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Hydrocarbons for Fuel— 75 Years of Materials Research at NBS

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Hydrocarbons for Fuel— 75 Years of Materials Research at NBS

George T. Armstrong

In this historical review the NBS work on hydrocarbons is discussed in terms of the three major classes of natural hydrocarbonaceous fuels: natural gas, petroleum, and coal. The work done on the measurement of properties of the pure components has included measurement of the values of the properties themselves and development of practical and accurate measurement procedures and instruments. In addition, combustion energies, densities, viscosities, vapor pressures, refractive indices, elemental compositions and other parameters have been determined for complex fuel mixtures and correlated to find methods of estimating properties. Extensive standard reference data tables have been compiled and a number of standard reference materials have been developed.

Key words: Coal; energy; fuel; graphite; hydrocarbons; metering; methane; natural gas; petroleum; physical properties; standard reference materials.

1. Introduction

The scope of NBS work on hydrocarbons for fuels over the years is so broad and complex that a brief review such as this can only point out highlights. Let us briefly outline first some of the principal features of the NBS fuel hydrocarbons work.

More or less broad coverage has been given to all the fossil fuels. The work has covered natural gas and petroleum more extensively than coal; however, even here some interesting and perhaps little appreciated work has been done. In each of these areas the practical fuels themselves have been studied, as well as well-characterized substances of which they are composed. Significant effort has gone into the measurement of properties of the pure components, both from the point of view of establishing the values of the properties themselves and from the point of view of practical and accurate measurement devices and procedures. In addition, combustion energies, densities, viscosities, vapor pressures, refractive indices, elemental compositions and other parameters have been determined for complex fuel mixtures and correlated to find methods of estimating one or more properties. The studies date from the earliest days of NBS, when natural gas was coming into widespread use as a fuel and beginning to displace gas manufactured from coal. Several very intensive well defined programs of research at NBS have revolved around the properties of gaseous and liquid hydrocarbon fuels. Extensive standard reference data compilations have been prepared, and a number of standard reference materials, related to the use of hydrocarbons and hydrocarbonaceous materials as fuels, have been developed and are in use.

In this review, work on hydrocarbons at the National Bureau of Standards is discussed in terms of the three major classes of natural hydrocarbon or hydrocarbonaceous fuels: natural gas, petroleum, and coal.

1.1. Gaseous Fuels

In the early days of NBS which was founded in 1901 natural gas was just coming into service as a

domestic heating and cooking fuel, its prior use having been mainly for illumination. Early NBS work was directed to the goals of safety and quality in this new fuel, and to measurement of its properties. Studies included methods of measurement of gas quantities (volumetrically) and of density, measurement of heating value and candlepower, and determination of impurities. Circulars were prepared describing how these could be determined accurately. For the States the NBS also tested calorimeters for measuring the heating value of gaseous fuels. In later years NBS evaluated automatic calorimeters for continuous recording of gas heating values.

One important result of NBS work has been the adoption of heating value as the measure of a gaseous fuel in trade; this is the current practice. In order to provide measurement validity a reference material (a good quality methane) is certified for real-gas heating value provided at intervals by NBS for the Institute of Gas Technology, which is the present source of reference fuels for the fuel gas industry.

Currently under way at NBS (Boulder) is a study, supported by the American Gas Association and other institutions, to provide better experimental data on the properties of liquefied natural gas. The properties of the principal pure components and of their binary and more complex mixtures are being determined.

1.2. Liquid Petroleum and Petroleum Products

For liquid petroleum and its components NBS has carried out, with the support of the American Petroleum Institute or of the Defense Department, several long-term studies, some of which have had major impact on U.S. and world petroleum technology. The studies include densities and coefficients of expansion of naturally occurring petroleum and refinery products, and their energies of combustion, heat capacities, and enthalpies of vaporization. The studies of density and coefficient of expansion form the initial basis of the widely used petroleum measurement tables, which are used in gauging quantities of petroleum products in transportation, transfer and storage. A new survey of densities and coefficients of expansion

of petroleum and refinery products representative of the world-wide sources is in progress.

It was found to be possible to correlate energy of combustion with various easily measured parameters such as aniline point and specific gravity; and several tables have been prepared, which are widely used in the industry for estimating heating values of well defined grades of commercial fuels such as aviation gasoline, jet fuels, and kerosines.

Procedures and instruments for accurate measurement of energies of combustion, freezing points, and purities of pure hydrocarbons were developed. Under the American Petroleum Institute Research Project 6, extensive studies were made of the composition of petroleum. More than two hundred high-purity hydrocarbons were prepared, and the purities of these materials were established. For more than a hundred hydrocarbons, accurate determinations of boiling points and vapor pressures, densities, refractive indices, freezing points, and energies of combustion were made. These form the classical studies of petroleum and hydrocarbons.

Under the American Petroleum Institute Research Project 44 was carried on a review and critical evaluation of the properties of the pure hydrocarbons determined from all published work. These reviews provided selected values of twenty-two different thermodynamic and physical properties for some twenty-five classes of hydrocarbons. The studies included correlation of properties in homologous series, and the calculation of thermal functions and equilibrium constants of the gases from statistical thermodynamic principles. An example of the use of the equilibrium constants of formation that were calculated is the prediction of equilibrium proportions of isomeric hydrocarbons.

In the NBS Thermochemical Laboratories, definitive studies were also made of the energies of formation of the principal products of combustion of all hydrocarbon fuels: H_2O , CO , and CO_2 .

1.3. Solid Fuels

With respect to coal components, the principal related work at NBS has been definitive studies of the energies of combustion of synthetic and naturally occurring graphite and diamond and of the relationship of these to the energy of combustion of coke containing various amounts of hydrogen. Studies have also been made of the thermal properties of graphite to elevated temperatures.

