NATIONAL BUREAU OF STANDARDS REPORT

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THE ENTHALPIES OF HYDROLYSIS OF ARSENIOUS OXIDE AND
ARSENIC TRICHLORIDE IN 1N-SODIUM HYDROXIDE:
THE ENTHALPY OF FORMATION OF ARSENIC TRICHLORIDE

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.
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THE ENTHALPIES OF HYDROLYSIS OF ARSENIOUS OXIDE AND ARSENIC TRICHLORIDE IN 1N-SODIUM HYDROXIDE: THE ENTHALPY OF FORMATION OF ARSENIC TRICHLORIDE

By

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ABSTRACT

The heats of hydrolysis in 1N NaOH were measured for three forms of $As_2O_3(c)$ and for $AsCl_3(\ell)$. These were found to be:

As_2O_3(c,octahedral) $\Delta H = -43.985\pm0.157$ kJ·mol^{-1}(-10.513 ± 0.038 kcal·mol^{-1})

As_2O_3(c,monoclinic) $\Delta H = -45.990\pm0.073$ kJ·mol^{-1}(-10.992 ± 0.017 kcal·mol^{-1})

As_2O_3(vitreous) $\Delta H = -63.957\pm0.222$ kJ·mol^{-1}(-15.286 ± 0.053 kcal·mol^{-1})

$AsCl_3(\ell)$ $\Delta H = -297.533\pm0.274$ kJ·mol^{-1}(-71.112 ± 0.065 kcal·mol^{-1})

The heat of formation of $AsCl_3$ was determined from direct chlorination of metallic arsenic to be; $\Delta Hf_{298.15} = -305.222\pm1.874$ kJ.mol (-72.950 ± 0.448 kcal·mol).

From these data a value for the heat of formation of As_2O_3 (c,octahedral) is derived, $\Delta Hf_{298.15} = -658.416\pm3.790$ kJ·mol^{-1} (-157.365 ± 0.906 kcal·mol^{-1}) and a value for the heat of transition As_2O_3(c,monoclinic) $\rightarrow As_2O_3$(c,octahedral), $\Delta H = +2.005\pm0.173$ kJ·mol^{-1}($+0.479\pm0.041$ kcal·mol^{-1}).

INTRODUCTION

The thermochemistry of every element revolves around certain so-called "key" compounds. The reliability of the total structure of thermodynamic values assigned to the family of compounds of an element depends greatly upon the accuracy of the values assigned to the key compounds. A key compound of the element arsenic is As_2O_3(c,octahedral).

The cell measurements of R. Schumann [1], and of Kirschning and Plieth [2], the specific heat measurements of C. T. Anderson [3], and the solubility measurements of J. Thomsen [4], of Stranski, Plieth and Zoll [5], and of Schulman and Schumb [6] were considered by NBS in selecting "best values" [7] for As_2O_3 and $AsCl_3$ heats of formation. These investigations were all performed prior to 1958.

In more recent years a series of investigations by Mortimer and Beezer [8,9] have questioned the NBS value for As_2O_3. Their work was done with 2N NaOH and followed the scheme:

$$As(c) + 3/2Br_2(g) \rightarrow AsBr_3(\ell)$$

$$AsBr_3(\ell) + 4NaOH(aq) \rightarrow NaAsO_2(aq) + 3NaBr(aq) + 2H_2O(\ell)$$

$$As_2O_3(c,octa) + 2NaOH(aq) \rightarrow 2NaAsO_2(aq) + H_2O(\ell)$$
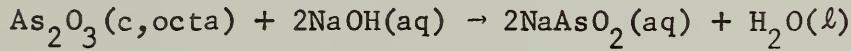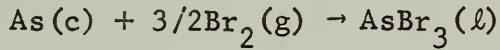
As will be seen later, this is the route used in this present investigation; substituting Cl_2 and $AsCl_3$ for Br_2 and $AsBr_3$ used above.

Four reactions were used in the course of these investigations:

1.a. As_2O_3(c,octa.) + 2NaOH(aq) → 2NaAsO_2(aq) + H_2O(ℓ)

   b. As_2O_3(c,mono.) + 2NaOH(aq) → 2NaAsO_2(aq) + H_2O(ℓ)

   c. As_2O_3(vitreous) + 2NaOH(aq) → 2NaAsO_2(aq) + H_2O(ℓ)

