. T. Hayes, J. Metals, 9 , 509 (1956).
1933	E. P. Mastrum, Jr. and G. Peick, ASD-TDR-62-204, Part II, University of Michigan, Ann Arbor, Michigan, May 1963.

Vaporization Data.

T_b is the temperature at which the Gibbs energy change (ΔG°) for the reaction $Ti(l) = Ti(g)$ approaches zero. The difference between $\Delta H^{\circ}_f(Ti, g)$ and $\Delta H^{\circ}_f(Ti, l)$ at T_b is ΔH_v° .

(Ideal Gas) GFW = 47.90

T, °K	C _p ^a	gibbs/mol S ^b - (G° - H° ₂₉₈)/T	gibbs/mol H° - H° ₂₉₈	ΔH° ^c kcal/mol	ΔG° ^c	Log K _p
0	.000	INFINITE	- 1.802	112.350	112.350	INFINITE
100	6.447	36.123	48.554	112.772	109.357	- 238.998
200	6.330	43.615	.596	112.868	105.851	- 115.668
298	5.359	43.686	.000	113.000	102.134	- 75.020
300	5.331	43.102	.066	.011	113.000	102.278
400	5.322	44.733	43.291	.577	112.948	98.710
500	5.344	45.945	43.706	1.120	112.845	95.161
600	5.337	46.009	44.142	1.688	112.707	91.434
700	5.170	46.711	44.812	2.168	112.541	88.137
800	5.128	46.398	45.044	2.683	112.346	84.554
900	5.104	46.001	45.451	3.194	112.121	81.217
1000	5.096	45.538	45.833	3.704	111.867	77.796
1100	5.106	50.024	46.493	4.214	111.588	74.404
1200	5.176	50.891	47.228	4.724	111.388	71.074
1300	5.237	51.267	47.850	5.241	110.149	67.810
1400	5.237	51.267	47.852	5.762	109.941	64.560
1500	5.313	51.631	47.438	6.289	109.723	61.326
1600	5.403	51.977	47.711	6.825	109.494	58.107
1700	5.504	52.307	47.773	7.370	109.258	54.902
1800	5.616	52.625	47.222	7.926	109.009	51.711
1900	5.737	52.932	48.461	8.494	108.750	48.535
2000	5.864	53.229	48.692	9.074	108.432	45.384
2100	5.996	53.518	48.915	9.666	108.074	42.240
2200	6.132	53.801	49.131	10.273	107.776	39.100
2300	6.271	54.076	49.340	10.893	107.511	35.970
2400	6.413	54.346	49.543	11.527	107.283	32.849
2500	6.557	54.611	49.740	12.176	107.084	29.741
2600	6.701	54.871	49.933	12.830	106.897	26.648
2700	6.847	55.121	50.124	13.516	106.724	23.569
2800	6.993	55.378	50.308	14.208	106.566	20.509
2900	7.140	55.626	50.483	14.915	106.423	17.462
3000	7.286	55.871	50.659	15.636	106.294	14.420
3100	7.432	56.112	50.831	16.372	106.180	11.392
3200	7.578	56.350	50.991	17.122	106.080	8.384
3300	7.722	56.585	51.165	17.887	105.995	5.397
3400	7.866	56.818	51.328	18.667	105.925	2.437
3500	8.007	57.048	51.488	19.461	105.869	- 1.600
3600	8.148	57.276	51.646	20.268	105.824	- 4.688
3700	8.283	57.500	51.801	21.090	105.790	- 7.800
3800	8.417	57.723	51.954	21.925	105.765	- 10.940
3900	8.548	57.944	52.105	22.773	105.750	- 14.100
4000	8.676	58.162	52.253	23.634	105.745	- 17.280
4100	8.799	58.378	52.400	24.508	105.750	- 20.480
4200	8.919	58.591	52.545	25.394	105.765	- 23.700
4300	9.035	58.802	52.688	26.292	105.780	- 26.940
4400	9.146	59.011	52.829	27.201	105.800	- 30.200
4500	9.252	59.218	52.969	28.121	105.820	- 33.480
4600	9.354	59.423	53.107	29.051	105.840	- 36.780
4700	9.451	59.625	53.244	29.991	105.860	- 40.100
4800	9.544	59.825	53.379	30.941	105.880	- 43.440
4900	9.631	60.022	53.512	31.900	105.900	- 46.800
5000	9.713	60.218	53.644	32.867	105.920	- 50.180
5100	9.791	60.411	53.775	33.842	105.940	- 53.580
5200	9.864	60.602	53.905	34.825	105.960	- 56.990
5300	9.933	60.790	54.033	35.815	105.980	- 60.420
5400	9.996	60.977	54.160	36.812	106.000	- 63.870
5500	10.056	61.161	54.285	37.814	106.020	- 67.340
5600	10.111	61.342	54.410	38.822	106.040	- 70.820
5700	10.161	61.522	54.533	39.836	106.060	- 74.320
5800	10.208	61.699	54.655	40.855	106.080	- 77.840
5900	10.251	61.874	54.776	41.878	106.100	- 81.380
6000	10.289	62.046	54.895	42.905	106.120	- 84.940

Dec. 31, 1960; Sept. 30, 1966; June 30, 1967

TITANIUM (Ti)

(IDEAL GAS)

GFW = 47.90

Ground State Configuration ³F₂ΔH_f⁰ = 112.4 ± 1.0 kcal/molΔH_f⁰ = 113.0 ± 1.0 kcal/molS₂₉₈⁰ = 43.066 gibbs/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0.00	5	11639.82	7	17467.00	15	35843.00	147
170.13	7	11776.82	9	18101.00	9	37685.00	105
386.87	9	[12000.00]	[1]	18392.00	76	38939.00	161
6556.86	3	12118.46	9	19789.00	44	40121.00	80
6598.83	5	13381.75	3	21381.00	38	41471.00	180
6661.00	7	14028.47	5	22270.00	12	42106.00	216
6742.79	9	14105.68	7	25405.00	87	43734.00	145
6843.00	11	15108.15	7	27178.00	123	44732.00	127
7255.29	5	15156.80	9	28745.00	65	46284.00	213
8436.63	1	15220.40	11	30144.00	89	48513.00	330
8492.44	3	16008.00	21	31849.00	76		
8602.35	5	16371.00	24	33751.00	54		
11531.81	5	17046.00	35	34698.00	28		

Heat of Formation

The vapor pressure of Ti(β), 1510-1822°K, has been measured in three separate investigations. Based on the reported vapor pressures, the enthalpies of sublimation (ΔH_s⁰298.15) are evaluated by both the second and third law methods. The results obtained are presented in the following table. The adopted value of ΔH_f⁰ for Ti(g) is 113.0 ± 1.0 kcal/mol.

Reference	Temperature, °K	Second Law Value	Third Law Value	Drift
1	1510 - 1822	112.23 ± 1.91	110.26 ± 0.81	-1.3 ± 1.2
2	1658 - 1808	112.41 ± 6.30	110.71 ± 1.10	-1.1 ± 3.7
3	1587 - 1764	111.79 ± 0.18	111.22	-0.2 ± 0.6

*Calculation based on the third law ΔH_s⁰298 and ΔH_f⁰298(β) = 1.43 kcal/mol.

1. J. M. Blocher, Jr., and I. E. Campbell, J. Am. Chem. Soc. **71**, 4040 (1949).

2. L. G. Carpenter and W. N. Hair, Proc. Phys. Soc. **54**, 57 (1951). The preliminary results were reported by L. G. Carpenter and F. R. Reavell, Nature, **163**, 527 (1949).

3. J. W. Edwards, H. L. Johnston and W. E. Ditmars, J. Am. Chem. Soc. **75**, 2467 (1953).

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from C. E. Moore, National Bureau of Standards Circular 467 (1949). However, above the level $\epsilon_i = 15877.17$ cm⁻¹, the values of ϵ_i and g_i listed in the above table are average values calculated from those given by Moore. The ²S₀ level of the ground multiplet which has not been observed is estimated to lie at 12000 cm⁻¹ by comparison with the corresponding levels for Ti⁴⁺ ion, Zr and Zr⁴⁺ ion reported by C. E. Moore, loc. cit.

Titanium Unipositive Ion (Ti⁺)

GEW = 47.89945

(Ideal Gas)

T, °K	Cp°	S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0						
100						
200						
298	6.257	43.854	-0.00	271.840	259.462	-190.190
300						
400	6.257	43.893	-0.12	271.850	259.385	-186.961
500	6.245	43.692	-0.37	272.354	259.153	-183.409
600	6.177	47.079	-1.254	272.826	250.797	-170.623
700	6.040	48.194	-1.871	273.270	246.349	-159.733
800	5.931	49.120	-2.470	273.679	241.828	-149.502
900	5.812	49.904	-3.057	274.053	237.253	-140.814
1000	5.712	50.583	-3.633	274.390	232.631	-132.691
1100	5.633	51.180	-4.200	274.590	227.974	-125.124
1200	5.572	51.714	-4.760	274.658	223.291	-118.164
1300	5.529	52.197	-5.315	274.598	218.624	-111.817
1400	5.499	52.639	-5.867	274.502	213.972	-106.072
1500	5.481	53.045	-6.414	274.399	209.297	-100.923
1600	5.474	53.423	-6.961	274.288	204.600	-96.310
1700	5.476	53.776	-7.511	274.163	199.884	-92.223
1800	5.484	54.109	-8.059	274.025	195.150	-88.658
1900	5.499	54.422	-8.608	273.875	190.401	-85.618
2000	5.521	54.720	-9.159	273.713	185.641	-83.104
2100	5.547	55.004	-9.712	273.539	180.861	-80.111
2200	5.578	55.274	-10.264	273.354	176.070	-76.645
2300	5.613	55.536	-10.820	273.158	171.264	-72.707
2400	5.650	55.786	-11.391	272.954	166.441	-68.291
2500	5.690	56.027	-11.974	272.744	161.601	-63.401
2600	5.731	56.261	-12.569	272.528	156.745	-58.031
2700	5.773	56.484	-13.174	272.308	151.874	-52.189
2800	5.817	56.705	-13.794	272.084	146.988	-45.874
2900	5.865	56.917	-14.427	271.856	142.088	-39.084
3000	5.904	57.124	-15.064	271.624	137.174	-31.814
3100	5.948	57.320	-15.704	271.388	132.248	-24.064
3200	6.029	57.711	-16.344	271.148	127.312	-15.812
3300	6.069	57.897	-17.251	270.913	122.368	-7.058
3400	6.107	58.079	-18.226	270.674	117.414	2.194
3500	6.144	58.256	-19.279	270.432	112.452	12.442
3600	6.179	58.430	-20.304	270.188	107.484	22.690
3700	6.212	58.600	-21.328	269.944	102.512	32.938
3800	6.243	58.766	-22.330	269.698	97.538	43.186
3900	6.273	58.928	-23.355	269.454	92.564	53.434
4000	6.300	59.087	-24.391	269.210	87.590	63.682
4100	6.326	59.243	-25.436	268.966	82.616	73.930
4200	6.351	59.396	-26.490	268.722	77.642	84.178
4300	6.373	59.546	-27.544	268.478	72.668	94.426
4400	6.394	59.692	-28.600	268.234	67.694	104.674
4500	6.414	59.836	-29.654	267.990	62.720	114.922
4600	6.432	59.978	-30.710	267.746	57.746	125.170
4700	6.448	60.116	-31.764	267.502	52.772	135.418
4800	6.463	60.252	-32.818	267.258	47.798	145.666
4900	6.477	60.385	-33.872	267.014	42.824	155.914
5000	6.490	60.516	-34.926	266.770	37.850	166.162
5100	6.502	60.645	-35.979	266.526	32.876	176.410
5200	6.511	60.771	-37.033	266.282	27.902	186.658
5300	6.523	60.896	-38.086	266.038	22.928	196.906
5400	6.533	61.018	-39.138	265.794	17.954	207.154
5500	6.541	61.138	-40.189	265.550	12.980	217.402
5600	6.549	61.255	-41.239	265.306	7.996	227.650
5700	6.557	61.371	-42.289	265.062	2.992	237.898
5800	6.563	61.486	-43.338	264.818	-2.002	248.146
5900	6.570	61.598	-44.386	264.574	-6.998	258.394
6000	6.576	61.708	-45.433	264.330	-11.994	268.642

Dec. 31, 1967

TITANIUM UNIPosITIVE ION (Ti⁺)

GEW = 47.89945

(IDEAL GAS)

Ground State Configuration $3d^2 4s^2$

$\Delta H_f^\circ = 269.62 \pm 1.0$ kcal/mol

$\Delta H_f^\circ = 271.84 \pm 1.0$ kcal/mol

Electronic Levels and Quantum Weights			
$\epsilon_i, \text{cm}^{-1}$	g_i	$\epsilon_i, \text{cm}^{-1}$	g_i
0	4	9508.611	14
93.94	6	9970.051	16
225.47	8	12722.863	32
393.22	10	15593.028	24
907.96	4	22758.664	26
983.80	6	30448.462	64
1087.21	8	32094.291	44
1215.58	10	36951.357	36
4782.319	14	40329.131	38
8945.376	28	43558.293	40

Heat of Formation

The heat of formation is calculated from the reaction $\text{Ti(g)} = \text{Ti}^+(\text{g}) + e^-(\text{g})$ with the JANAF auxiliary value for Ti(g) and an ionization potential = 6.82 eV or 157.276 kcal/mol, obtained from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. I, 1949.