1.4. Standard Reference Materials

Standard reference materials for use in natural gas technology, petroleum fuel technology, and coal combustion technology have been developed and are available. Some of these relate to the properties of the fuels themselves; others refer to pollution problems created by their use. Examples of the latter are standard samples for analysis of trace heavy metals in coal and coal ash, and sulfur in fuel oil and coal.

2. Methane and Natural Gas

2.1. Industrial Gas Measurement, Analysis, and Calorimetry

Study of natural gas began at NBS as part of an extensive program guided by E. B. Rosa (1901-1921) in the early years of NBS to establish standards of safety, quality, measurement, and performance, in the public utilities industries. Natural gas was in transition from its principal use for illumination to its later use for heating [1].¹ At the turn of the century gas was measured to individual customers by volume and charged for on that basis. Important properties were "candlepower" and "heating value." E. B. Rosa almost immediately began advocating the use of heating value as a measure of quality and value of natural gas [2]. Heating value was ultimately adopted as the measure of the commodity as a result of this NBS activity [1]. The procedure is still in practice.

Early NBS work included studies of the measurement of quantity of gas (M. H. Stillman [3]; see also [4]); measurement of heating value (C. W. Waidner and E. F. Mueller [5]); determination of candlepower [6]; determination of impurities, in particular ammonia [7] and hydrogen sulfide [8]; determination of gas density [9]. Other aspects of commercial gas technology were also involved, including safety and fittings for gas service.

Calorimetry of gaseous methane on a routine basis required the conduct of the combustion process in a reproducible way, the use of commercial gas calorimeters (such as the Junkers or the Boys calorimeters)² together with commercial gas metering devices (usually the wet test meter), and associated temperature and mass measurements. The process was fairly complex for a routine quality-test procedure. It consisted of measuring volumetrically the amount of gas flowing into the system, burning the gas with a controlled amount of combustion air in the calorimeter, in which the heat was absorbed in flowing water, and observing the heat affect of the combustion when a steady state was achieved.

The NBS studies established the conditions for carrying out the measurements accurately, with inaccuracies lying between 0.2 and 0.5 percent. Factors requiring measurement or control include temperature, pressure, and humidity of the gas, amount of gas burned, amount of combustion air used, degree of completeness of combustion, rate of water flow in the calorimeter, temperature rise of the flowing water in the calorimeter, heat losses due to extraneous processes, and mass of water condensed from the combustion gases.

With heating value proposed as a criterion of value for trade in natural gas, methods for determining it and adequate auxiliary data for interpreting the measurements were needed. These were prepared as

¹ Figures in brackets refer to literature references at the end of this publication.

² Certain trade names and company products are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products are necessarily the best available for the purpose.

NBS Circulars: Standard Methods of Gas Testing (Circular No. 48 [4]) and Gas Calorimeter Tables (Circular No. 65, revised and reissued at intervals as Circulars C417 and C464) [10].

The NBS also undertook to test calorimeters for the States that adopted heating value as a measure for pricing fuel. This was to provide regulatory commissions with the necessary equipment and measurement verification to enable them to test fuels and approve of charges by public utilities corporations. Although the gas-flow calorimeter is an absolute instrument for which calibration is not appropriate, demonstration of the accuracy of the complete process in a particular calorimeter required analysis of combustion gas and products and a careful mathematical treatment of the results. This was a relatively time consuming process. The testing of manually operated calorimeters for the States continued until about 1955, when the number tested annually had become very small. The gas industry by that time had almost universally adopted the automatic recording calorimeter and this accounted for the absence of manually operated instruments.

The automatic recording gas calorimeter of the type principally in use in the United States was the subject of two extensive investigations at NBS. R. S. Jessup [11] compared the Thomas Recording Calorimeter (later called Cutler-Hammer Automatic Recording Calorimeter) with the Junkers calorimeter, and established the reliability of the former as being well within 1.0 percent. Figure 1 shows the Cutler-Hammer calorimeter schematically. The calorimeter suffered to a certain extent from a lag in responding to sudden changes of heating value of the gas. However, the convenience of use and the continuous record obtained provided sufficient incentive to cause this calorimeter and its later versions to displace the manually operated calorimeters.

J. H. Eiseman and E. A. Potter [12] later established that with gas of high heating value (methane-like) the calorimeter could provide measurements with uncertainties of 0.25 percent or less. Their study

was necessitated by the higher heating value of gases that had come into the market since the earlier study.

The Cutler-Hammer calorimeter operates on the following principle. Gas is burned at a constant rate and the heat developed is absorbed by a stream of air. The rates of flow of the gas, the air for combustion, and the air for absorption of heat are regulated by metering devices similar to the ordinary wet-gas meter. These metering devices are geared together and driven by an electric motor so that the ratios of the three rates of flow are constant. The products of combustion are kept separate from the heat-absorbing air and are cooled very nearly to the initial temperature of the air. The water formed in the combustion is condensed to the liquid state. The rise in temperature of the heat-absorbing air is proportional to the total or gross heating value of the gas. The rise in temperature is measured by means of resistance thermometers and is recorded graphically.

Gas calorimeters of the above type, with public reliance justified by these NBS studies, give the basis for calculating heating values of fuels delivered to the homeowner and exchanged in trade between producers, transmission companies, and industrial or public utilities consumers.

The above problems have been primarily metrology problems and relate primarily to the adequate measurement of important parameters of this commonly used fuel. Other work at NBS has provided further important information for the fuel gas trade.

In the period of World War I (see ref. [61]) the NBS became involved intensively in measures for conservation and rationing of natural gas.