2. $AsCl_3(\ell) + 4NaOH(aq) \rightarrow NaAsO_2(aq) + 3NaCl(aq) + 2H_2O(\ell)$

3. $3NaCl(c) + NaAsO_2(aq) \rightarrow NaAsO_2(aq) + 3NaCl(aq)$

4. $As(c,\alpha) + 3/2Cl_2(g) \rightarrow AsCl_3(\ell)$
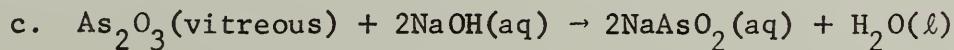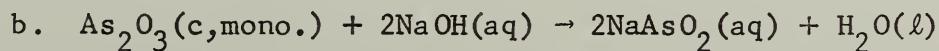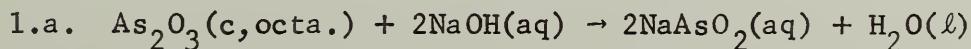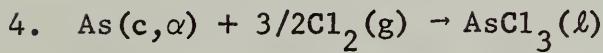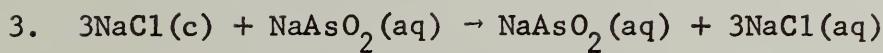
Equations 1b and 1c, when used in conjunction with 1a, allow an evaluation of the heats of transition between the various solid forms of As_2O_3. However, equation 1a is the one used for all other calculations.

MATERIALS

Arsenic: metallic arsenic, identified by Fisher Scientific Co. as

"purified" was used. Analysis in this laboratory indicated a

purity > 99.8%.

Arsenious oxide: samples of arsenolite, As_2O_3(c,octahedral), of

claudetite, As_2O_3(c,monoclinic), and of the vitreous

oxide, As_2O_3(amorp.) were supplied by A. Bestul and

S. Chang of NBS [10]

Chlorine: chlorine gas with an assay value of 99.85% was obtained from

The Matheson Co., Inc.

Sodium chloride
Sodium hydroxide: from Baker Chemical Co., Reagent Grade. The sodium

hydroxide solutions were prepared carbonate free and

stored protectively from CO_2.

EXPERIMENTAL PROCEDURES

These investigations required two separate calorimetric assemblies.
one for the solution reactions (Eq. 1,2,3) and one for the formation
reaction (Eq. 4)

In each instance the controlled temperature water bath was the same.
The temperature was controlled to ±0.002°C by a system consisting of a
resistance bridge with a nickel sensing element as one arm, a D.C.
null detector and a current-adjusting type (C.A.T.) control unit. The
power was supplied by an audio-amplifier to a 126 Ω heat coil.

The calorimeter vessel used in the solution experiments was described in an earlier work by Johnson, Gilliland and Prosen [11]. The solution calorimetric vessel was placed directly into the controlled temperature water bath. Temperature measurements were made on the solution within the vessel.

For the heat of formation experiments the reaction vessel consisted of a closed-end glass tube (approx. 17mm dia.) with a 6mm side-arm approximately one inch from the bottom. The side-arm leads directly to the outside of the system and serves as a means of ingress for the gaseous reactant. The open end of the vessel is a 19/22 standard taper (inner part). The cap for the vessel is a 19/22 standard taper (outer part) leading through a succession of coils and terminating outside of the system. A drainage bulb is sealed onto the lowest of the coils to facilitate the collection of the liquid products. A small glass wool sample support plug sits in the vessel just above the side-arm. The exit end of the coils is fastened to a series of gas scrubbers containing alkali.

The heat-of-formation reaction vessel was placed in a copper calorimeter can (approx. 2000 cm^3) which was suspended within a closed submersible container. In usage the entire system is submerged in the water bath. The calorimeter can is filled with distilled water and temperature measurements are made on the water in the calorimeter can. A 170 Ω immersion heater was used for the electrical calibration for these reactions.

All samples, with the exception of the metallic arsenic, were sealed off in pre-weighed soft glass bulbs. The sealed bulb and sample were then weighed along with the excess glass tip. The difference in weights was

taken as the sample weight which was corrected to "in vacuo" weight. Weighing was done on an analytical balance using NBS calibrated brass weights. The As_2O_3 and NaCl were poured directly into the bulbs. The $AsCl_3$ was vacuum distilled into the bulbs from a break-off tip ampoule. The metallic arsenic was weighed directly into the reaction vessel using a Mettler single-pan balance. All weighings were to ±0.01 mg.

Each experiment consisted of an electrical calibration followed immediately by the chemical reaction. The sequence of events was: an initial rating period, an electrical heating period, a middle rating period (which served both as the final rating period for the calibration and the initial rating period for the reaction), a chemical reaction period, and a final rating period.

The rating periods were of twelve minute duration, the electrical heating periods thirty minutes (during ten of which power was being introduced), and the chemical heating periods from thirty to sixty minutes.

At the appropriate time after the middle rating period, the hydrolysis reactions were initiated by depressing the bulb crusher. In order to insure complete breakage the rod was passed entirely through the sample holder two or three times. It was then withdrawn to the upper boundary of the holder to prevent interference with the mixing of sample and solvent.

Prior to the first rating period in the $AsCl_3$ formation experiments, the vessel was flushed for approximately 5 minutes with He. This was then diverted to a by-pass so that the rating was done with an internally static atmosphere. The Cl_2 was introduced into the line near the end of the middle rating period. The rate of flow of the gas mixture was adjusted while flowing through the by-pass.