Heat Capacity and Entropy

The electronic levels and quantum weights are taken from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. I, 1949. The electronic levels above 4700 cm^{-1} are averaged. The $H^\circ - H_{298}^\circ$ value at 0°K is -1.886 kcal/mol.

Ti⁺

Tungsten (W)

(Reference State) GFW = 183.85

T, °K	Cp ^o	gibbs/mol S ^o - (G ^o - H ^o ₂₉₈)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0	.000	.000	INFINITE	- 1.189	.000	.000
100	3.832	2.297	12.624	- 1.033	.000	.000
200	5.375	5.562	8.327	-.553	.000	.000
298	5.807	7.806	7.806	.000	.000	.000
300	5.811	7.842	7.806	.011	.000	.000
400	5.958	9.515	8.036	.600	.000	.000
500	6.061	10.875	8.474	1.201	.000	.000
600	6.164	11.889	8.970	1.812	.000	.000
700	6.267	12.797	9.551	2.423	.000	.000
800	6.370	13.591	10.208	3.034	.000	.000
900	6.480	14.288	10.848	3.708	.000	.000
1000	6.598	15.237	10.875	4.362	.000	.000
1100	6.696	15.869	11.301	5.026	.000	.000
1200	6.782	16.307	11.705	5.689	.000	.000
1300	6.859	16.602	12.095	6.387	.000	.000
1400	7.025	17.522	12.662	7.094	.000	.000
1500	7.137	18.011	12.816	7.792	.000	.000
1600	7.250	18.474	13.155	8.511	.000	.000
1700	7.362	18.912	13.482	9.240	.000	.000
1800	7.477	19.342	13.795	9.984	.000	.000
1900	7.592	19.749	14.098	10.737	.000	.000
2000	7.709	20.142	14.391	11.502	.000	.000
2100	7.826	20.521	14.673	12.279	.000	.000
2200	7.943	20.885	14.946	13.068	.000	.000
2300	8.063	21.243	15.216	13.868	.000	.000
2400	8.182	21.599	15.472	14.680	.000	.000
2500	8.302	21.925	15.724	15.504	.000	.000
2600	8.424	22.233	15.968	16.340	.000	.000
2700	8.546	22.526	16.200	17.186	.000	.000
2800	8.670	22.805	16.420	18.072	.000	.000
2900	8.795	23.071	16.668	18.987	.000	.000
3000	8.800	23.215	16.892	19.943	.000	.000
3100	10.380	23.870	17.112	20.952	.000	.000
3200	11.000	24.559	17.329	23.154	.000	.000
3300	11.700	25.291	17.554	24.363	.000	.000
3400	12.500	26.019	17.754	25.660	.000	.000
3500	13.500	25.295	17.964	25.660	.000	.000
3600	14.750	25.092	18.173	27.071	.000	.000
3700	16.000	24.804	18.380	28.482	.000	.000
3800	17.250	24.604	18.600	30.000	.000	.000
3900	18.500	24.422	18.817	31.627	.000	.000
4000	19.750	24.237	19.168	33.477	.000	.000
4100	21.000	24.047	19.411	35.437	.000	.000
4200	22.250	23.852	19.576	37.507	.000	.000
4300	23.500	23.652	19.774	39.687	.000	.000
4400	24.750	23.447	20.102	42.877	.000	.000
4500	26.000	23.238	20.321	43.727	.000	.000
4600	27.250	23.025	20.534	44.577	.000	.000
4700	28.500	22.807	20.742	45.427	.000	.000
4800	29.750	22.587	20.946	46.277	.000	.000
4900	31.000	22.362	21.144	47.127	.000	.000
5000	32.250	22.134	21.338	47.977	.000	.000
5100	33.500	21.902	21.528	48.827	.000	.000
5200	34.750	21.667	21.714	49.677	.000	.000
5300	36.000	21.429	21.896	50.527	.000	.000
5400	37.250	21.188	22.074	51.377	.000	.000
5500	38.500	20.944	22.248	52.227	.000	.000
5600	39.750	20.697	22.419	53.077	.000	.000
5700	41.000	20.447	22.587	53.927	.000	.000
5800	42.250	20.195	22.751	54.777	.000	.000
5900	43.500	20.000	22.912	55.627	.000	.000
6000	44.750	19.755	23.068	56.477	.000	.000

TUNGSTEN (W)

GFW = 183.85

(REFERENCE STATE)
0 to 3680°K Crystal
3680 to 5936°K Liquid
5936 8000°K Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	-0.00	INFINITE	-	1.180	.000	.000	.000
100	3.892	2.297	12.433	1.033	.000	.000	.000
200	5.235	5.562	8.427	.953	.000	.000	.000
298	5.807	7.806	7.806	.000	.000	.000	.000
300	5.811	7.842	7.806	.011	.000	.000	.000
400	5.998	9.255	8.036	.600	.000	.000	.000
500	6.401	10.875	8.414	1.201	.000	.000	.000
600	6.164	11.989	8.970	1.812	.000	.000	.000
700	6.269	12.947	9.471	2.433	.000	.000	.000
800	6.374	13.791	9.959	3.066	.000	.000	.000
900	6.468	14.549	10.429	3.704	.000	.000	.000
1000	6.558	15.237	10.875	4.362	.000	.000	.000
1100	6.696	15.869	11.301	5.026	.000	.000	.000
1200	6.805	16.457	11.706	5.701	.000	.000	.000
1300	6.914	17.006	12.093	6.387	.000	.000	.000
1400	7.025	17.522	12.462	7.084	.000	.000	.000
1500	7.137	18.011	12.816	7.792	.000	.000	.000
1600	7.250	18.475	13.155	8.511	.000	.000	.000
1700	7.363	18.918	13.481	9.242	.000	.000	.000
1800	7.477	19.342	13.795	9.984	.000	.000	.000
1900	7.591	19.749	14.096	10.737	.000	.000	.000
2000	7.706	20.142	14.391	11.502	.000	.000	.000
2100	7.826	20.521	14.673	12.279	.000	.000	.000
2200	7.944	20.887	14.948	13.068	.000	.000	.000
2300	8.063	21.243	15.214	13.868	.000	.000	.000
2400	8.182	21.589	15.472	14.680	.000	.000	.000
2500	8.302	21.925	15.724	15.504	.000	.000	.000
2600	8.424	22.253	15.968	16.340	.000	.000	.000
2700	8.650	22.575	16.207	17.193	.000	.000	.000
2800	8.950	22.895	16.440	18.072	.000	.000	.000
2900	9.350	23.215	16.668	18.987	.000	.000	.000
3000	9.800	23.540	16.892	19.944	.000	.000	.000
3100	10.380	23.870	17.112	20.952	.000	.000	.000
3200	11.000	24.209	17.328	22.020	.000	.000	.000
3300	11.700	24.558	17.542	23.154	.000	.000	.000
3400	12.500	24.919	17.754	24.363	.000	.000	.000
3500	13.500	25.295	17.964	25.660	.000	.000	.000
3600	14.750	25.693	18.173	27.073	.000	.000	.000
3700	16.063	26.115	18.382	28.613	.043	.043	.000
3800	17.375	26.561	18.591	30.285	.260	.260	.015
3900	18.688	27.029	18.801	32.088	.454	.454	.025
4000	20.000	27.519	19.013	34.023	.634	.634	.034
4100	21.313	28.029	19.227	36.088	.755	.755	.040
4200	22.625	28.558	19.443	38.295	.863	.863	.045
4300	23.938	29.106	19.661	40.613	.934	.934	.047
4400	25.250	29.671	19.882	43.073	.956	.956	.048
4500	26.563	30.253	20.102	45.683	.969	.969	.047
4600	27.875	30.852	20.333	48.385	.968	.924	.044
4700	29.188	31.465	20.563	51.238	.943	.843	.039
4800	30.500	32.091	20.797	54.223	.717	.717	.033

$$\Delta H_{298}^{\circ} = 0 \text{ kcal/mol}$$

$$\Delta H_{298}^{\circ} = 0 \text{ kcal/mol}$$

$$\Delta H_{298}^{\circ} = [8.46 \pm 2.5] \text{ kcal/mol}$$

$$\Delta H_{298}^{\circ} = 203.4 \pm 1.5 \text{ kcal/mol}$$

$$S_{298}^{\circ} = 7.806 \text{ gibbs/mol}$$

$$T_m = 3680 \pm 20^{\circ} \text{K}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

There have been several investigations of the low temperature heat capacity of tungsten: F. Lange, Z. physik. Chem. **110**, 343 (1924), covered the range 28-91°K. M. Horowitz and J. O. Daunt, Phys. Rev. **91**, 1099 (1953), reported values in the range 1-77°K, while T. R. Waite, R. S. Craig, and W. E. Wallace, Phys. Rev. **104**, 1240 (1956), worked from 4-15° and W. DeSorbo, J. Phys. Chem. **62**, 985 (1958), from 15-90°K. C. Zwikker and G. Schmidt, Z. Physik. **52**, 668 (1928), covered the range from 90 to 2521°K. K. Cluissius and P. Franzosini, Z. Naturforsch. **14d**, 99 (1959), made a thorough study of the heat capacity in the range 12-274°K, and their measurements were adopted leading to $S_{298}^{\circ} = 7.806$ eu based on $S_{12}^{\circ} = 0.0088$ eu. This value is in disagreement with the quoted value of 7.63 eu but agrees exactly with a separate integration by V. A. Kirillin, A. E. Sheindlin, V. Ye. Chekhovskoi and V. A. Petrov, Zhur. Fiz. Khim. **37**, 2249 (1963). In the intermediate temperature range the adiabatic heat capacity measurements of H. L. Bronson, H. M. Chisholm and S. M. Docketty, Can. J. Res. **B**, 282 (1953), from 253 to 773°K joined well with the low temperature measurements and were adopted. The high temperature enthalpies have been measured by several investigators from which were selected the values of P. M. Jaeger and E. Rosenblum, Rec. trav. chim. **51**, 1 (1932), from 273-1800°K; A. Magnus and H. Holzmam, Ann. Physik Ser. **5**, 3, 585 (1929), who covered the range 373 to 1173°K; M. Hoch and H. L. Johnston, J. Phys. Chem. **65**, 855 (1961) who made measurements between 1382 and 2900°K; Kirillin et al., loc. cit., who have made several determinations over the range 600 to 3100°K, and have also analysed the above data and have presented smooth functions from 0 to 3500°K. The present table agrees with that of Kirillin et al. up to 2700°K. Above this temperature the values of Cp adopted follow those reported by I. I. Novikov and P. G. Streikov, Vestnik. Akad. Nauk SSSR **54**, 26(1964), measured by an electric modulation method, up to the melting point. These values rise rapidly above 2700°K and are not inconsistent with the individual measurements of Kirillin et al. at their highest temperatures.