Toward the end of the war period the necessity of obtaining helium from natural gas created a need for measurement of physical and thermodynamic properties of methane as a cryogenic fluid, in order to establish conditions for separation of methane from the helium. This led to an initiation of studies on the physical properties of methane [16] such as the vapor pressure measurements by Cragoe [62, 63b] which are comparatively obscure.

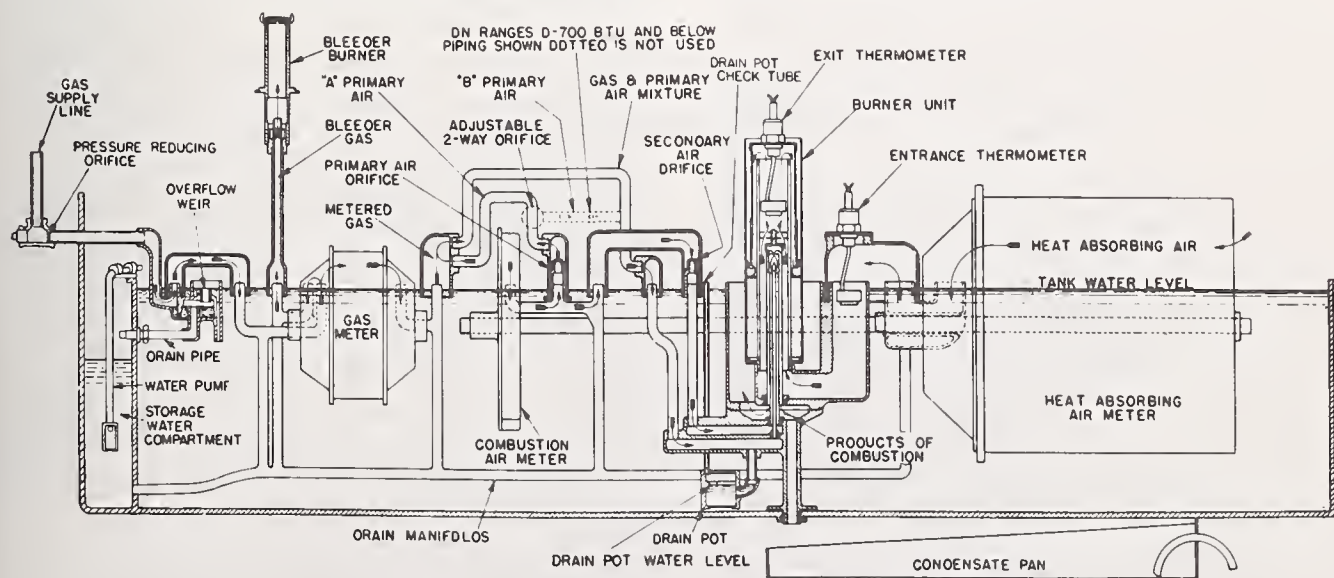


FIGURE 1. Flow diagram of the Cutler-Hammer recording gas calorimeter.

2.2. Physical and Thermodynamic Properties of Pure Components and Well-Defined Mixtures of Components

With the discovery of deuterium in 1932 by Urey, Brickwedde, and Murphy [34], the theoretical interest in isotope effects led Brickwedde and Scott to undertake a study of the thermodynamic properties of deuterated methanes. This work, including the original vapor pressure work on CH_4 by Cragoe, unpublished for many years, was finally summarized by Armstrong and published [63]. The vapor pressure study of the deuteromethanes is unique in the number of closely related deuterium-substituted molecules for which precise data were reported, and showed a strong and very regular isotope substituent effect.

Three of the most important thermochemical studies made by F. D. Rossini, and among his earliest studies at NBS, were the definitive determinations of the enthalpies of combustion of hydrogen [13], methane [14], and carbon monoxide [14]. Not only are these substances important ingredients of commercial fuels, but the products of combustion, water and carbon dioxide, are universal products of combustion of hydrocarbon fuels. The enthalpies of formation of the products are essential in fuel energy calculations.

Rossini's studies reduced the uncertainties in the combustion energies by a factor of three or more. These studies were followed by other studies covering the principal hydrocarbon constituents of gaseous fuels, the low-molecular-weight aliphatic hydrocarbons ethane, propane, and the butanes. The measured values are generally accepted as standard reference data for the ideal gas hydrocarbons. See later for additional calorimetric measurements by Rossini and his colleagues.

In further support of the combustion calorimetry of natural gas as a pricing measurement, a standard reference material consisting of a natural gas of good quality was certified as to its heating value and issued by NBS for some years. This reference material is used in the industry to verify the accuracy of calorimeters in the natural gas range of heating values. The responsibility for distribution of this reference material was transferred to the Institute of Gas Technology in 1961, with the provision that NBS would supply a certification of a reference fuel as needed to provide traceability of the energy measurement to the national standards.

The last certification of such a reference material was prepared in 1965 [15]. The material certified was analyzed by mass spectrometric and gas chromatographic techniques by E. E. Hughes and J. K. Taylor. It was about 99.95 percent methane, with 0.04 percent ethane and much smaller amounts of non-combustible constituents. The heating value was calculated for unit volume of the real gas both dry and water-saturated under the standard pressure and temperature conditions in use by the gas industry. The calculation, which was done by G. T. Armstrong, was based upon Rossini's determination of the standard enthalpies of combustion of methane and ethane (adopted as standard reference data), the compressibility data of Dous-

lin (Bureau of Mines) and the vapor pressure of water measured by H. F. Stimson (NBS).