The reaction is quite spontaneous. At the desired time the flow of the gas mixture is turned from the by-pass to the vessel. After approximately 2-4 minutes the Cl_2 was shut off and the vessel was flushed with He for 10 minutes. This was then shut off also, so that the final rating period could be taken with a static atmosphere as were the previous two.

Temperature measurements were made using a 25 Ω platinum resistance thermometer in conjunction with an L & N G-2 Mueller Resistance Bridge and an L & N Microvolt Indicating Amplifier which served as a galvanometer. In the heat of formation experiments the galvanometer output was fed into an M-H Brown Recorder.

These measurements were made at two-minute intervals during the rating periods and at one-minute intervals during the heating periods. For the rating periods, a galvanometer reading is taken 5 seconds before the minute. The thermometer current is then reversed and a second reading is taken 5 seconds after the minute. In the experiments using the recorder, these intervals were increased to 10 seconds before and after. The readings during the heating period were taken with no current reversal.

Power for the electrical heating came from a Lambda Regulated Power Supply which was fed by a Sola Harmonic Neutralized Constant Voltage Transformer.

Power measurements for the As_2O_3 experiments were made using a White Double Potentiometer (10^4-10^1 μv) in conjunction with the L & N Microvolt Indicating Amplifier as galvanometer. In all other experiments the White Potentiometer was replaced with a Wenner Potentiometer (10^4-10^0 μV). This afforded an increase in resolution by a factor of ten, but necessitated a manual switching for readings of e_e, the voltage readings for calculation of the voltage drop across the heater, and e_i, the voltage readings for

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calculation of the current through the heater. The e_i readings were made across a 0.1 Ω standard resistor, the e_e readings were made across a 10 Ω standard resistor which was in series with a 10^4 Ω standard resistor. This 10010 Ω system was in parallel with the heater. (See sketch).

The readings were made alternately, beginning with e_e, at 30-second intervals, for a period of ten minutes. This gave eleven e_e readings and ten e_i readings. Their respective averages were used in the computations. The observed values were corrected not only for potentiometer zero and calibration corrections, but also for the variation of the indicated emf from the true emf.

The products of the $AsCl_3$ reactions (Eq. 2,4) were titrated with standard iodine solution to determined the As^{+3} involved. Products from Eq. 4 experiments were first reduced with hydrazine sulphate as described by Morries [12].

Analysis of the products of the early $AsCl_3$ (Eq. 2) hydrolysis experiments was not made immediately following the experiment. These gave results that were appreciably low in comparison with the results obtained when analysis immediately followed the experiment. (See Table 6). Because of this, the original mass of sample was used for all calculations in the $AsCl_3$ hydrolysis series.

Analyses of the products of Eq. 4 experiments were used to determine the amount of As used in the reaction.
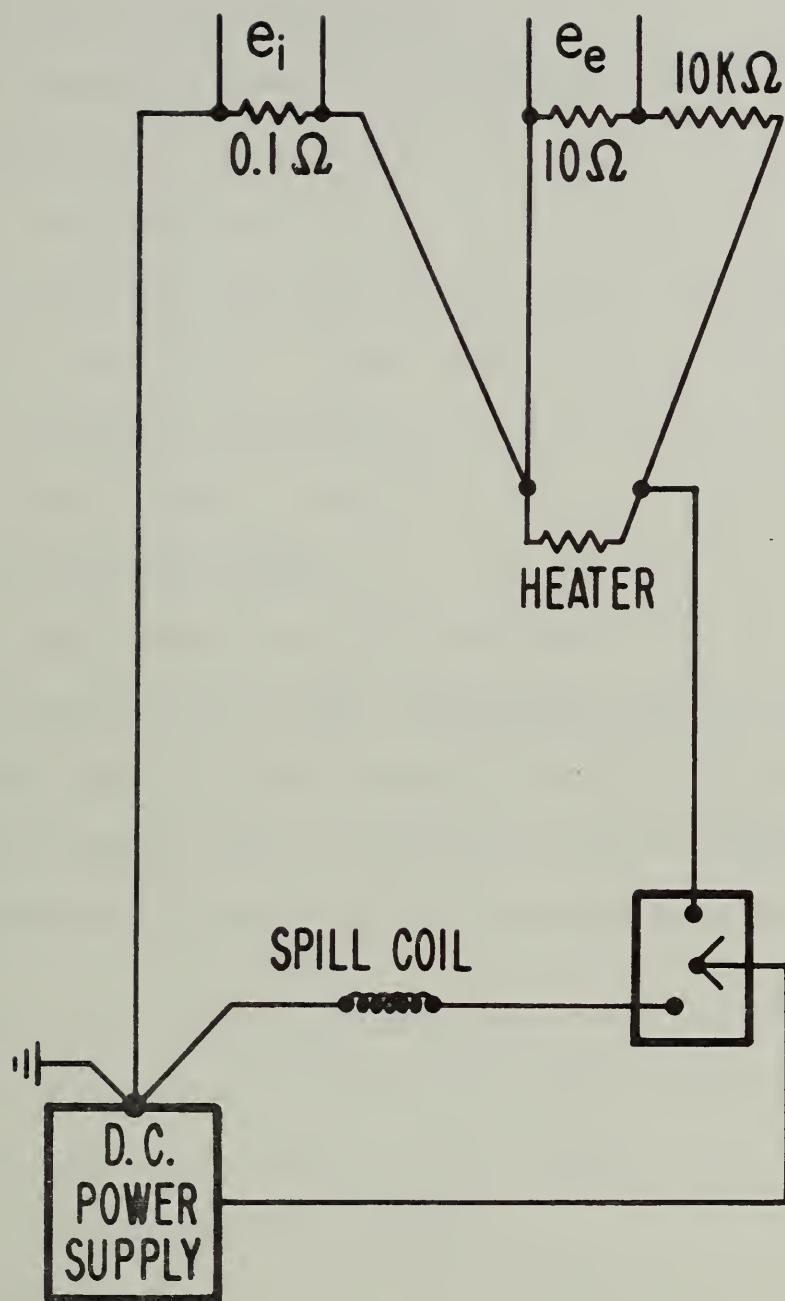
Sketch 1