Melting Data.

I. Langmuir, Phys. Rev. **63**, 138 (1915), determined the melting point as 3540°K from intrinsic brilliance measurements; this was later corrected to 3655 ± 30°K by H. A. Jones, I. Langmuir and O. M. J. Mackay, Phys. Rev. **30**, 201 (1927). M. Firani and H. Alterthum, Z. Elektrochem. **29**, 5 (1923), from pyrometer measurements on a black body hole found 3660 ± 60°K. Using the same technique C. P. Zalabak, NASA Tech. Note D-761 (1961), reports 3680°K on a low carbon specimen; he reports a decrease of the melting point with increasing carbon content. E. Rudy and S. Windisch, Aerojet-General Tech. Rept. No. APWU-VR-65-2 Part 1, Vol. III July 1965, report a melting point of 3698 ± 20°K. The value adopted was 3680 ± 20°K. The heat of melting was obtained by assuming an entropy of melting of 2.3 eu obtained from a comparison of several high melting metals (Fe, Cu, Co, Mg, Al).

Sublimation Data.

See W(g) for details.

Tungsten (W)

(Liquid) GFW = 183.85

T, °K	Cp°	S° -(C°-H° ₂₉₈)/T	gibbs/mol	H°-H° ₂₉₈	kcal/mol	ΔHf°	ΔGf°	Log Kp
0								
100								
200								
298	5.807	10.923	10.923	•000	11.223	10.294	-	7.545
300	5.810	10.959	10.923	+0.11	11.223	10.288	-	7.495
400	6.000	11.223	11.223	+0.00	11.223	10.288	-	7.495
500	6.091	13.992	11.591	1.200	11.222	9.666	-	6.224
600	6.164	15.106	12.087	1.812	11.223	9.353	-	5.407
700	6.269	16.064	12.493	2.433	11.223	9.041	-	4.823
800	6.374	16.908	13.077	3.066	11.223	8.729	-	4.385
900	6.480	17.645	13.635	3.708	11.223	8.416	-	3.947
1000	6.588	18.284	13.992	4.362	11.223	8.106	-	3.511
1100	6.696	18.987	14.418	5.026	11.223	7.793	-	3.074
1200	6.805	19.574	14.823	5.701	11.223	7.482	-	2.637
1300	6.914	20.123	15.210	6.387	11.223	7.170	-	2.200
1400	7.023	20.645	15.581	7.084	11.223	6.857	-	1.763
1500	7.137	21.128	15.933	7.797	11.223	6.547	-	1.326
1600	7.250	21.592	16.273	8.511	11.223	6.236	-	0.889
1700	7.363	22.035	16.599	9.242	11.223	5.924	-	0.452
1800	7.477	22.459	16.912	10.000	11.223	5.617	-	0.015
1900	7.591	22.865	17.213	10.777	11.223	5.310	-	-0.422
2000	7.709	23.259	17.508	11.582	11.223	4.998	-	-0.855
2100	7.826	23.638	17.791	12.279	11.223	4.677	-	-1.287
2200	7.944	24.005	18.065	13.068	11.223	4.363	-	-1.719
2300	8.062	24.360	18.331	13.868	11.223	4.054	-	-2.151
2400	8.180	24.704	18.588	14.679	11.223	3.742	-	-2.583
2500	8.300	25.042	18.841	15.504	11.223	3.431	-	-3.015
2600	8.500	25.376	19.086	16.354	11.237	3.118	-	-3.447
2700	8.500	25.697	19.325	17.204	11.234	2.805	-	-3.879
2800	8.500	26.006	19.558	18.054	11.205	2.495	-	-4.311
2900	8.500	26.304	19.784	18.904	11.176	2.182	-	-4.743
3000	8.500	26.592	20.007	19.754	11.034	1.878	-	-5.175
3100	8.500	26.871	20.224	20.604	10.875	1.572	-	-5.607
3200	8.500	27.141	20.436	21.454	10.657	1.275	-	-6.039
3300	8.500	27.402	20.643	22.304	10.373	0.988	-	-6.471
3400	8.500	27.656	20.846	23.154	10.024	0.693	-	-6.903
3500	8.500	27.902	21.044	24.004	9.567	0.443	-	-7.335
3600	8.500	28.117	21.238	24.854	9.006	0.186	-	-7.767
3700	8.500	28.375	21.428	25.704	8.000	0.000	-	-8.199
3800	8.500	28.601	21.613	26.554	0.000	0.000	-	-8.631
3900	8.500	28.807	21.792	27.404	0.000	0.000	-	-9.063
4000	8.500	29.037	21.974	28.254	0.000	0.000	-	-9.495
4100	8.500	29.247	22.149	29.104	0.000	0.000	-	-9.927
4200	8.500	29.452	22.320	29.954	0.000	0.000	-	-10.359
4300	8.500	29.652	22.488	30.804	0.000	0.000	-	-10.791
4400	8.500	29.848	22.650	31.654	0.000	0.000	-	-11.223
4500	8.500	30.039	22.815	32.504	0.000	0.000	-	-11.655
4600	8.500	30.225	22.974	33.354	0.000	0.000	-	-12.087
4700	8.500	30.408	23.131	34.204	0.000	0.000	-	-12.519
4800	8.500	30.587	23.284	35.054	0.000	0.000	-	-12.951
4900	8.500	30.762	23.434	35.904	0.000	0.000	-	-13.383
5000	8.500	30.934	23.583	36.754	0.000	0.000	-	-13.815
5100	8.500	31.102	23.729	37.604	0.000	0.000	-	-14.247
5200	8.500	31.268	23.872	38.454	0.000	0.000	-	-14.679
5300	8.500	31.431	24.013	39.304	0.000	0.000	-	-15.111
5400	8.500	31.591	24.151	40.154	0.000	0.000	-	-15.543
5500	8.500	31.744	24.289	41.004	0.000	0.000	-	-15.975
5600	8.500	31.897	24.423	41.854	0.000	0.000	-	-16.407
5700	8.500	32.048	24.556	42.704	0.000	0.000	-	-16.839
5800	8.500	32.196	24.686	43.554	0.000	0.000	-	-17.271
5900	8.500	32.341	24.813	44.404	0.000	0.000	-	-17.703
6000	8.500	32.484	24.931	45.254	0.000	0.000	-	-18.135

Dec. 31, 1961, June 30, 1966

TUNGSTEN (W) (LIQUID)

GFW = 183.85

S°_{298.15} = 10.923 gibbs/molΔHf°_{298.15} = 11.223 kcal/mol

Tm° = 3680 ± 20°K

ΔHm° = [8.46 ± 2.5] kcal/mol

Tb° = [5936]°K

ΔHv° = [192.824] kcal/mol

Heat of Formation.

The heat of formation at 298°K was calculated from that of the crystal by adding ΔHm° and the difference between H°₃₆₈₀-H°₂₉₈ for (c) and (l).

Heat Capacity and Entropy.

The heat capacity was estimated as 8.5 gibbs/g-atom by analogy with other monatomic metals. The entropy at 298°K was calculated in a manner analogous to that of the heat of formation. At 2500°K a glass transition was assumed, below which the heat capacity was that of the crystal.

Melting Data.

See crystal table for details.

Vaporization Data.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

Ground State Configuration $5d_0$
 $S_{298.15}^\circ = 41.549 \text{ gibbs/mol}$
 $\Delta H_f^\circ = 203.1 \pm 1.5 \text{ kcal/mol}$
 $\Delta H_f^\circ = 203.4 \pm 1.5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	g_1	$\epsilon_2, \text{cm}^{-1}$	g_2	$\epsilon_3, \text{cm}^{-1}$	g_3
0.0	1	17701.14	7	20983.06	5
1670.3	3	17107.02	9	20427.81	3
3325.53	5	15459.99	7	20174.28	1
4830.00	7	14976.21	5	26035.67	35
6219.33	9	18082.80	3	26585.14	68
2951.29	7	18116.84	5	28413.86	60
9528.07	1	18974.47	7	30061.53	47
13307.06	3	19256.23	9	33420.02	44
19253.58	5	19535.04	11	34874.19	45
12161.95	9	19648.58	13	38611.26	277
15069.94	11	18280.48	5	43092.16	307
17008.50	13	19389.43	1	45985.57	309
13348.54	7	20756.53	8	48987.49	305
16431.28	9	23905.35	16	52348.75	321
19826.04	11	28159.77	24	55770.38	367
13777.70	5	19827.67	7	59180.98	183

Heat of Formation.

ΔH_f° is the heat of sublimation of the crystal at 298°K; this has been obtained by 2nd and 3rd law analysis of the vapor pressure data of three investigators. The results are summarized below:

Ref.	Range*°K	Points	$\Delta H_f^\circ, 298.15 \text{ kcal/mol}$		
			2nd law	3rd law	3rd law drift eu
1	2511-3053	12*	200.9 $\pm$ 3.6	201.57 $\pm$ 1.6	0.1 $\pm$ 1.4
2	2383-3123	14	214.8 $\pm$ 1.4	202.17 $\pm$ 2.5	-4.7 $\pm$ 0.5
3	2574-3183	10	202.4 $\pm$ 2.7	203.35 $\pm$ 1.2	0.4 $\pm$ 1.0

*1 point rejected due to failure of a statistical test.

**All temperatures are taken from Ref. 3, in which the earlier measurements have been corrected.

References:

1. H. A. Jones, I. Langmuir and G. M. J. Mackay, *Phys. Rev.* **30**, 201 (1927).
2. C. Zwicker, *Physica* **5**, 249 (1925).
3. R. Szwarc, E. R. Pante, and J. J. Diamond, *J. Res. Natl. Bur. Std.* **69A**, 417 (1965).

The values are remarkably good, since even at the highest temperature the pressures are less than 10^{-6} atm; all workers used the Langmuir technique. Since the data of Refs. 1 and 3 do not drift, it may be assumed that the accommodation coefficient is unity or close to unity. The drift in the second set cannot be eliminated by assuming a non-unity accommodation coefficient, nor does there appear to be a constant pressure error. Most probably the drift is due to slight errors in temperature. For example, if the readings were 24° high at the low end and 10° low at the high end, the drift would be eliminated; errors of this magnitude are quite possible. The value adopted for $\Delta H_f^\circ, 298.15$ is $203.4 \pm 1.5 \text{ kcal/mol}$.

Heat Capacity and Entropy.

The electronic energy levels were taken from those listed by C. E. Moore, U. S. Natl. Bur. Std. Circular 467 (1956). Levels above 25000 cm^{-1} were averaged.