Calculation of the heating value of gas mixtures from composition has long been considered attractive as an alternative to calorimetry for many purposes requiring less than the highest accuracy. To meet the needs of the gas industry in particular, and to prepare users for coming metric practice, a recommended set of values of combustion energies of the ideal gases was prepared in 1972 [16]. This compilation gives heating values on a dry and on a water-saturated basis for ideal gases: H_2 , H_2S , CO , CH_4 , and 49 other selected gaseous hydrocarbons (C_1 to C_6) in kilojoules per mole, megajoules per cubic meter, and British thermal units per cubic foot. Values are tabulated under two standard conditions: 288.71 K (60°F), $101591.3 \text{ N} \cdot \text{m}^{-3}$ (30 in Hg) used for many years by ASTM; and 288.71 K (60°F), $101559.8 \text{ N} \cdot \text{m}^{-3}$ (14.73 psia) recently proposed by ANSI. An outline is given of a procedure to derive data for the real gases, and to adjust temperature and pressure bases.

In deriving these values, advantage was taken of a recent critical review and compilation by E. S. Domalski [65] of the enthalpies of combustion of organic substances including many hydrocarbons. This review was a partial updating of the well known compilation made at NBS by Kharasch [66], which for many years stood as the only extensive authoritative collection of enthalpies of combustion of organic compounds.

Within recent years, research on natural gas and liquefied natural gas has been resumed at the NBS Boulder laboratories to meet the needs resulting from large scale use of liquefied natural gas (LNG). This extensive program has several tasks which are still underway.

One of the most significant contributions of this program has been new, comprehensive, accurate data on thermophysical properties of compressed and liquefied methane, the predominant constituent of natural gas. A recent publication by R. D. Goodwin [17] covers the temperature region from 90 to 500 K at pressures to 70 MPa. It gives a critical evaluation and correlation of all relevant equation-of-state and thermodynamic data, original equation-of-state and heat capacity measurements, and comprehensive accurate tables of thermodynamic data.

Other work completed in this program includes new measurements and correlations of data on heat capacities [18], sound velocities [19], dielectric constants [20], refractive indices [21], viscosities and thermal conductivity coefficients [22, 23] of methane in the temperature range 90 to 300 K, and pressures to 35 MPa.

With respect to mixtures of compressed and liquefied constituents of natural gas, the most significant contribution to date from this group is a comprehensive bibliography of experimental data by M. J. Hiza, et al. [24]. Also, new liquid-vapor equilibrium measurements have been reported for methane-nitrogen mixtures in the temperature range 95-180 K [25, 26].

Other projected work includes measurements of densities of liquid methane, ethane, propane, butane, nitrogen and mixtures of these substances, and methods for estimating heating values of flowing LNG.

3. Liquid Petroleum Products

3.1. Densities and Enthalpies of Combustion

Among the properties of petroleum that are most important commercially are the density and coefficient of expansion. They are widely used in the measurement of shipments of petroleum. Ten million cubic meters (approximately sixty million barrels) of crude petroleum are measured each day as it enters the world market, and similar quantities of petroleum products are delivered in various stages of processing. The measurement of much of this material is made volumetrically. To assure that the measured amounts of material are equitable for trade, despite fluctuations in density due to thermal expansion, the measurements are adjusted to a reference temperature. (60 °F or 15 5/9 °C has been used for many years. A change to 15 °C is currently under way.) The adjustments are made using internationally accepted petroleum measurement tables [27], which are based on average measured coefficients of expansion of petroleum and petroleum products. These measurement tables have been largely based on NBS measurements in the past and indications are that they will continue to be so based.

NBS involvement in the petroleum measurement tables began with experimental density determinations in the period 1912 to 1914 by H. W. Bearce and E. L. Peffer [28]. They made determinations on refined oils, crude oils, fuel oils and heavy lubricating oils, representing the commercial petroleum oils produced in the United States at that time. Densities were determined by hydrostatic weighing and by picnometer at 0, 10, 20, 25, 30, 40, 50, 75, 85, and 95 °C. The data for each fuel were fitted to equations of the form

$$D_t = D_r + \alpha(t - T) + \beta(t - T)^2$$

which were found to represent the data closely. In these equations T is a reference temperature such as 25 °C and t is a variable temperature. The coefficients α and β thus found vary regularly on the average with the density at 25 °C (D_{25}). For their historical interest, the plotted data from this research are shown as figure 2. In retrospect, the qualitative statistical treatment of the data in this paper appears to be hardly adequate in view of the fact that the deviations from the selected curve are large compared to the total range of the curve and the fact that the smoothed values were to be used to measure materials from all the sources involved, and others.

Smoothed densities from the above paper were transformed to specific gravities (determined in air) and degrees Baumé and tabulated in various ways to allow volumes measured at ambient temperature to be reduced to volumes and weights at the reference