In Tables 1, 2, 3, and 4 the column headings have the following meanings:

M_s - the mass of sample as weighed

E_s' - the energy equivalent of the system as determined by electrical calibration

R_m - the mean temperature

$E_{s_{corr}}$ - the energy equivalent of the system at the mean temperature of the reaction; E_s' + Temp. Coeff. $(R_{m_{react}} - R_{m_{calib}})$

ΔR_c - the corrected temperature rise of the reaction

Q' - the heat evolved by the reaction; $E_{s_{corr}}$ x ΔR_c

M.W. - the molecular weight

R_f - the final temperature of the reaction

ΔT - the variance of the final temperature from 25°C; $R_{25} - R_f$

$Corr_1$ - the correction for temperature of the heat evolution; ΔT x Δc_p

$\Delta H_{25}'$ - the observed heat of reaction at 25°C; $(\dfrac{Q' \text{ x M.W.}}{M_s}) - corr_1$

ΔH_{25} - the heat of reaction at 25°C adjusted for dilution effects.

Table 3 has the following additional designations:

m_1 - the arsenic from analysis of the liquid product

m_2 - the arsenic from analysis of the gaseous product

m_a - the total arsenic from analysis

r - the ratio M_s/m_a

m_g - the adjusted mass of arsenic appearing as $AsCl_3(g)$; $(r$ x $m_2)/$M.W. (arsenic)

$Corr_2$ - the correction to the observed heat for the vaporization of part of the product; $(m_2/$M.W. (arsenic)$)$ x ΔH_{vap}

Q - the observed heat evolved plus the vaporization correction;

$$(E_s \times \Delta R_c) + [(m_2/M.W.) \times \Delta H_{vap}]$$

The following constants were used in calculating:

Es temperature coefficient

Table 1	364.705	$J \cdot \Omega^{-2}$
Table 2	364.705	
Table 3	630.	
Table 4	100.	for H_2O
	250.	for $As_2O_3(aq)$

$\overline{\Delta c}p$ Reaction

Table 1	0.757	$KJ \cdot mol\Omega^{-1}$
Table 2	-2.341	
Table 3	0.374	
Table 4	negligible	

$R_{25} = 0.503780$

In Table 1, the A, C, and V following experiment designations indicate, respectively, the octahedral, monoclinic, and vitreous forms of As_2O_3.

The change of energy equivalent with temperature was calculated from data obtained in Expts. 2 and 3 of the $AsCl_3$ hydrolysis. This value was also used for the As_2O_3 experiments.

The value for Δcp was calculated from data obtained in Expt. 4A of the As_2O_3 series and Expts. 9 and 10 of the $AsCl_3$ series. The equation used was:

$$\frac{(-Q_F) - (-Q_I)}{R_F - R_I} = \Delta cp$$

where Q_F is calculated using the calibration preceding the reaction and Q_I is calculated using the calibration following the reaction. Similar calculations were made for the solution of NaCl in $(As_2O_3 + NaOH)$. See Table 4.