Dec. 31, 1961; June 30, 1966

T, °K	C_p	S°	$-(C_p^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	<0.00	INFINITE	-	1.486	203.103	INFINITE	
100	4.968	36.105	-4.965	989	203.444	-37.238	
200	4.973	39.549	-4.909	4392	203.461	-206.664	-214.904
298	5.092	41.549	-4.900	4000	203.400	-141.722	
300	5.097	41.581	-4.909	4009	203.398	-140.802	
400	5.166	44.111	-4.815	4215	203.356	-103.763	
500	5.236	44.411	-4.715	4127	203.316	-81.345	
600	7.251	45.641	-4.2635	1.804	203.392	-66.731	
700	8.217	46.833	-4.3150	2.578	203.545	-56.144	
800	9.026	47.985	-4.3683	3.442	203.776	-48.196	
900	9.685	49.109	-4.4216	4.386	204.086	-42.004	
1000	9.855	50.109	-4.4760	5.348	204.586	-37.047	
1100	9.904	51.052	-4.5290	6.338	204.712	-32.983	
1200	9.787	51.910	-4.5807	7.324	205.023	-29.591	
1300	9.599	52.685	-4.6305	8.292	205.305	-26.717	
1400	9.359	53.392	-4.6782	9.240	205.558	-24.242	
1500	9.007	54.016	-4.7249	10.151	205.759	-22.110	
1600	8.721	54.588	-4.7690	11.037	205.926	-20.236	
1700	8.451	55.108	-4.8111	11.896	206.054	-18.581	
1800	8.205	55.584	-4.8513	12.728	206.144	-17.109	
1900	7.980	56.027	-4.8894	13.537	206.197	-15.801	
2000	7.786	56.427	-4.9264	14.326	206.224	-14.605	
2100	7.634	56.803	-4.9614	15.098	206.219	-13.532	
2200	7.499	57.155	-4.9949	15.854	206.186	-12.556	
2300	7.389	57.486	-5.0269	16.598	206.130	-11.666	
2400	7.298	57.800	-5.0573	17.331	206.055	-10.850	
2500	7.240	58.095	-5.0871	18.060	205.956	-10.100	
2600	7.197	58.378	-5.1155	18.781	205.841	-9.407	
2700	7.174	58.649	-5.1427	19.500	205.707	-8.767	
2800	7.167	58.910	-5.1690	20.217	205.545	-8.172	
2900	7.173	59.162	-5.1944	20.934	205.357	-7.619	
3000	7.200	59.405	-5.2188	21.652	205.100	-7.104	
3100	7.236	59.642	-5.2425	22.374	204.822	-6.622	
3200	7.264	59.872	-5.2654	23.100	204.480	-6.171	
3300	7.282	60.097	-5.2876	23.831	204.077	-5.748	
3400	7.290	60.318	-5.3092	24.569	203.606	-5.351	
3500	7.284	60.533	-5.3301	25.313	203.053	-4.978	
3600	7.265	60.745	-5.3505	26.066	202.495	-4.626	
3700	7.236	60.954	-5.3703	26.827	193.300	-4.297	
3800	7.194	61.159	-5.3897	27.596	193.219	-3.997	
3900	7.139	61.361	-5.4086	28.375	193.148	-3.712	
4000	7.073	61.561	-5.4270	29.164	193.087	-3.442	
4100	6.998	61.758	-5.4450	29.963	193.036	-3.184	
4200	6.914	61.953	-5.4627	30.772	192.995	-2.940	
4300	6.824	62.146	-5.4799	31.591	192.964	-2.706	
4400	6.728	62.337	-5.4968	32.420	192.943	-2.483	
4500	6.628	62.525	-5.5134	33.260	192.933	-2.270	
4600	6.520	62.712	-5.5297	34.110	192.933	-2.066	
4700	6.405	62.897	-5.5457	34.970	192.943	-1.871	
4800	6.284	63.080	-5.5614	35.840	192.963	-1.684	
4900	6.158	63.262	-5.5768	36.720	192.993	-1.505	
5000	6.029	63.441	-5.5920	37.609	193.032	-1.335	
5100	5.896	63.619	-5.6069	38.508	193.081	-1.168	
5200	5.760	63.796	-5.6216	39.416	193.139	-1.008	
5300	5.621	63.971	-5.6360	40.334	193.207	-0.855	
5400	5.479	64.144	-5.6503	41.259	193.282	-0.707	
5500	5.335	64.315	-5.6645	42.194	193.367	-0.565	
5600	5.188	64.485	-5.6783	43.136	193.459	-0.428	
5700	5.041	64.653	-5.6919	44.084	193.559	-0.295	
5800	4.894	64.820	-5.7053	45.044	193.667	-0.167	
5900	4.746	64.985	-5.7186	46.009	193.782	-0.044	
6000	4.598	65.148	-5.7318	46.981	193.900	0.000	

Tungsten Unipositive Ion (W⁺)
(Ideal Gas)

GFW = 183.8495

T, °K	Cp°	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0							
100							
200							
298	5.108	42.931	42.931	•000	388.918	376.958	- 276.318
300	5.113	42.963	42.931	•009	388.925	376.883	- 276.559
400	5.471	44.478	43.534	1.947	389.851	378.451	- 203.151
500	5.934	45.748	43.534	1.107	389.827	368.612	- 161.120
600	6.380	46.870	43.998	1.723	390.329	364.323	- 132.704
700	6.762	47.884	44.482	2.381	390.862	359.946	- 112.380
800	7.093	48.796	44.966	3.076	391.417	355.491	- 97.116
900	7.358	49.657	45.448	3.795	391.985	350.967	- 83.847
1000	7.553	50.442	45.902	4.540	392.563	346.377	- 75.701
1100	7.731	51.170	46.348	5.304	393.180	341.728	- 67.895
1200	7.897	51.849	46.779	6.085	393.783	337.025	- 61.381
1300	8.051	52.480	47.196	6.885	394.366	332.268	- 55.050
1400	8.081	53.080	47.593	7.682	394.900	327.458	- 48.874
1500	8.146	53.640	47.978	8.494	395.591	322.625	- 47.006
1600	8.189	54.167	48.348	9.311	396.186	317.741	- 43.401
1700	8.213	54.665	48.705	10.131	396.772	312.819	- 40.216
1800	8.222	55.136	49.049	10.956	397.348	307.858	- 37.380
1900	8.222	55.579	49.385	11.775	397.904	302.858	- 34.842
2000	8.214	56.001	49.702	12.597	398.448	297.842	- 32.549
2100	8.202	56.401	50.012	13.418	399.009	292.818	- 30.474
2200	8.190	56.782	50.311	14.238	399.537	287.748	- 28.595
2300	8.173	57.146	50.600	15.056	400.051	282.654	- 26.858
2400	8.152	57.496	50.878	15.864	400.544	277.542	- 25.244
2500	8.172	57.828	51.151	16.691	401.044	272.406	- 23.814
2600	8.179	58.148	51.414	17.508	401.522	267.250	- 22.464
2700	8.194	58.457	51.670	18.327	401.985	262.079	- 21.214
2800	8.186	58.756	51.917	19.147	402.423	256.888	- 20.051
2900	8.153	59.041	52.151	19.967	402.836	251.680	- 18.967
3000	8.292	59.325	52.392	20.768	403.196	246.464	- 17.955
3100	8.342	59.598	52.620	21.629	403.515	241.230	- 17.007
3200	8.399	59.863	52.843	22.466	403.781	235.996	- 16.118
3300	8.464	60.123	53.059	23.309	403.987	230.747	- 15.282
3400	8.537	60.377	53.269	24.159	404.134	225.482	- 14.495
3500	8.609	60.625	53.477	25.016	404.181	220.202	- 13.753
3600	8.688	60.869	53.679	25.881	404.132	214.985	- 13.051
3700	8.770	61.108	53.877	26.754	395.646	209.777	- 12.391
3800	8.837	61.343	54.070	27.635	386.174	204.749	- 11.776
3900	8.902	61.581	54.257	28.516	376.741	199.741	- 11.205
4000	9.020	61.801	54.445	29.423	397.255	194.697	- 10.633
4100	9.101	62.025	54.628	30.329	397.808	189.573	- 10.105
4200	9.180	62.245	54.806	31.243	398.369	184.452	- 9.600
4300	9.257	62.462	54.982	32.165	398.938	179.393	- 9.118
4400	9.334	62.676	55.154	33.094	399.514	174.344	- 8.656
4500	9.394	62.886	55.324	34.030	400.096	169.311	- 8.215
4600	9.455	63.093	55.490	34.972	400.685	164.015	- 7.793
4700	9.511	63.297	55.654	35.921	401.281	158.864	- 7.387
4800	9.564	63.496	55.816	36.875	401.882	153.698	- 6.998
4900	9.604	63.695	55.977	37.833	402.487	148.527	- 6.625
5000	9.641	63.890	56.131	38.795	403.095	143.355	- 6.265
5100	9.672	64.081	56.285	39.761	403.708	138.130	- 5.919
5200	9.696	64.269	56.437	40.729	404.323	132.920	- 5.586
5300	9.715	64.454	56.586	41.699	404.941	127.692	- 5.265
5400	9.724	64.634	56.732	42.672	405.560	122.447	- 4.957
5500	9.730	64.814	56.879	43.644	406.179	117.209	- 4.657
5600	9.729	64.990	57.022	44.617	406.798	111.942	- 4.369
5700	9.723	65.162	57.163	45.590	407.418	106.675	- 4.090
5800	9.711	65.331	57.303	46.562	408.037	101.391	- 3.821
5900	9.695	65.495	57.438	47.534	408.656	96.094	- 3.560
6000	9.674	65.659	57.576	48.501	409.275	90.806	- 3.303

Dec. 31, 1966

TUNGSTEN UNIPOSITIVE ION (W⁺)

(IDEAL GAS)

GFW = 183.8495

Ground State Configuration $5d_{1/2}$ $\Delta H_f^\circ = 387.139$ kcal/mol
 $S_{298.15}^\circ = 42.931$ gibbs/mol $\Delta H_f^{298.15} = 388.918$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	g_1	$\epsilon_1, \text{cm}^{-1}$	g_1	$\epsilon_1, \text{cm}^{-1}$	g_1
0	2	16553	10	26929	12
1518.8	4	17437	12	36185	2
3172.5	6	18001	10	39441	12
4716.3	8	18991	10	42256	18
6147.2	10	19071	10	44709	30
7420.4	6	19277	6	45522	6
8711.3	4	19404	6	46373	26
11301.1	6	19443	20	47397	14
13412.0	8	19837	10	48543	30
14857.2	10	[20000]	[30]	49176	28
8632.7	2	20040	8	50605	20
10592.5	4	20628	28	51443	38
13434.1	6	[21000]	[20]	52486	36
13173.4	2	[22000]	[20]	53323	34
14634.4	4	22187	40	54406	66
14967.8	6	23166	36	55342	20
15147.0	8	23921	36	56554	56
16234.8	6	25081	8	59910	194
16589.7	8	26189	18	63560	16

Heat of Formation.

The heat of formation is obtained by adding the heat of ionization at 0°K to the ΔH_f° W(g). The heat of ionization, 184.036 kcal (7.98 eV), is obtained from C. E. Moore, Natl. Bur. Std. Circular 467, Vol. III, Washington D. C. (1959).

Heat Capacity and Entropy.

The electronic energy levels are obtained from C. E. Moore, loc. cit. In the low lying configuration [Xe] $4f^{14}5d^5$ the F_2, G_2, F_2, H and S multiplets have not been observed. The total degeneracy of these levels (70) is split among three estimated levels of 20000, 21000, and 22000 cm^{-1} , obtained by analogy with Mo^+ . A realistic uncertainty in these levels would produce a maximum uncertainty of 0.03 gibbs/mol in the free energy function and 0.09 gibbs/mol in the entropy at 6000°K.

The enthalpy at 0°K is -1.487 kcal/mol.