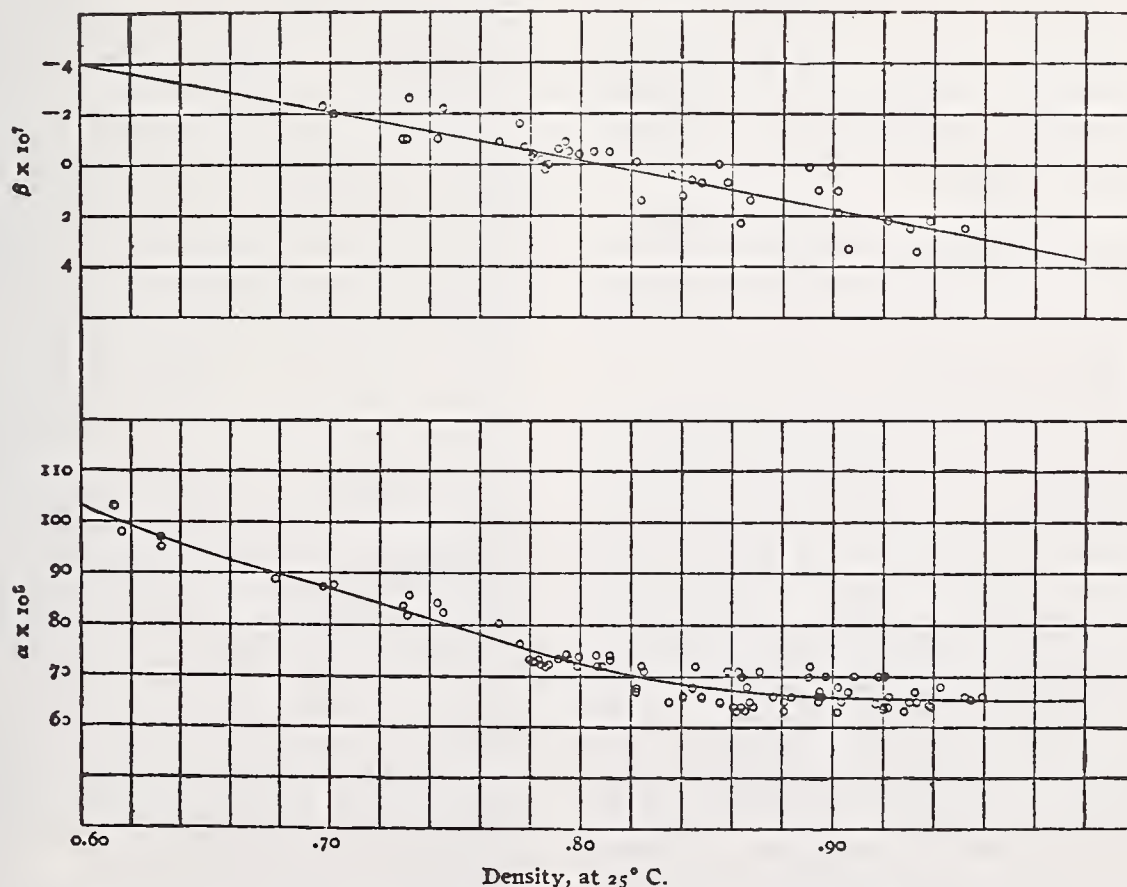


FIGURE 2. Summary data of Bearce and Peffer showing the variation of coefficients of expansion with density (at the reference temperature) for petroleum oils.

temperature. Thus treated they formed the first authoritative United States Standard Tables for Petroleum Oils [29]. The justification for using smoothed tables for measuring oils showing such wide individual deviations is that on the average the measurement errors will cancel, a justification whose validity has been questioned from time to time.

Additional experimental measurements of thermal expansion of petroleum oils were made by R. S. Jessup [30] and of gasolines by C. S. Cragoe and E. E. Hill [31]. These studies were undertaken to provide data on materials prepared using cracking processes not encountered in the earlier study. Jessup's study indicated that the viscosity of an oil and its density provided good correlating parameters for estimating volume as a function of temperature and pressure. The work of Cragoe and Hill showed systematic differences in the thermal expansions of cracked gasolines and straight run gasolines. Distillation curves provided a better correlating device than the specific gravity.

The work that went into the preparation of the Standard Petroleum Oil Tables (NBS Circular 57 and its successors C154, C410, and finally the ASTM-IP Petroleum Measurement Tables) is described by Hyams and Holmes [32].

Diversification of world petroleum resources in recent years has led to renewed speculation as to the validity of the averages. A new, extremely comprehensive survey of densities and coefficients of thermal expansion of crude and refined petroleum representing known supplies has been inaugurated and is under way at the National Bureau of Standards (1975). The new survey links densities to the prototype SI units. The measurements on oil samples are based upon the natural oscillation frequency of a tube filled with the liquid under investigation [33]. This technique is sensitive enough to detect changes of less than a part per million in density.

Other thermal properties of petroleum also vary systematically with temperature, with the density, and with other parameters associated with the oils. A substantial amount of work was carried out at NBS to establish equations and tables of data that would represent averages for petroleum products.

An early and very well known and widely used example of this is NBS Miscellaneous Publication No. 97, "Thermal Properties of Petroleum Products." This publication prepared by Cragoe [34] gives tables and discussion of thermal expansion, energies of combustion, specific volume of vapor, thermal conductivity, specific heat capacity, enthalpy of vaporization, and enthalpy of a range of petroleum oils. This publication was prepared primarily as a critical review and summary of data in the literature, compiled at the initiation of American Petroleum Institute (API) Project 38, which began in 1927 at NBS (see note following reference [34]). This compilation proved to be very popular and calls for it are still received forty years later. It is still one of the few, if not the only, source of federally authorized average data for hydrocarbon fuels in certain regions of density.

In the above publication energies of combustion

were tabulated as functions of the gravity (degrees API). The API gravity is a Baumé scale of reciprocal specific gravity, modulus 141.5.³ The use of API gravity is widespread in the petroleum industry; and NBS staff found it convenient to assist this technology in the succeeding years, by establishing other correlations based on it. Several studies were carried out for the U.S. Air Force to provide correlations for estimating the enthalpy of combustion of aviation fuels of various grades. The work carried out over a period of years ending in 1962 apparently was initiated by C. S. Cragoe as part of API project 38. However, it was continued primarily by R. S. Jessup and included studies of aviation gasoline (several grades), jet fuels, and kerosine. The latter work [35] provided the basic data for the kerosine fuel used in first stage engines of such rockets as Atlas and many others. These studies were adopted by the American Society for Testing and Materials, by the Institute of Petroleum, the American National Standards Institute, and the Federal Government as standard methods of test for estimating the net heat of combustion of specified fuels, based on the so-called aniline-gravity product (product of aniline point temperature in degrees Fahrenheit and specific gravity in degrees API). See Annual Book of ASTM Standards [36] for the correlations adopted and their sources.