Table 1

Heat of Solution of As_2O_3 in $1N$ $NaOH$

	M_s	E'_s	R_m Calib.	R_m React.	$E_{s\ corr}$	ΔR_c	Q'
	g	$J \cdot \Omega^{-1}$	Ω	Ω	$J \cdot \Omega^{-1}$	Ω	J
1A	4.34296	20808.390	0.420383	0.466808	20825.321	0.046233	962.817
2A	3.53898	20817.776	0.454094	0.565559	20858.428	0.037787	788.177
3A	3.50111	20813.823	0.444080	0.548726	20851.988	0.037124	774.109
4A	3.84889	20795.591	0.355218	0.472916	20838.516	0.041042	855.254
1C	2.93445	20806.795	0.428834	0.546354	20849.655	0.032592	679.532
2C	2.83046	20807.966	0.419690	0.536971	20850.739	0.031378	654.254
1V	3.67722	20816.929	0.417244	0.539732	20861.601	0.056964	1188.360
2V	3.71024	20804.717	0.407038	0.533878	20850.976	0.057541	1199.786
3V	3.98752	20812.230	0.401812	0.530130	20859.028	0.061505	1282.935

	$\dfrac{Q' \times M.W.}{M_s}$	R_F	ΔT	$Corr_1$	$\Delta H'_{25}$	ΔH_{25}	
	$KJ \cdot mol^{-1}$	Ω	Ω	$KJ \cdot mol^{-1}$	$KJ \cdot mol^{-1}$	$KJ \cdot mol^{-1}$	
1A	43.861	0.496771	0.007009	0.005	43.855	43.855	
2A	44.062	0.590056	-0.086276	-0.065	44.127	44.204	
3A	43.744	0.573244	-0.069464	-0.053	43.797	43.879	
4A	43.962	0.500160	0.003620	0.003	43.959	44.003	
						ave = 43.985	± 0.157
1C	45.814	0.568474	-0.064694	-0.049	45.863	46.027	
2C	45.731	0.558582	-0.054802	-0.041	45.772	45.952	
						ave = 45.990	± 0.073
1V	63.936	0.574038	-0.070258	-0.053	63.989	64.050	
2V	63.976	0.571842	-0.068062	-0.052	64.028	64.086	
3V	63.653	0.569800	-0.066020	-0.050	63.703	63.735	
						ave = 63.957	± 0.222

Table 2

Heat of Solution of $AsCl_3(\ell)$ in 1N NaOH

	M_s	E'_s	R_m Calib.	React.	$E_{s\,corr}$	ΔR_c	Q'
	g	$J \cdot \Omega^{-1}$	Ω	Ω	$J \cdot \Omega^{-1}$	Ω	J
1	2.56649	20799.786	0.342808	0.505472	20859.110	0.187816	3917.675
2	1.72883	20834.899	0.410100	0.522742	20875.980	0.132146	2758.677
3	3.26580	20814.934	0.398788	0.568840	20876.953	0.249239	5203.351
4	2.64335	20756.285	0.306010	0.457174	20811.415	0.202093	4205.841
5	1.34298	20798.222	0.418136	0.533256	20840.207	0.102468	2135.454
6	2.98697	20738.442	0.387590	0.555626	20799.726	0.228066	4743.710
7	1.21587	20816.435	0.422838	0.534436	20857.135	0.093496	1950.059
8	0.67854	20723.558	0.387260	0.479845	20857.234	0.052613	1092.100
9	2.59940	20804.594	0.334406	0.541312	20880.054	0.199422	4163.942
10	2.43583	20847.861	0.343832	0.543699	20920.753	0.186238	3896.239

	$\dfrac{Q' \times M.W.}{M_s}$	R_F	ΔT	$Corr_1$	$\Delta H'_{25}$	ΔH_{25}
	$KJ \cdot mol^{-1}$	Ω	Ω	$KJ \cdot mol^{-1}$	$KJ \cdot mol^{-1}$	$KJ \cdot mol^{-1}$
1	276.720	0.600056	-0.096276	+0.224	276.496	
2	289.268	0.590361	-0.086581	+0.203	289.065	290.017
3	288.832	0.693362	-0.189582	+0.444	288.388	288.971
4	288.436	0.560072	-0.056292	+0.132	288.304	288.985
5	288.252	0.587321	-0.083541	+0.196	288.056	288.266
6	287.898	0.671592	-0.167812	+0.393	287.505	287.689
7	290.745	0.585350	-0.081570	+0.191	290.554	290.766
8	291.768	0.510421	-0.006641	+0.016	291.753	291.998
9	290.391	0.645868	-0.142088	+0.333	290.058	290.560
10	289.968	0.641914	-0.138134	+0.323	289.645	290.171

ave = 289.714 ± 0.902

Table 3

$$As(c) + 3/2\ Cl_2(g) \rightarrow AsCl_3(\ell)$$
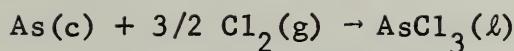
Exp.	M_s g	m_1 g	m_2 g	m_a g	r	m_g moles
2	1.31200	0.43040	0.77472	1.20512	1.088688	0.0112575
4	1.87233	0.94738	0.91924	1.86662	1.003059	0.0123069
5	1.92053	1.65088	0.33768	1.98856	0.965789	0.0043530
8	2.09335	1.89653	0.65373	2.55026	0.820838	0.0071623
9	2.28166	1.60196	0.96670	2.56866	0.888269	0.0114612
10	1.95554	1.34002	0.52719	1.86721	1.047306	0.0073694
11	1.84983	1.73716	0.34206	2.07922	0.889675	0.0040618
13	2.03404	1.73007	0.27121	2.00128	1.016370	0.0036792
14	2.36237	2.01723	0.34389	2.36112	1.000529	0.0045924