T, °K	C _p ^a	gibbs/mol S ^b	-(G ^c -H ²⁹⁸)/T	H ^c -H ²⁹⁸ ΔH ^c	ΔG ^c	log K _p
0	.000	.000	INFINITE	- 1.321	.000	.000
100	6.466	3.352	14.443	- 1.109	.000	.000
200	5.754	6.946	9.862	.563	.000	.000
298	6.068	9.314	9.314	.000	.000	.000
300	6.097	9.352	9.314	.011	.000	.000
400	6.367	11.143	9.556	.634	.000	.000
500	6.642	12.593	10.023	1.285	.000	.000
600	6.919	13.428	10.557	1.963	.000	.000
700	7.197	14.516	11.103	2.669	.000	.000
800	7.475	15.895	11.642	3.402	.000	.000
900	7.753	16.791	12.165	4.164	.000	.000
1000	8.032	17.623	12.670	4.953	.000	.000
1100	8.311	18.401	13.156	5.770	.000	.000
1200	8.586	19.286	13.667	6.606	.000	.000
1300	8.867	20.444	14.167	8.160	.000	.000
1400	9.108	20.966	14.634	8.865	.000	.000
1500	9.219	21.461	15.073	9.581	.000	.000
1600	9.330	21.930	15.487	10.309	.000	.000
1700	9.441	22.378	15.879	11.047	.000	.000
1800	9.552	22.806	16.252	11.797	.000	.000
1900	9.663	23.218	16.608	12.558	.000	.000
2000	9.774	23.613	16.949	13.330	.000	.000
2100	9.885	24.005	17.275	14.113	.000	.000
2200	9.996	24.379	17.669	14.910	.000	.000
2300	10.107	24.745	18.071	15.710	.000	.000
2400	10.218	25.103	18.453	16.510	.000	.000
2500	10.329	25.453	18.818	17.310	.000	.000
2600	10.440	25.806	19.167	18.110	.000	.000
2700	10.551	26.158	19.502	18.910	.000	.000
2800	10.662	26.499	19.824	19.710	.000	.000
2900	10.773	26.829	20.133	20.510	.000	.000
3000	10.884	27.151	20.430	21.310	.000	.000
3100	10.995	27.463	20.718	22.110	.000	.000
3200	11.106	27.767	20.995	22.910	.000	.000
3300	11.217	28.063	21.263	23.710	.000	.000
3400	11.328	28.351	21.522	24.510	.000	.000
3500	11.439	28.634	21.774	25.310	.000	.000
3600	11.550	28.919	22.017	26.110	.000	.000
3700	11.661	29.206	22.254	26.910	.000	.000
3800	11.772	29.494	22.484	27.710	.000	.000
3900	11.883	29.782	22.707	28.510	.000	.000
4000	11.994	30.070	22.924	29.310	.000	.000
4100	12.105	30.358	23.136	30.110	.000	.000
4200	12.216	30.646	23.342	30.910	.000	.000
4300	12.327	30.934	23.543	31.710	.000	.000
4400	12.438	31.222	23.739	32.510	.000	.000
4500	12.549	31.510	23.931	33.310	.000	.000
4600	12.660	31.798	24.118	34.110	.000	.000
4700	12.771	32.086	24.301	34.910	.000	.000
4800	12.882	32.374	24.479	35.710	.000	.000
4900	12.993	32.662	24.652	36.510	.000	.000
5000	13.104	32.950	24.824	37.310	.000	.000
5100	13.215	33.238	25.000	38.110	.000	.000
5200	13.326	33.526	25.171	38.910	.000	.000
5300	13.437	33.814	25.342	39.710	.000	.000
5400	13.548	34.102	25.513	40.510	.000	.000
5500	13.659	34.390	25.684	41.310	.000	.000
5600	13.770	34.678	25.855	42.110	.000	.000
5700	13.881	34.966	26.026	42.910	.000	.000
5800	13.992	35.254	26.197	43.710	.000	.000
5900	14.103	35.542	26.368	44.510	.000	.000
6000	14.214	35.830	26.539	45.310	.000	.000

Dec. 31, 1960; June 30, 1961; Dec. 31, 1967

See crystal, liquid and monatomic gas for details.

0 to 1135°K Crystal alpha
1135. to 2125°K Crystal beta
2125. to 4776.9°K Liquid
4776.9 to 6000°K Ideal Monatomic gas

Zirconium, Alpha (Zr)
(Crystal)

ZIRCONIUM, ALPHA (Zr)

(CRYSTAL)

GFW = 91.22

GFW = 91.22

T, °K	Cp*	S° -(C°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal/mol	ΔHf°	ΔGf°	Log Kp
0	0.00	INFINITE	-1.321	0.00	0.00	0.00
100	6.046	3.35	-1.321	0.00	0.00	0.00
200	5.754	6.246	-1.583	0.00	0.00	0.00
298	6.058	9.314	0.00	0.00	0.00	0.00
300	6.097	9.352	0.11	0.00	0.00	0.00
400	6.267	11.43	0.556	0.00	0.00	0.00
500	6.342	12.593	1.295	0.00	0.00	0.00
600	6.919	13.828	1.963	0.00	0.00	0.00
700	7.197	14.916	2.669	0.00	0.00	0.00
800	7.475	15.995	3.402	0.00	0.00	0.00
900	7.753	16.41	4.164	0.00	0.00	0.00
1000	8.032	17.023	4.953	0.00	0.00	0.00
1100	8.311	18.401	5.770	0.00	0.00	0.00
1200	8.589	19.136	6.615	0.00	0.00	0.00
1300	8.868	19.835	7.488	0.00	0.00	0.00
1400	9.145	20.502	8.389	0.00	0.00	0.00
1500	9.423	21.143	9.317	0.00	0.00	0.00

S°_{298.15} = 9.314 ± 0.10 Gibbs/mol

T_f = 1135 ± 5°K

ΔHf°₀ = 0 kcal/mol

ΔHf°_{298.15} = 0 kcal/mol

ΔHc° = 0.96 kcal/mol

ΔHf°_{298.15} = 148.3 ± 3.5 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacities, 1.1 - 288.2°K, have been measured by Todd (1), Skinner (2), Eastermann (3), Wolcott (4), Burk (5), and Kneip (6). Values of Cp_{298.15} were reported as 6.19 and 6.01 Gibbs/mol by Todd (1) and Skinner (2), respectively. The difference (beginning at 150°K) is probably caused by different amounts of impurities (e.g. O₂, H₂, N₂) in the samples. Neither sample was analyzed for hydrogen and oxygen content. Small amounts of either of these impurities would cause important changes in Cp. Remasurement of Cp using a high purity sample is desirable to resolve the difference. Tentatively, we adopt smooth Cp values which are intermediate between those of Todd and Skinner in the temperature range 200 - 298°K. The curve at lower temperatures is based on references 1, 2, 4, 5 and 6. S°_{298.15} is derived from the adopted Cp based on S°₁₁₆ = 0.0008 eu.

Enthalpies have been measured using drop calorimetry by Jaeger (7), Coughlin (8), Skinner (9), Redmond (10), Adenstedt (11) and Douglas (13). Cp above 298°K has been measured by Scott (12) and Vollmer (15) using adiabatic calorimetry and by Klein (14) using pulse heating. The data lead to differences in Cp which are even greater than those noted at 298°K. Observed Cp's are lower than the adopted curve by roughly 3 to 6 per cent, but the observed enthalpies are generally higher by 0 to 10 per cent. Impurities are partly to blame but there also may be a systematic difference between the methods. The purest and best-characterized samples are those of Douglas (13) and Vollmer (15). Even the high-purity sample of Douglas gives H values which are abnormally high at 573°K, suggesting the presence of thermal effects of solid solution and precipitation due to a small amount of hydrogen in the sample (12).

The adopted Cp is based mainly on Douglas (13), but references (7, 8, 15) were also given some weight. Deviations of (13) from the adopted values range from +3.3 per cent at 573°K to +0.3 at 1123°K. Other deviations (each in order of increasing T) are 3 to 0 per cent (7), 1.3 to -1.7 per cent (8), -4 to -6 per cent (15), 5.4 to 1.7 per cent (9) and -1 to 9.5 per cent (10) in terms of enthalpy. Cp is extrapolated linearly above 1133°K.

Transition Data

See Zr(β) table for details.

Heat of Sublimation

ΔH°_{298.15} is calculated as the difference between ΔHf°_{298.15} for Zr(g) and Zr(α).

References

1. S. S. Todd, J. Am. Chem. Soc. **72**, 2914 (1950), 53.2 - 296.8°K.
2. G. B. Skinner and H. L. Johnston, J. Am. Chem. Soc. **73**, 4549 (1951), 14.4 - 298.2°K. Purity is atom per cent.
3. I. Eastermann, S. A. Friedberg and J. E. Goldman, Phys. Rev. **87**, 582 (1952), 1.8 - 4.2°K.
4. N. M. Wolcott, Phil. Mag. **2**, 1246 (1957), 1.2 - 20°K.
5. D. L. Burk, I. Eastermann and S. A. Friedberg, Z. Physik. Chem. **16**, 183 (1958), 20 - 200°K.
6. G. D. Kneip, Jr., J. O. Berterton, Jr., and J. O. Scarbrough, Phys. Rev. **130**, 1687 (1963), 1.1 - 4.5°K.
7. F. M. Jaeger and W. A. Veenstra, Rec. Trav. Chim. **53**, 917 (1934), 670.6 - 902.4°K.
8. J. P. Coughlin and E. G. King, J. Am. Chem. Soc. **72**, 2262 (1950), 390 - 1371°K.
9. G. B. Skinner, Ph.D. Thesis, The Ohio State University, 1951, 1102 - 1798°K.
10. R. F. Redmond and J. Lones, Oak Ridge Natl. Lab., Oak Ridge, Tenn., ORNL-1342, 1952, 404 - 1309°K.
11. H. K. Adenstedt, Trans. Am. Soc. Metals **44**, 949 (1952), 373.2°K.
12. J. L. Scott, Oak Ridge Natl. Lab., Oak Ridge, Tenn., ORNL-2328, 1957, 333 - 1213°K.
13. T. B. Douglas and A. C. Victor, J. Res. Natl. Bur. Std. **61**, 13 (1958), 67A, 403 (1963), 373 - 1173°K.
14. A. H. Klein and G. C. Danielson, Iowa State University, Iowa, WP-14281, 1962, 298 - 2118°K. Cp given graphically.
15. O. Vollmer, M. Braun and R. Kohlhaas, Z. Naturforsch. **22**, 833 (1967), 300 - 1700°K.

$$S_{298.15}^{\circ} = 11.152 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = 1.706 \text{ kcal/mol}$$

$$T_c = 1135 \pm 10^{\circ}\text{K}$$

$$\Delta H_c^{\circ} = 0.96 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 5.0 \pm 0.3 \text{ kcal/mol}$$

Heat of Formation

The heat of formation is obtained from $\Delta H_{298.15}^{\circ}(\alpha)$ by adding ΔH_c° and the difference between $H_{T_c}^{\circ}$ for Zr(α) and Zr(β).

Heat Capacity and Entropy

The enthalpies and Cp of Zr(β), at temperatures 1135 - 2118.2 °K, have been measured by many investigators (see Zr(α) table for details). The selected Cp values are based on the data reported by Douglass (1) and Skinner (2). Deviations from the adopted enthalpies are -1.4 to 0.8 per cent (1), -0.4 to 0.3 (2), and 0.2 to 3.0 per cent (3). Deviations of the measured Cp from the adopted values are -5 to -3 per cent (14) and about -6 per cent (10). The heat capacities below 1143.2 end above 1798 °K are estimated by linear extrapolation.

The entropy is obtained in a manner analogous to that of the heat of formation.

Transition Data

Zirconium has two crystal forms, i.e., the hexagonal-close-packed α -form and the cubic-body-centered β -form (3, 4, 5). The value and range of Tt for $\alpha \rightarrow \beta$ depends strongly on the kind and amount of impurities (5, 13). For example, nitrogen and oxygen increase Tt while hydrogen decreases it. The adopted value is Tt = 1135 $\pm$ 10 °K, although recent measurements using purer samples indicate a somewhat higher value. These are summarized below along with the data for ΔH_c° . The value $\Delta H_c^{\circ} = 0.96 \text{ kcal/mol}$ is derived from the adopted enthalpy and Cp data on Zr(α) and Zr(β).

Investigator	Tt, °K	ΔH_c° , kcal/mol	Purity, Percent	Method or Property Measured
3. Vogel (1931)	1135 $\pm$ 5	-	unavailable	cooling and dilatometric curves
7. Coughlin (1950)	1135*	0.920	97.85	drop calorimetry
5. Komar (1957)	1135*	-	unavailable	Electron microscope
8. Hertzicken (1962)	1135	0.712 $\pm$ 0.060	unavailable	differential calorimetry
1. Douglass (1958)	1136*	0.894	99.91	drop calorimetry
9. Dwez (1951)	1138 $\pm$ 10	-	unavailable	cooling curve
10. Klein (1962)	1138 $\pm$ 7	-	unavailable	resistivity
15. Kneip (1956)	1142 $\pm$ 4	-	$\sim$ 99.95	unavailable
2. Skinner (1951)	1143 $\pm$ 5	1.042	99.05	drop calorimetry
12. Scott (1967)	1143 $\pm$ 2	0.993 $\pm$ 0.025	unavailable	adiabatic calorimetry
13. Rudy (1965)	1145 $\pm$ 15	-	99.81	differential thermal analysis
11. Jaeger (1934)	<1150	-	unavailable	drop calorimetry
14. Vollmer (1967)	1155 $\pm$?	0.950	99.8	adiabatic calorimetry

* Adopted by the original authors.