From a scientific point of view the above studies leave much to be desired. The correlating parameters could be only very qualitatively related to the quantity of interest—the enthalpy of combustion to gaseous water, carbon dioxide, sulfur dioxide, and nitrogen. The aniline point (the minimum solution temperature of an equivolume mixture of aniline and the liquid under test) is a rough measure of aromatic hydrocarbon content in mixed hydrocarbon fuels, and to a lesser extent a measure of naphthenic hydrocarbons. These have significantly lower specific enthalpies of combustion than have aliphatic hydrocarbons and differences from each other because of variations in hydrogen content, hydrocarbon chain length, ring size, and degree of ring formation, all of which affect the enthalpy of combustion. The parameters correlated do not show as good a correlation for pure hydrocarbons as they do for the naturally occurring and derived mixtures. Thus the success of the correlation schemes depends on the presence of large numbers of hydrocarbons to provide reasonably constant and regularly varying average values. Within well defined classes of fuels the correlations allow estimation of the enthalpy of combustion within 55 kJ/kg (23 Btu/lb) at the 95 percent confidence level (approximately 0.15 percent uncertainty in the enthalpy of combustion).

Better and more rationally justified correlations have been obtained, based on analysis for hydrocarbon type and assignment of a characteristic enthalpy of combustion to each hydrocarbon type [35]. For practical purposes this improvement helps not at all; the necessary measurements are as complex as the combustion measurement itself.

³ The functional relationship is: Gravity/degrees API = 141.5/(*sp gr* 60/60 F) —131.5, where *sp gr* 60/60 F is the specific gravity at 60°F with respect to water at 60°F.

A technical problem arises in attempting to make these correlations useful in nations using SI measurements. The conversions are not trivial in terms of the amount of effort involved compared to the length of the test itself. Recorrelations based on SI measurements would probably be more satisfactory.

The current interest in energy thrift together with the high prices of fuels revived interest in reliable information about enthalpies of combustion of burner fuels and diesel fuels. However, the chances of success in empirical correlations of the types given above are diminished because of the high molecular weights of the substances of which they are composed. The more complex molecules of which these materials are composed permit a wider range of energies of combustion because of more possibilities for polycyclic aromatics and naphthenes. The paraffinic and asphaltic base petroleum also differ more as the residuals are included. Heavy oils derived from shale or coal are different from those derived from petroleum. Their composition and properties may vary greatly with conditions of their formation (temperature, hydrogen pressure, etc.).

3.2. Composition of Petroleum and Properties of its Components

American Petroleum Institute Research Project 6 was carried out at the National Bureau of Standards, and in its course made a notable contribution to the fractionation, analysis, isolation, purification, and properties of petroleum hydrocarbons. This project was initiated in January 1927, with E. W. Washburn, Chief of the Division of Chemistry as its first Director, followed in 1934 by F. D. Rossini, who continued as its Director after it was transferred from NBS to the Carnegie Institute of Technology in June 1950. A detailed summary account of the work of this project was given by Rossini, Mair, and Streiff [37]. The remarkable scope of this work is hinted at from a listing of chapter headings which is given in table 1. The principal investigators on this work, under Washburn, 1927-34, were Mair, White, Leslie, Schick Tanz, Rose, Bruun, and Hicks-Bruun, and, under Rossini, from 1934, were Mair, Forziati, Willingham, Glasgow, Streiff, Krouskop, and Camin.

The monograph and the technical papers of this work are noteworthy for their meticulous analysis of procedures and mathematical formulations, the intricacy and the detailed description of instruments, apparatus, and experimental results. As examples are shown in figure 3a and 3b the boiler used to determine boiling points, and the manometer assembly used to regulate the boiling point pressure at 20 fixed points.

In the course of their work, the project scientists made accurate measurements of boiling points and vapor pressures on 119 different compounds in the range 5 to 105 kPa (40 to 785 mm Hg), with the pictured apparatus. These data were fitted with Antoine (3 constant) equations. Standard deviations of temperature were 0.001 to 0.002 K, and of the pressure 2.5 to 5 Pa (0.02 to 0.04 mm Hg).

TABLE 1. Chapter headings of *Hydrocarbons from Petroleum* [37].

1. Introduction
2. Fractionation and Fractionating Processes
3. Regular Distillation
4. Azeotropic Distillation
5. Regular Distillation at Different Pressures
6. Distillation at Very Low Pressures
7. Extraction
8. Adsorption
9. Crystallization
10. Solid Molecular Compounds, Clathrate Compounds
11. Boiling Points and Vapor Pressures
12. Densities
13. Refractive Indices
14. Freezing Points; Evaluation of Purity from Freezing Points
15. Molecular Weights
16. Analysis for Carbon and Hydrogen
17. Purification of Hydrocarbons
18. Summary of the Work of Other Laboratories on the Composition of Petroleum
19. Analysis of the Gasoline Fraction of Petroleum
20. Analysis of the Kerosine Fraction of Petroleum
21. Analysis of the Gas-Oil Fraction of Petroleum
22. Analysis of the Lubricant Fraction of Petroleum
23. Hydrocarbons in One Crude Petroleum
24. Hydrocarbons in Different Crude Petroleum
25. Analysis of the Hydrocarbons in Certain Gasoline Distillates
26. Analysis of Alkylates and Hydrocodimers
27. Analysis of Codimers
- Appendices and Indices

Densities were measured at 20, 25, and 30 °C for 115 hydrocarbons, with overall uncertainties estimated at about $50 \mu\text{g} \cdot \text{cm}^{-3}$.

In the freezing point studies a method was developed for estimating impurities, of sufficient simplicity that it could be used in the routine test laboratory. In addition to the compounds for which freezing points are listed in table 2, the study found fifteen compounds that could not be crystallized.