Exp.	R_m Calib. Ω	R_m React. Ω	E_s' $J \cdot \Omega^{-1}$	$E_{s\ corr}$ $J \cdot \Omega^{-1}$	ΔR_c Ω	Q' J
2	0.404986	0.547674	89412.052	89501.945	0.050202	4493.177
4	0.485807	0.636473	89567.836	89662.756	0.079896	7163.696
5	0.492601	0.641226	89655.280	89748.914	0.088137	7910.200
8	0.553944	0.699592	89665.249	89757.007	0.092123	8268.685
9	0.415034	0.581845	89493.691	89598.782	0.097763	8759.446
10	0.494150	0.629142	88963.406	89048.451	0.097394	8672.785
11	0.583686	0.698118	89468.333	89540.425	0.081974	7339.987
13	0.508752	0.638965	89391.408	89473.442	0.089790	8033.820
14	0.437188	0.582690	89428.736	89520.402	0.105433	9438.405

Exp.	R_F Ω	ΔT Ω	$Corr_1$ $KJ \cdot \Omega^{-1}$	$Corr_2$ J	Q J	$\dfrac{Q \times M.W.}{M_s}$ $KJ \cdot mol^{-1}$	$\Delta H_{25}' = \Delta H_{25}$ $KJ \cdot mol^{-1}$
2	0.590805	-0.087025	-0.033	494.564	4987.741	284.824	284.857*
4	0.694686	-0.190906	-0.071	540.667	7704.363	308.291	308.362
5	0.699630	-0.195850	-0.073	191.236	8101.436	316.044	316.117*
8	0.758092	-0.254312	-0.095	314.654	8583.339	307.200	307.295
9	0.649733	-0.145953	-0.055	503.513	9262.959	304.163	304.218
10	0.686814	-0.183034	-0.068	323.752	8996.537	344.680	344.748*
11	0.744450	-0.240670	-0.090	178.443	7518.430	304.511	304.601
13	0.692056	-0.188276	-0.070	161.635	8195.455	301.870	301.940
14	0.645499	-0.141719	-0.053	201.753	9640.158	305.734	305.787

ave = 305.367 ± 1.880

Table 4

Heat of Solution of NaCl(c) in H_2O and in As_2O_3(aq)

Exp.	Solvent	M_s g	E'_s Calib I $J \cdot \Omega^{-1}$	Calib II $J \cdot \Omega^{-1}$	R_m Calib I Ω	Reaction Ω	Calib II Ω
1	H_2O	2.0698	20971.524	20975.709	0.353104	0.457848	0.558960
2	H_2O	1.7026	20958.109	20960.749	0.444269	0.545944	0.644838
2a	H_2O	1.5449	20993.917	21012.807	0.337339	0.705236	0.526779
3	As_2O_3(aq)	2.3348	20892.048	20926.757	0.323676	0.430666	0.534306
3a	As_2O_3(aq)	1.5521	20931.993	20978.465	0.333020	0.703396	0.523275

Exp.	ΔR_c Ω	$E_{s\ corr}$ $J \cdot \Omega^{-1}$	Q' J	Added heat J	Q J	$\dfrac{Q \times M.W.}{M_s}$ $KJ \cdot mol^{-1}$
1	-0.007313	II 20965.598	-153.441	0.0	-153.441	-4.333
		I 20981.998	-153.321	0.0	-153.321	-4.329
2	-0.005462	II 20950.860	-114.529	0.0	-114.529	-3.931
		I 20968.277	-114.434	0.0	-114.434	-3.928
2a	0.161384	21030.653	3394.011	3502.981	-108.970	-4.122
3	-0.005007	II 20917.958	-104.736	0.0	-104.736	-2.622
		I 20900.009	-104.646	0.0	-104.646	-2.619
3a	0.163216	21009.986	3431.371	3499.466	-68.095	-2.564

$$ave = H_2O = -4.129$$
$$As_2O_3(aq) = -2.602$$

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Table 5

Normalities of NaOH and Coefficients for Equations 5 and 6

Compound	Exp.	Normality	x	y	m	n
As$_2$O$_3$ (octa.)	1	1.057	21.734	19.734	52.382	57.741
	2	1.057	26.671	24.671	52.382	56.669
	3	1.057	26.959	24.959	52.382	56.620
	4	1.057	24.524	22.524	52.382	57.078
As$_2$O$_3$ (monoclinic)	1	1.057	32.165	30.165	52.382	55.888
	2	1.057	33.348	31.348	52.382	55.756
As$_2$O$_3$ (vitreous)	1	1.057	25.665	23.665	52.382	56.851
	2	1.057	25.437	23.437	52.382	56.895
	3	1.057	23.668	21.668	52.382	57.263
AsCl$_3$ (ℓ)	2	1.057	49.967	45.967	52.382	56.984
	3	1.057	26.451	22.451	52.382	61.804
	4	1.057	32.678	28.678	52.382	59.758
	5	1.0	60.982	56.982	55.371	59.293
	6	1.0	27.419	23.419	55.371	64.914
	7	1.0	67.356	63.356	55.371	58.898
	8	1.0	120.693	116.693	55.371	57.286
	9	1.038	32.660	28.660	53.339	60.853
	10	1.038	34.852	30.852	53.339	60.319