Melting Data

See the Zr(β) table for details.

References

1. T. B. Douglass and A. C. Victor, *J. Res. Natl. Bur. Std.*, **51**, 13 (1958). The Tt value was evaluated from enthalpy data.
2. G. B. Skinner, Ph. D. Thesis, The Ohio State University, 1951. Sample purity is atom percent.
3. R. Vogel and W. Tonn, *Z. Anorg. Allgem. Chem.*, **202**, 292 (1931).
4. W. G. Burgers, *Physica*, **1**, 561 (1934).
5. A. P. Komar and V. N. Shrednik, *Fiz. Metal. Metalloved.*, **5**, No. 3, 452 (1957).
6. A. P. Komar and V. N. Shrednik, *Soviet Phys. JETP*, **5**, 127 (1957).
7. J. P. Coughlin and E. G. King, *J. Am. Chem. Soc.*, **72**, 2262 (1950). The Tt value.
8. S. D. Hertzicken and B. F. Siyuear, *Ukr. Fiz. Zhur.*, **7**, 339 (1962).
9. P. Dwez, *Trane. AIME*, **151**, 765 (1951).
10. A. H. Klein and G. C. Denileon, Iowa State University, NP-14281, 1962.
11. F. M. Jaeger and W. A. Veenstra, *Rec. Trav. Chim.*, **53**, 917 (1934).
12. J. L. Scott, Oak Ridge Natl. Lab. ORNL-1342, 1952 and ORNL-2226, 1957.
13. E. Rudy, D. P. Hermon and C. E. Brucki, Aerojet-General Corporation, AFML-TR-65-2, Part 1, Vol. II, 1965.
14. O. Vollmer, M. Braun and R. Kohlhaas, *Z. Naturforsch.*, **22**, 833 (1967).
15. G. D. Kneip, Jr., and J. O. Betterton, Jr., *J. Electrochem. Soc.*, **103**, 684 (1956).

Dec. 31, 1967

Zirconium (Zr)

(Liquid)

GFW = 91.22

T, °K	Cp	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0							
100							
200							
298	5.887	13.289	13.289	.000	6.351	5.166	- 3.787
300	5.889	13.325	13.289	.011	6.351	5.159	- 3.758
400	5.999	15.034	13.521	.805	6.352	4.466	- 2.005
500	6.110	16.385	13.763	1.211	6.277	4.361	- 1.915
600	6.221	17.509	14.463	1.827	6.215	4.007	- 1.460
700	6.332	18.476	14.969	2.455	6.137	3.645	- 1.138
800	6.443	19.329	15.462	3.094	6.043	3.295	- .900
900	6.554	20.076	15.935	3.740	5.938	2.956	- .739
1000	6.665	20.790	16.386	4.405	5.803	2.635	- .576
1100	6.776	21.431	16.816	5.077	5.658	2.325	- .462
1200	6.887	22.025	17.225	5.760	5.495	2.030	- .379
1300	6.997	22.581	17.616	6.454	5.314	1.767	- .314
1400	7.108	23.103	17.990	7.159	5.118	1.537	- .268
1500	7.219	23.595	18.349	7.879	4.909	1.337	- .230
1600	7.330	24.067	18.697	8.609	4.681	1.165	- .196
1700	7.441	24.517	19.034	9.359	4.435	.989	- .167
1800	7.552	24.944	19.359	10.129	4.173	.797	- .142
1900	7.663	25.349	19.677	10.919	3.890	.593	- .120
2000	7.774	25.733	19.977	11.729	3.580	.379	- .100
2100	7.885	26.097	20.261	12.559	3.247	.158	- .086
2200	7.996	26.442	20.530	13.409	2.895	.000	- .076
2300	8.107	26.767	20.782	14.279	2.525	.000	- .069
2400	8.218	27.075	21.019	15.169	2.140	.000	- .064
2500	8.329	27.367	21.238	16.079	1.743	.000	- .060
2600	8.440	27.644	21.441	17.009	1.337	.000	- .057
2700	8.551	27.907	21.629	17.959	.925	.000	- .054
2800	8.662	28.157	21.802	18.929	.509	.000	- .051
2900	8.773	28.394	21.961	19.919	.089	.000	- .048
3000	8.884	28.619	22.107	20.929	.000	.000	- .045
3100	8.995	28.832	22.241	21.959	.000	.000	- .042
3200	9.106	29.034	22.363	23.009	.000	.000	- .039
3300	9.217	29.226	22.475	24.079	.000	.000	- .036
3400	9.328	29.409	22.577	25.169	.000	.000	- .033
3500	9.439	29.583	22.669	26.279	.000	.000	- .030
3600	9.550	29.748	22.752	27.409	.000	.000	- .027
3700	9.661	29.904	22.827	28.559	.000	.000	- .024
3800	9.772	30.051	22.893	29.729	.000	.000	- .021
3900	9.883	30.189	22.950	30.919	.000	.000	- .018
4000	9.994	30.319	23.000	32.129	.000	.000	- .015
4100	10.105	30.441	23.035	33.359	.000	.000	- .012
4200	10.216	30.556	23.065	34.609	.000	.000	- .009
4300	10.327	30.663	23.091	35.879	.000	.000	- .006
4400	10.438	30.763	23.113	37.169	.000	.000	- .003
4500	10.549	30.857	23.131	38.479	.000	.000	- .000
4600	10.660	30.946	23.146	39.809	.000	.000	- .000
4700	10.771	31.031	23.158	41.159	.000	.000	- .000
4800	10.882	31.112	23.167	42.529	.000	.000	- .000
4900	10.993	31.189	23.173	43.919	.000	.000	- .000
5000	11.104	31.263	23.177	45.329	.000	.000	- .000
5100	11.215	31.334	23.178	46.759	.000	.000	- .000
5200	11.326	31.401	23.177	48.209	.000	.000	- .000
5300	11.437	31.464	23.173	49.679	.000	.000	- .000
5400	11.548	31.523	23.167	51.169	.000	.000	- .000
5500	11.659	31.578	23.158	52.679	.000	.000	- .000
5600	11.770	31.630	23.146	54.209	.000	.000	- .000
5700	11.881	31.679	23.131	55.759	.000	.000	- .000
5800	11.992	31.725	23.113	57.329	.000	.000	- .000
5900	12.103	31.768	23.091	58.919	.000	.000	- .000
6000	12.214	31.808	23.065	60.529	.000	.000	- .000

ZIRCONIUM (Zr)

(LIQUID)

GFW = 91.22

S°_{298.15} = [13.289] gibbs/mol

T_m = 2125 ± 5 °K

T_b = [4776.9] °K

ΔH_f°_{298.15} = [6.351] kcal/mol

ΔH_m° = 5.0 ± 0.4 kcal/mol

ΔH_v° = 141.13 kcal/mol

Heat of Formation

The heat of formation is obtained from ΔH_f°₂₉₈(β) by adding ΔH_m° and the difference between H°₂₁₂₅ - H°₂₉₈ for Zr(β) and Zr(L).

Heat Capacity and Entropy

A glass transition temperature at 1400°K is assumed. The heat capacities below 1400°K are taken from those for Zr(β). The Cp value above 1400°K is estimated by comparison with that of Zr(β) at T_m and assumed to be constant in the temperature range 1400 - 3500°K. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting point of Zr(β) has been determined by many investigators. The results reported show wide discrepancies, probably caused by the differences in purity of the samples used for determination. The T_m value adopted is obtained from Oriani and Jones. The other values of T_m reported are presented in the table below.

The adopted heat of melting was determined calorimetrically by V. P. Elyutin, M. A. Maurakh and G. M. Sverdlov, Izv. Vysshikh Uchebn. Zavedenii, Tsvertn. Met. 10, No. 2, 87 (1967). Zirconium samples from two different sources were melted in an Arc-crucible furnace. The crucible contained an insert of graphite which had a thick lining (presumably of zirconium carbide) in order to minimize carbonization of Zr(L). The molten Zr was poured through an opening in the bottom of the crucible into a calorimeter containing molten Mg as the calorimetric fluid. The method of calculating the value of ΔH_m° was described in detail by V. P. Elyutin, M. A. Maurakh, V. Y. Mishuk, and G. M. Sverdlov, Izv. Vysshikh Uchebn. Zavedenii, Tsvertn. Met. 10, 60 (1967). The authors estimated the uncertainty as about 7 percent in ΔH_m°.

Reference

- H. K. Adenstedt, Trans. Am. Soc. Metals 44, 949 (1952).
J. L. Scott, Oak Ridge Natl. Lab., Oak Ridge, Tenn., ORNL-2328, 1957.
R. A. Oriani and T. S. Jones, Rev. Sci. Instr. 23, 248 (1954).
D. K. Deardorff and E. T. Hayes, Trans. AIME 208, 509 (1956).
J. H. deBoer, Ind. Eng. Chem. 49, 1256 (1957); J. H. deBoer, and J. D. East, Z. Anorg. Allgem. Chem. 187, 193 (1930); and F. H. Jaeger and W. A. Veenstra, Rec. Trav. Chim. 53, 917 (1934).
R. V. Sara, J. Am. Ceram. Soc. 48, 243 (1965).
R. A. Oriani and T. S. Jones, Rev. Sci. Instr. 2, 248 (1954). This value is not adopted.
E. Rudy and S. Windisch, Aerojet-General Corporation, AFML-TR-65-2, Part I, Vol. VIII, January 1966.
E. Rudy, D. P. Harmon, and C. E. Bruki, Aerojet-General Corporation, AFML-TR-65-2, Part I, Vol. II, May 1965.

Vaporization Data

T_b is the temperature at which the Gibbs energy change (ΔG°) for the reaction Zr(L) = Zr(g) approaches zero. The difference between ΔH_f°(Zr, g) and ΔH_f°(Zr, l) at T_b is ΔH_v°.

Zirconium Unipositive Ion (Zr⁺)

GFW = 91.21945

ZIRCONIUM UNIPosITIVE ION (Zr⁺)

(IDEAL GAS)

Zr⁺

GFW = 91.21945

Ground State Configuration $4f_{7/2}^2$

$S_{298.15}^\circ = 43.864 \pm 0.01$ gibbs/mol

$\Delta H_{298.15}^\circ = 43.864 \pm 0.01$ kcal/mol

$\Delta H_{298.15}^\circ = 43.864 \pm 0.01$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i	$\epsilon_i, \text{cm}^{-1}$	g_i
0	4	15611.151	30
6	6	24311.416	46
783.44	8	30405.276	54
1322.91	10	31980.999	40
3003.126	18	34607.328	36
4080.140	20	37180.173	38
6466.284	26	38077.586	40
8624.116	36	40045.807	26
12983.250	40	41556.750	50

Heat of Formation

The heat of formation is calculated from the reaction $\text{Zr(g)} - \text{e}^-(\text{g}) = \text{Zr}^+(\text{g})$ with the JANAF auxiliary value for Zr(g) ; and an ionization potential = 6.84 eV or 157.737 kcal/mol, obtained from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. II, 1952 and Vol. III, 1958. The electronic levels above 2500 cm^{-1} are averaged. The $H^\circ - H_{298}^\circ$ value at 0°K is -1.786 kcal/mol.

Heat Capacity and Entropy

The electronic levels and quantum weights are taken from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. II, 1952 and Vol. III, 1958. The electronic levels above 2500 cm^{-1} are averaged. The $H^\circ - H_{298}^\circ$ value at 0°K is -1.786 kcal/mol.