As part of the above program, a cooperative sample preparation program involving twenty-seven laboratories was carried out. As a result of this program, over two hundred different hydrocarbon substances were prepared as standard hydrocarbons or research hydrocarbons having measured purities. The participating laboratories included the NBS group, Ohio State University, Pennsylvania State College, NACA Flight Propulsion Laboratory, General Motors Corporation, California Research Corporation, Phillips Petroleum Company, Standard Oil Development Company, Atlantic Refining Company, and Ethyl Corporation, supplying from 3 to 99 samples each, and sixteen other laboratories supplying one or two samples each. The collection of materials, the preparation and purification of additional materials, and the management of their distribution was transferred to the Carnegie Institute of Technology in 1950.

The hydrocarbons were prepared at NBS under the direction of Rossini, with B. J. Mair as the principal supervisor, principally by regular distillation and azeotropic distillation, with occasional use of distillation at reduced pressure, adsorption, crystallization, and fractionation with urea. Purity changes during

purification were followed by measurements of freezing points. In the course of the work, reliable procedures were developed for preserving the samples by sealing under vacuum in glass ampoules.

Of the more than two hundred different compounds that thus became available as research materials, well over half were obtained in purities greater than 99.9 mole percent. Essentially all had purities greater than 99.5 percent. These became the basis of extensive physical properties measurements of high quality. In table 2 are summarized the principal archival measurements of physical properties as distinguished from the large numbers of test data measured for process control in the preparation of the materials.

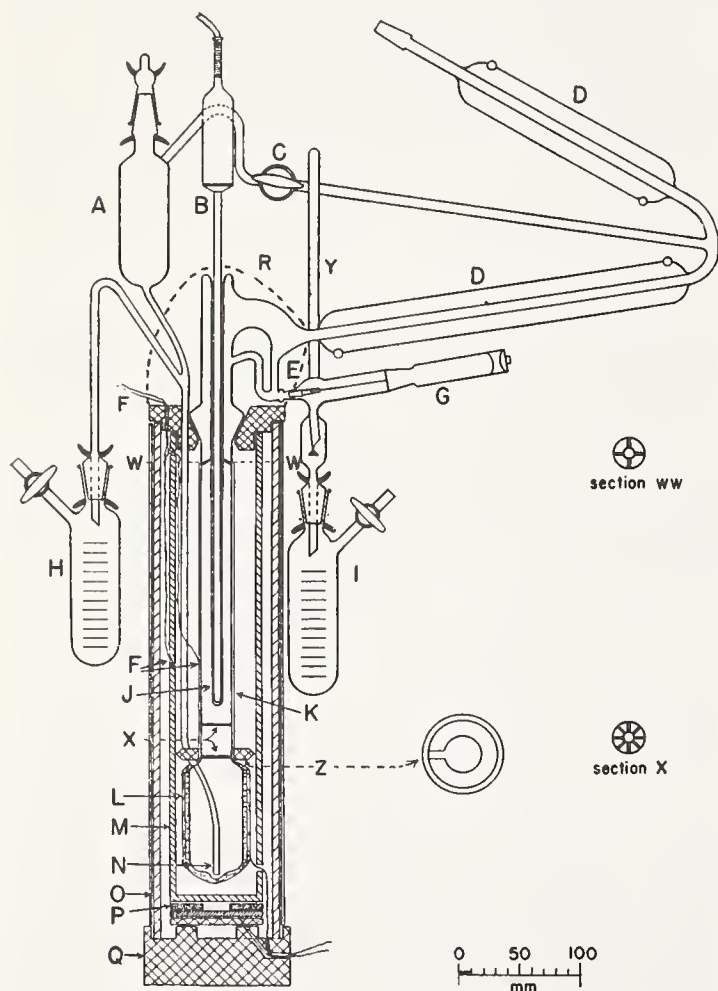


FIGURE 3a. Details of the boiler and related parts of the boiling-point apparatus.

The letters have the following significance: A, tube through which the sample is introduced; B, platinum resistance thermometer; C, stopcock; D, condensers; E, ground glass valve for withdrawing distillate; F, thermocouple, for measuring difference in temperature between the wall of the glass boiler and the jacket; G, metal control for the ground-glass valve; H, receiver for recovering sample at the conclusion of the measurements; I, receiver for collecting distillate removed from the head during the experiment; J, glass well for the platinum resistance thermometer; K, radiation shield of aluminum foil; L, electric heater for boiling the liquid in the pot; M, jacket 1/4 in wall, of aluminum; N, tube for withdrawing sample from the pot; O, thermal insulating jacket, Pyrex glass cylinder with an asbestos layer covered with aluminum foil; P, flat electric heater for the aluminum jacket; Q, transite support; R, thermal insulation, covered with aluminum foil; W, glass rod supports for the thermometer well; X, glass rod "spiders"; Y, connecting tube for equalizing pressure; Z, transite collar for centering boiler.

The other aspect of the program of API Project 6 was the fractionation, analysis, and isolation of hydrocarbons from petroleum. Before this project began, only a few low boiling hydrocarbons such as propane, n-butane, isobutane, n-pentane, and isopentane had been isolated from petroleum and identified. In the early days of the project the distilling columns used for gasoline fractionation had a separating power equivalent to about 20 theoretical plates. By the time the project transferred away from NBS distilling