Table 6

Analysis of $AsCl_3$ Hydrolysis Products

Exp.	Mass of Sample g	Solution Aliquot cm^3	Iodine Solution cm^3	Normality Iodine Soln.	$As^{+3}_{(obs.)}$ g	$As^{+3}_{(cal.)}$ g	Ratio (obs/cal.)
1	2.56649	20	33.425	0.01604	1.00420	1.06070	0.94673
2	1.72883	20	23.150	0.01604	0.69550	0.71451	0.97339
3	3.26580	20	43.950	0.01604	1.32040	1.34972	0.97828
4	2.64335	20	35.567	0.01604	1.06855	1.09247	0.97810
5	1.34298	20	18.425	0.01604	0.55355	0.55504	0.99732
6	2.98697	20	41.383	0.01604	1.24330	1.23448	1.00714
7	1.21587	20	14.725	0.01826	0.50360	0.50251	1.00217
8	0.67854	40	17.225	0.01766	0.28488	0.28043	1.01587
9	2.59940	50	48.233	0.02936	1.06098	1.07431	0.98759
10	2.43583	50	45.817	0.02936	1.00784	1.00670	1.00113

All product solutions were diluted to 1000 cm^3 before the aliquot samples were taken.

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Experiments 1, 3, 6, 7, 12, and 15 of the $AsCl_3$ formation
were not calculated for the following reasons:

#1 - the final temperature greatly exceeded the jacket
temperature

#3 - some of the liquid product was visibly carried into
the gaseous product receivers

#6 and 7 - chlorine leak into the system gave spurious
temperature rise

#12 and 15 - analysis unobtainable

Experiments 2, 5, and 10 were omitted from the final
considerations for obvious reasons.

All of the hydrolysis experiments except the first $AsCl_3$
hydrolysis were considered.

The energy equivalent, E_S, of the system is calculated from
the electrical calibration data and is assigned to the mid-point
of the calibration temperature rise. The change of energy equivalent
with temperature has been determined experimentally. The $E_{S(corr)}$
reported is the measured E_S adjusted to the mid-point of the reaction
temperature rise.

In the Eq. 2 experiments some of the product left the system
in a gaseous state. Corrections to the calculated heats were
made on the basis of $\Delta H_{vap}(AsCl_3)$ = 43932 J/g or 10.5 Kcal/mol. [13].
These corrections appear in Table 3 as "$Corr_2$".

Evaluation of the hydrolysis data was based on the following
equations:

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5. $As_2O_3(c) + x(NaOH*mH_2O) \rightarrow [2NaAsO_2 + y(NaOH*nH_2O)] + H_2O(\ell)$

6. $AsCl_3(\ell) + x\,NaOH*mH_2O \rightarrow [NaAsO_2 + y(NaOH*nH_2O) + 3NaCl] + 2H_2O(\ell)$

7. $3NaCl(c) + [NaAsO_2 + y(NaOH*nH_2O)] \rightarrow [NaAsO_2 + y(NaOH*nH_2O) + 3NaCl]$

The volume of alkali used in the solution experiments was always 450 cm^3. The difference in sample size and some slight variations in alkali strength caused the coefficients x, y, m, and n in equations 5-7 to differ from experiment to experiment. (See Table 5). By use of appropriate dilution data from Parker [14] all experiments were reduced to a common basis wherein x=21.734 and m=52.382. A typical set of such calculations is shown here for the 4th As_2O_3(c,octa.) experiment:

$As_2O_3 + 24.524(NaOH*52.382H_2O) \rightarrow$
$[2NaAsO_2 + 22.524(NaOH*57.078H_2O)] + H_2O(\ell)$ $\qquad \Delta H=-43.959$ KJ/mol

$2.790[(NaOH*52.382H_2O) \rightarrow$
$(NaOH*57.078H_2O)$ $\quad \Delta H=0.0368$ KJ/mol] $\qquad +0.103$

$As_2O_3 + 21.734(NaOH*52.382H_2O) \rightarrow$
$[2NaAsO_2 + 19.734(NaOH*57.078H_2O)] + H_2O(\ell)$ $\qquad -44.063$

$19.734[NaOH*57.741H_2O) \rightarrow$
$(NaOH*57.078H_2O)$ $\quad \Delta H=-0.003$ KJ/mol] $\qquad -0.059$