T, °K	C_p°	$S^\circ - (C_p^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH°	ΔG°	Log K _p
0						
100	6.759	43.864	0.000	306.200	294.412	-215.810
200	6.760	43.864	0.013	306.211	294.339	-214.425
300	6.754	43.853	0.069	306.761	290.786	-158.611
400	6.757	43.830	0.186	307.278	286.121	-125.063
500	6.758	43.795	0.322	307.758	281.844	-102.662
600	6.758	43.755	0.487	308.200	277.488	-86.636
700	6.757	43.712	0.673	308.613	273.073	-74.600
800	6.754	43.666	0.879	308.996	268.607	-65.227
900	6.752	43.618	1.104	309.355	264.100	-57.719
1000	6.750	43.566	1.348	309.689	259.559	-51.570
1200	6.747	43.473	1.828	309.149	255.040	-46.449
1400	6.743	43.366	2.359	308.613	250.511	-42.115
1600	6.738	43.245	2.934	308.086	245.988	-38.394
1800	6.732	43.112	3.554	307.569	241.438	-35.165
2000	6.725	42.969	4.218	307.050	236.876	-32.335
2200	6.717	42.816	4.925	306.532	232.324	-29.835
2400	6.708	42.653	5.674	306.015	227.784	-27.609
2600	6.698	42.480	6.464	305.500	223.250	-25.615
2800	6.687	42.300	7.294	305.000	218.726	-23.818
3000	6.675	42.112	8.164	304.500	214.204	-22.190
3200	6.662	41.917	9.074	304.000	209.689	-20.726
3400	6.648	41.717	10.024	303.500	205.173	-19.393
3600	6.633	41.512	11.014	303.000	200.654	-18.170
3800	6.618	41.303	12.044	302.500	196.139	-17.043
4000	6.602	41.090	13.114	302.000	191.624	-16.002
4200	6.586	40.873	14.224	301.500	187.109	-15.036
4400	6.569	40.653	15.374	301.000	182.594	-14.138
4600	6.551	40.430	16.564	300.500	178.079	-13.302
4800	6.533	40.203	17.794	300.000	173.564	-12.520
5000	6.515	39.973	19.064	299.500	169.049	-11.787
5200	6.496	39.740	20.374	299.000	164.534	-11.100
5400	6.477	39.503	21.724	298.500	160.019	-10.453
5600	6.458	39.263	23.114	298.000	155.504	-9.844
5800	6.438	39.019	24.544	297.500	151.000	-9.269
6000	6.418	38.772	26.014	297.000	146.489	-8.725
6200	6.397	38.522	27.524	296.500	141.974	-8.210
6400	6.376	38.269	29.074	296.000	137.459	-7.721
6600	6.354	38.013	30.664	295.500	132.944	-7.257
6800	6.332	37.754	32.294	295.000	128.429	-6.816
7000	6.310	37.492	33.964	294.500	123.914	-6.395
7200	6.288	37.227	35.674	294.000	119.400	-6.000
7400	6.265	36.960	37.424	293.500	114.885	-5.625
7600	6.242	36.690	39.214	293.000	110.370	-5.265
7800	6.219	36.417	41.044	292.500	105.855	-4.925
8000	6.196	36.142	42.914	292.000	101.340	-4.595
8200	6.173	35.867	44.824	291.500	96.825	-4.275
8400	6.150	35.592	46.774	291.000	92.310	-3.965
8600	6.127	35.317	48.764	290.500	87.795	-3.665
8800	6.104	35.042	50.794	290.000	83.280	-3.375
9000	6.081	34.767	52.864	289.500	78.765	-3.095
9200	6.058	34.492	54.974	289.000	74.250	-2.825
9400	6.035	34.217	57.124	288.500	69.735	-2.565
9600	6.012	33.942	59.314	288.000	65.220	-2.315
9800	5.989	33.667	61.544	287.500	60.705	-2.075
10000	5.966	33.392	63.814	287.000	56.190	-1.845

Zr⁺

(Reference State) At. Wt. = 0.00054876

ELECTRON GAS (e⁻)

(REFERENCE STATE)

AT. WT. = 0.00054876

0 to 6000°K. IDEAL GAS

S_{298.15}⁰ = 4.988 cal. deg.⁻¹ mole⁻¹ΔH_f⁰ 298.15 = 0

T. °K.	C _p	S ⁰ - (F ⁰ -H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0							
100	4.968	4.989	4.989	.000	.000	.000	.000
200	4.968	5.019	4.989	.009	.000	.000	.000
300	4.968	5.049	5.006	.000	.000	.000	.000
400	4.968	5.079	5.022	.000	.000	.000	.000
500	4.968	5.109	5.035	.000	.000	.000	.000
600	4.968	5.139	5.048	.000	.000	.000	.000
700	4.968	5.169	5.061	.000	.000	.000	.000
800	4.968	5.199	5.074	.000	.000	.000	.000
900	4.968	5.229	5.087	.000	.000	.000	.000
1000	4.968	5.259	5.100	.000	.000	.000	.000
1100	4.968	5.289	5.113	.000	.000	.000	.000
1200	4.968	5.319	5.126	.000	.000	.000	.000
1300	4.968	5.349	5.139	.000	.000	.000	.000
1400	4.968	5.379	5.152	.000	.000	.000	.000
1500	4.968	5.409	5.165	.000	.000	.000	.000
1600	4.968	5.439	5.178	.000	.000	.000	.000
1700	4.968	5.469	5.191	.000	.000	.000	.000
1800	4.968	5.499	5.204	.000	.000	.000	.000
1900	4.968	5.529	5.217	.000	.000	.000	.000
2000	4.968	5.559	5.230	.000	.000	.000	.000
2100	4.968	5.589	5.243	.000	.000	.000	.000
2200	4.968	5.619	5.256	.000	.000	.000	.000
2300	4.968	5.649	5.269	.000	.000	.000	.000
2400	4.968	5.679	5.282	.000	.000	.000	.000
2500	4.968	5.709	5.295	.000	.000	.000	.000
2600	4.968	5.739	5.308	.000	.000	.000	.000
2700	4.968	5.769	5.321	.000	.000	.000	.000
2800	4.968	5.799	5.334	.000	.000	.000	.000
2900	4.968	5.829	5.347	.000	.000	.000	.000
3000	4.968	5.859	5.360	.000	.000	.000	.000
3100	4.968	5.889	5.373	.000	.000	.000	.000
3200	4.968	5.919	5.386	.000	.000	.000	.000
3300	4.968	5.949	5.399	.000	.000	.000	.000
3400	4.968	5.979	5.412	.000	.000	.000	.000
3500	4.968	6.009	5.425	.000	.000	.000	.000
3600	4.968	6.039	5.438	.000	.000	.000	.000
3700	4.968	6.069	5.451	.000	.000	.000	.000
3800	4.968	6.099	5.464	.000	.000	.000	.000
3900	4.968	6.129	5.477	.000	.000	.000	.000
4000	4.968	6.159	5.490	.000	.000	.000	.000
4100	4.968	6.189	5.503	.000	.000	.000	.000
4200	4.968	6.219	5.516	.000	.000	.000	.000
4300	4.968	6.249	5.529	.000	.000	.000	.000
4400	4.968	6.279	5.542	.000	.000	.000	.000
4500	4.968	6.309	5.555	.000	.000	.000	.000
4600	4.968	6.339	5.568	.000	.000	.000	.000
4700	4.968	6.369	5.581	.000	.000	.000	.000
4800	4.968	6.399	5.594	.000	.000	.000	.000
4900	4.968	6.429	5.607	.000	.000	.000	.000
5000	4.968	6.459	5.620	.000	.000	.000	.000
5100	4.968	6.489	5.633	.000	.000	.000	.000
5200	4.968	6.519	5.646	.000	.000	.000	.000
5300	4.968	6.549	5.659	.000	.000	.000	.000
5400	4.968	6.579	5.672	.000	.000	.000	.000
5500	4.968	6.609	5.685	.000	.000	.000	.000
5600	4.968	6.639	5.698	.000	.000	.000	.000
5700	4.968	6.669	5.711	.000	.000	.000	.000
5800	4.968	6.699	5.724	.000	.000	.000	.000
5900	4.968	6.729	5.737	.000	.000	.000	.000
6000	4.968	6.759	5.750	.000	.000	.000	.000

Mar. 31, 1965

Electronic Levels and Multiplicities

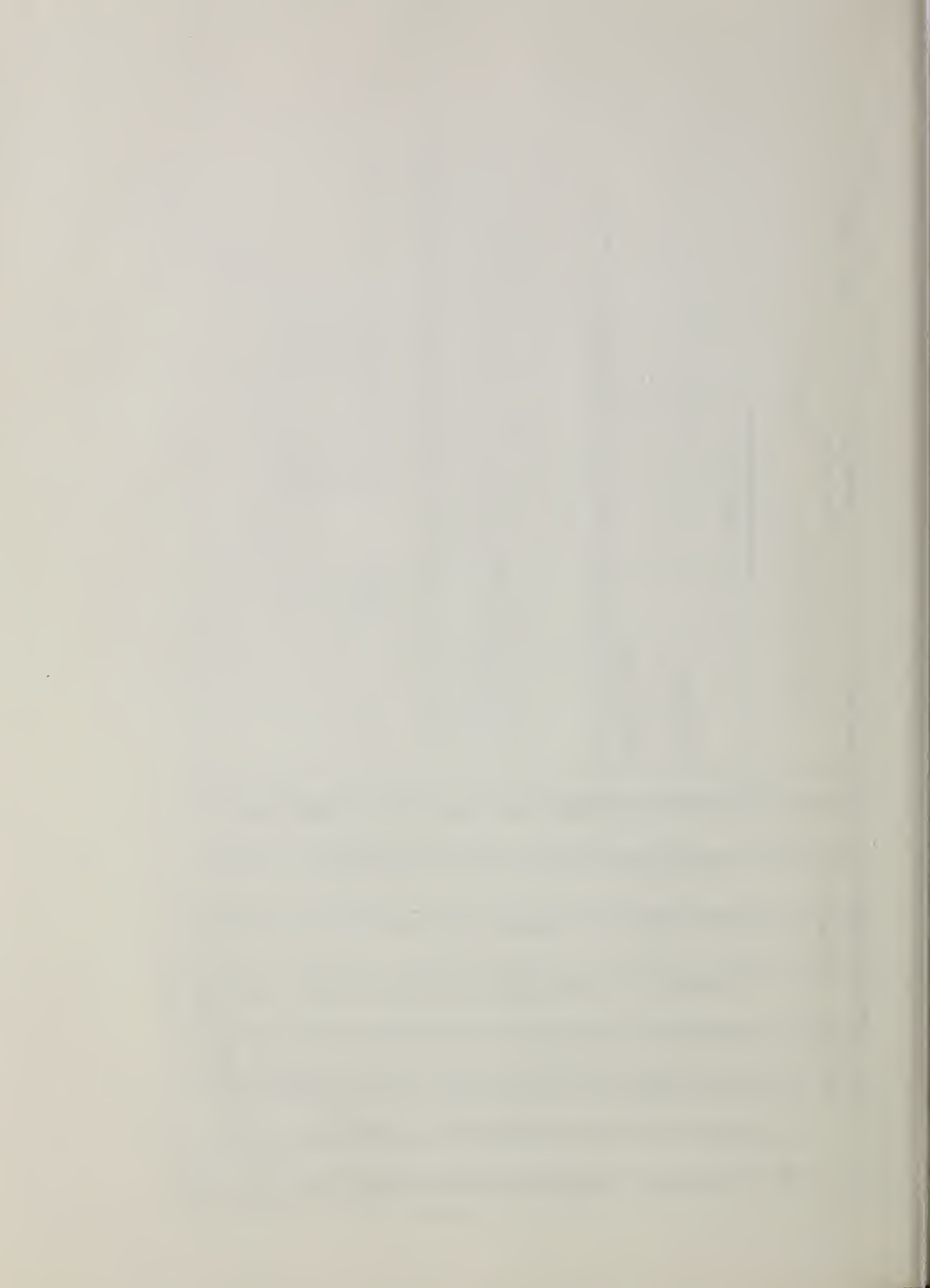
$$\frac{E_i \text{ cm.}^{-1}}{0} \cdot \frac{g_i}{2}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Calculated by assuming to be an ideal monatomic gas of mass 0.00054876 with two equivalent spin states. The enthalpy between 298 and 0°K. is 1.481 kcal. mole⁻¹ as for all unexcited monatomic gases.



Publications in the National Standard Reference Data Series National Bureau of Standards

You may use this listing as your order form by checking the proper box of the publication(s) you desire or by providing the full identification of the publication you wish to purchase. The full letter symbols with each publication number and full title of the publication and author must be given in your order, e.g. NSRDS-NBS-17, Tables of Molecular Vibrational Frequencies, Part 3, by T. Shimanouchi.

Pay for publications by check, money order, or Superintendent of Documents coupons or deposit account. Make checks and money orders payable to Superintendent of Documents. Foreign remittances should be made either

by international money order or draft on an American bank. Postage stamps are not acceptable.

No charge is made for postage to destinations in the United States and possessions, Canada, Mexico, and certain Central and South American countries. To other countries, payments for documents must cover postage. Therefore, one-fourth of the price of the publication should be added for postage.

Send your order together with remittance to Superintendent of Documents, Government Printing Office, Washington, D.C. 20402.

- ☐ NSRDS-NBS 1, National Standard Reference Data System—Plan of Operation, by E. L. Brady and M. B. Wallenstein, 1964 (15 cents), SD Catalog No. C13.48:1.
- ☐ NSRDS-NBS 2, Thermal Properties of Aqueous Uni-univalent Electrolytes, by V. B. Parker, 1965 (45 cents), SD Catalog No. C13.48:2.
- ☐ NSRDS-NBS 3, Sec. 1, Selected Tables of Atomic Spectra, Atomic Energy Levels and Multiplet Tables, Si II, Si III, Si IV, by C. E. Moore, 1965 (35 cents), SD Catalog No. C13.48:3/Sec.1.
- ☐ NSRDS-NBS 3, Sec. 2, Selected Tables of Atomic Spectra, Atomic Energy Levels and Multiplet Tables, Si I, by C. E. Moore, 1967 (20 cents), SD Catalog No. C13.48:3/Sec.2.
- ☐ NSRDS-NBS 3, Sec. 3, Selected Tables of Atomic Spectra, Atomic Energy Levels and Multiplet Tables, C I, C II, C III, C IV, C V, C VI, by C. E. Moore, 1970 (\$1), SD Catalog No. C13.48:3/Sec.3.
- ☐ NSRDS-NBS 3, Sec. 4, Selected Tables of Atomic Spectra, Atomic Energy Levels and Multiplet Tables, N IV, N VI, N VII, by C. E. Moore, (in press).
- ☐ NSRDS-NBS 4, Atomic Transition Probabilities, Volume I, Hydrogen Through Neon, by W. L. Wiese, M. W. Smith and B. M. Glennon, 1966 (\$2.50), SD Catalog No. C13.48:4/Vol.1.
- ☐ NSRDS-NBS 5, The Band Spectrum of Carbon Monoxide, by P. H. Krupenie, 1966 (70 cents), SD Catalog No. C13.48:5.
- ☐ NSRDS-NBS 6, Tables of Molecular Vibrational Frequencies, Part 1, by T. Shimanouchi, 1967 (40 cents), SD Catalog No. C13.48:6/Pt.1.
- ☐ NSRDS-NBS 7, High Temperature Properties and Decomposition of Inorganic Salts, Part 1, Sulfates, by K. H. Stern and E. L. Weise, 1966 (35 cents), SD Catalog No. C13.48:7/Pt.1.
- ☐ NSRDS-NBS 8, Thermal Conductivity of Selected Materials, by R. W. Powell, C. Y. Ho, and P. E. Liley, 1966 (\$1), PB189698
- ☐ NSRDS-NBS 9, Tables of Bimolecular Gas Reactions, by A. F. Trotman-Dickenson and G. S. Milne, 1967 (\$2), SD Catalog No. C13.48:9.
- ☐ NSRDS-NBS 10, Selected Values of Electric Dipole Moments for Molecules in the Gas Phase, by R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, 1967 (40 cents), SD Catalog No. C13.48:10.
- ☐ NSRDS-NBS 11, Tables of Molecular Vibrational Frequencies, Part 2, by T. Shimanouchi, 1967 (30 cents), SD Catalog No. C13.48:11/Pt.2.
- ☐ NSRDS-NBS 12, Tables for the Rigid Asymmetric Rotor: Transformation Coefficients from Symmetric to Asymmetric Bases and Expectation Values of P_2^2 , P_2^0 , and P_2^{-2} , by R. H. Schwendeman, 1968 (60 cents), SD Catalog No. 13.48:12.
- ☐ NSRDS-NBS 13, Hydrogenation of Ethylene on Metallic Catalysts, by J. Horiuti and K. Miyahara, 1968 (\$1), SD Catalog No. C13.48:13.
- ☐ NSRDS-NBS 14, X-Ray Wavelengths and X-Ray Atomic Energy Levels, by J. A. Bearden, 1967 (40 cents), SD Catalog No. C13.48:14.
- ☐ NSRDS-NBS 15, Molten Salts, Vol. 1, Electrical Conductance, Density, and Viscosity Data, by G. J. Janz, F. W. Dampier, G. R. Lakshminarayanan, P. K. Lorenz, and R. P. T. Tomkins, 1968 (\$3), SD Catalog No. C13.48:15/Vol.1.
- ☐ NSRDS-NBS 16, Thermal Conductivity of Selected Materials, Part 2, by C. Y. Ho, R. W. Powell, and P. E. Liley, 1968 (\$2), SD Catalog No. C13.48:16/Pt.2.
- ☐ NSRDS-NBS 17, Tables of Molecular Vibrational Frequencies, Part 3, by T. Shimanouchi, 1968 (30 cents), SD Catalog No. C13.48:17/Pt.3.
- ☐ NSRDS-NBS 18, Critical Analysis of the Heat-Capacity Data of the Literature and Evaluation of Thermodynamic Properties of Copper, Silver, and Gold From 0 to 300°K, by G. T. Furukawa, W. G. Saba, and M. L. Reilly, 1968 (40 cents), SD Catalog No. C13.48:18.
- ☐ NSRDS-NBS 19, Thermodynamic Properties of Ammonia as an Ideal Gas, by L. Haar, 1968 (20 cents), SD Catalog No. C13.48:19.
- ☐ NSRDS-NBS 20, Gas Phase Reaction Kinetics of Neutral Oxygen Species, by H. S. Johnston, 1968 (45 cents), SD Catalog No. C13.48:20.
- ☐ NSRDS-NBS 21, Kinetic Data on Gas Phase Unimolecular Reactions, by S. W. Benson and H. E. O'Neal, 1970 (\$7), SD Catalog No. C13.48:21.
- ☐ NSRDS-NBS 22, Atomic Transition Probabilities, Vol II, Sodium Through Calcium, A Critical Data Compilation, by W. L. Wiese, M. W. Smith, and B. M. Miles, 1969 (\$4.50), SD Catalog No. C13.48:22/Vol.II.
- ☐ NSRDS-NBS 23, Partial Grottrian Diagrams of Astrophysical Interest, by C. E. Moore and P. W. Merrill, 1968 (55 cents), SD Catalog No. C13.48:23.
- ☐ NSRDS-NBS 24, Theoretical Mean Activity Coefficients of Strong Electrolytes in Aqueous Solutions from 0 to 100° C, by Walter J. Hamer, 1968 (\$4.25), SD Catalog No. C13.48:24.
- ☐ NSRDS-NBS 25, Electron Impact Excitation of Atoms, by B. L. Moiseiwitsch and S. J. Smith, 1968 (\$2), SD Catalog No. C13.48:25.
- ☐ NSRDS-NBS 26, Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions, by J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, 1969 (\$4), SD Catalog No. C13.48:26.
- ☐ NSRDS-NBS 27, Thermodynamic Properties of Argon from the Triple Point to 300 K at Pressures to 1000 Atmospheres, by A. L. Gosman, R. D. McCarty, and J. G. Hust, 1969 (\$1.25), SD Catalog No. C13.48:27.
- ☐ NSRDS-NBS 28, Molten Salts, Vol. 2, Section 1, Electrochemistry of Molten Salts: Gibbs Free Energies and Excess Free Energies From Equilibrium-Type Cells, by G. J. Janz and C. G. M. Dijkhuis. Section 2, Surface Tension Data, by G. J. Janz, G. R. Lakshminarayanan, R. P. T. Tomkins, and J. Wong, 1969 (\$2.75), SD Catalog No. C13.48:28/Vol.2.
- ☐ NSRDS-NBS 29, Photon Cross Sections, Attenuation Coefficients and Energy Absorption Coefficients From 10 keV to 100 GeV, by J. H. Hubbell, 1969 (75 cents), SD Catalog No. C13.48:29.
- ☐ NSRDS-NBS 30, High Temperature Properties and Decomposition of Inorganic Salts, Part 2, Carbonates, by K. H. Stern and E. L. Weise, 1969 (45 cents), SD Catalog No. C13.48:30.
- ☐ NSRDS-NBS 31, Bond Dissociation Energies in Simple Molecules, by B. deB. Darwent, 1970 (55 cents), SD Catalog No. C13.48:31.
- ☐ NSRDS-NBS 32, Phase Behavior in Binary and Multicomponent Systems at Elevated Pressures: *n*-Pentane and Methane-*n*-Pentane, by V. M. Berry and B. H. Sage, 1970 (70 cents), SD Catalog No. C13.48:32.
- ☐ NSRDS-NBS 33, Electrolytic Conductance and the Conductances of the Halogen Acids in Water, by W. J. Hamer and H. J. DeWane, 1970 (50 cents), SD Catalog No. C13.48:33.
- ☐ NSRDS-NBS 34, Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra, by C. E. Moore, 1970 (75 cents), SD Catalog No. C13.48:34.

**Announcement of New Publications in
National Standard Reference Data Series**

Superintendent of Documents,
Government Printing Office,
Washington, D.C. 20402

Dear Sir:

Please add my name to the announcement list of new publications to be issued in the series: National Standard Reference Data Series—National Bureau of Standards.

Name_____

Company_____

Address_____

City_____ State_____ Zip Code_____

(Notification key N-337)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET		1. PUBLICATION OR REPORT NO. NSRDS-NBS 37	2. Gov't Accession No.	3. Recipient's Accession No.
4. TITLE AND SUBTITLE JANAF Thermochemical Tables, Second Edition			5. Publication Date	
			6. Performing Organization Code	
7. AUTHOR(S) D. R. Stull, H. Prophet, et al.			8. Performing Organization	
9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234			10. Project/Task/Work Unit No.	
			11. Contract/Grant No. F04611-67-C-0009 F04611-70-0028	
12. Sponsoring Organization Name and Address The Thermal Research Laboratory Dow Chemical Company Midland, Michigan			13. Type of Report & Period Covered NA	
			14. Sponsoring Agency Code	
15. SUPPLEMENTARY NOTES Superseding PB168-370 and Addenda 1, 2, and 3				
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.) This monograph is the second edition of the JANAF Thermochemical Tables. It contains thermodynamic properties for some 1099 chemical species. The following properties are tabulated as functions of temperatures: C_p° , S° , $(F^\circ - H_{298}^\circ)/T$, $H^\circ - H_{298}^\circ$, ΔH_f° and Log Kp.				
17. KEY WORDS (Alphabetical order, separated by semicolons) Evaluated Data; Thermal Functions; Thermodynamic Properties of Materials; Thermodynamics.				
18. AVAILABILITY STATEMENT ☒ UNLIMITED. ☐ FOR OFFICIAL DISTRIBUTION. DO NOT RELEASE TO NTIS.		19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED	21. NO. OF PAGES 1141	
		20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED	22. Price \$9.75	