$As_2O_3 + 21.734(NaOH*52.382H_2O) \rightarrow$
$[2NaAsO_2 + 19.734(NaOH*57.741H_2O)] + H_2O(\ell)$ $\qquad -44.003$ KJ/mol
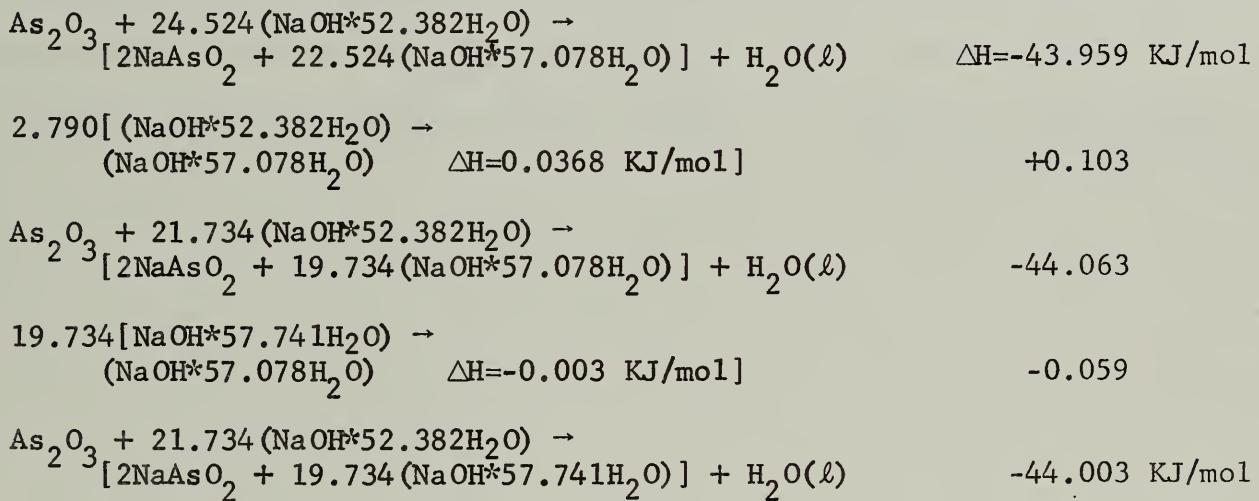
Experiments were made on the solution of NaCl(c) in both H_2O and $As_2O_3 + NaOH$. The water experiments were made as a check of the system and procedure. The values obtained were compared with the published value of the heat of solution of NaCl.

Both of the above reactions are endothermic, so some experiments were run with the addition of measured electrical heat during the reaction period. The data are given in Table IV. In the "a" experiments the two calibrations were run consecutively prior to

the reaction, in the others the calibrations bracketed the reaction.

From these data we calculate:

$$3NaCl(c) + [NaAsO_2 + 17.734(NaOH*57.741H_2O)] \rightarrow$$
$$[NaAsO_2 + 17.734(NaOH*57.741H_2O) + 3NaCl] \qquad \Delta H = +7.806 \ KJ$$
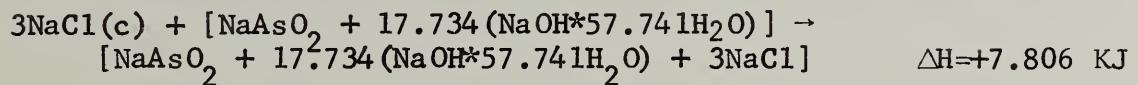
The heat of reaction for Eq. 7 was determined as +7.806 KJ. (See

Table 4).

Combining Eqs. 5, 6, and 7 leads to the following:

8. $2AsCl_3(\ell) + 21.734(NaOH*52.382H_2O) \rightarrow As_2O_3(c, octa.) + 6NaCl(c)$
   $+ 3H_2O(\ell) + 15.734(NaOH*57.741H_2O)$
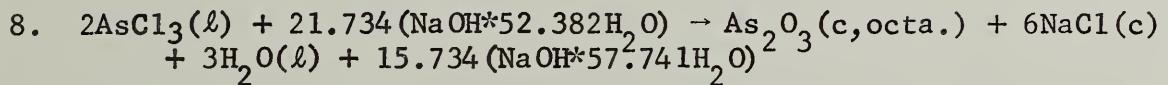
$$\Delta H = -551.035 \pm 0.570 \ KJ/mol \qquad (-131.712 \pm 0.136 \ kcal/mol)$$

Our experiments give $\Delta Hf_{298.15} \ AsCl_3(\ell) = -305.367 \ KJ/mol$

(-72.984 kcal/mol). Inserting this value into Eqn. 8 along with

the accepted values of $\Delta Hf_{298.15}$ for NaCl(c), $H_2O(\ell)$, and the NaOH

solutions, we get for As_2O_3(c, octa.) $\Delta Hf_{298.15} = -658.416 \pm 1.96 \ KJ/mol$
$(-157.365 \pm 0.468 \ kcal/mol)$

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