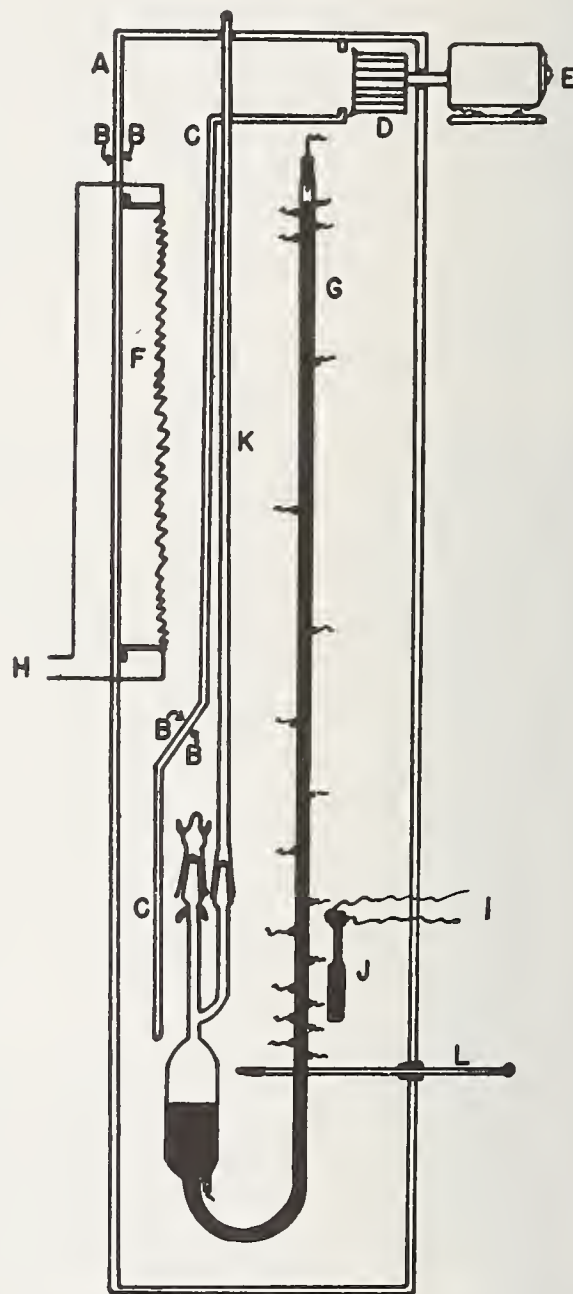


FIGURE 3b. Manometer assembly, showing the air thermostat.

The letters have the following significance: A, box enclosure with walls of transite (the cover is not shown); B, aluminum foil, covering inside and outside surface of the transite box; C, partial partition wall of transite (both sides covered with aluminum foil: serving to guide flow of air); D, rotary air circulator; E, electric motor, mounted independently of the thermostat housing; F, electric space heater, 100 watts; G, mercury manometer; H, connection to electric power through relay contacts; I, connection to relay coil; J, mercury thermoregulator; K, connection to pressure system; L, mercury-in-glass thermometer.

TABLE 2. *Physical properties measurements on pure hydrocarbons under API Project 6.*

Property	Number of hydrocarbons	Range of values	Uncertainties	Other
Boiling point ^a vapor pressure	119	20 points 5 to 105 kPa	2.5 to 5 Pa	Antoine equations
Density ^b	115	20, 25, 30 °C	50 $\mu\text{g}\cdot\text{cm}^{-3}$	
Refractive ^c Index	119	20, 25, 30 °C 7 wavelengths	0.0001	Hartman equation Couchy equation
Freezing ^d point	214	-160 to +80 °C normal atm air pressure	.001 K	Cryoscopic constant, impurity

Principal investigators in addition to Rossini, Mair, and Streiff [37].

(^a) Willingham, Taylor, Pignocco, Forziati, Norris, and Camin, see [37, pp. 188-208]

(^b) Forziati and Camin, see [37, pp. 209-219]

(^c) Forziati and Camin, see [27, pp. 220-238]

(^d) Glasgow and Krouskop, see [37, pp. 239-281]

columns with about 200 theoretical plates were used by the project. (These numbers of plates, of course, are hardly comparable to the much more effective separating capability of a gas-liquid chromatograph of the 1970's.)

The separation procedures adopted in Project 6 for the gasoline fraction of petroleum included (1) an initial adsorption stage by which the aromatic hydrocarbons were separated from the paraffin and naphthene hydrocarbons and (2) a distillation process to resolve each of these two components separately. The distillation of the two portions yielded directly (a) concentrates of pure compounds, or (b) concentrates of mixtures of two or more compounds. The constant boiling mixtures of compounds of the same type were resolved by further distillation (regular or azeotropic) or by crystallization. The constant boiling mixtures of paraffin and naphthene hydrocarbons were separated by special procedures. Non-hydrocarbon components, such as sulfur compounds, were concentrated with the aromatic fraction and were separated by further adsorption. The key feature in simplifying the separation process was the initial segregation of aromatic and non-aromatic portions, which greatly mitigated the difficulties of the later fractional distillations. Separation procedures were also devised for the kerosine fraction, gas-oil fraction, and the lubricant fraction of petroleum.

Using the above procedures devised and tested on the Project, a single representative crude petroleum was analyzed in detail in one of the most complex and sustained chemical analyses in history. The sample was 600 gallons (2.5 m³) of a Midcontinent crude petroleum from Ponca City, Oklahoma (courtesy of the Maryland Oil Company, later part of Continental Oil Company) selected to be intermediate in composition in terms of then known petroleum from different fields. The sample was taken in 1928 and by 1952 one hundred thirty compounds had been isolated, most of them identified and their relative abundances determined.

The number of compounds actually found in significant amounts is a small fraction of those for which

physical properties would place them in the ranges analyzed. As an example, of perhaps 500 petroleum compounds in the boiling range 40 to 180 °C, 92 were isolated. These constitute 82 percent of the gasoline fraction; so the remaining >400 compounds must have been present in relatively small amounts.

The analysis of this single petroleum was unique at the time it was being done. We shall not here attempt to place this in perspective in terms of current (1975) knowledge of the composition of petroleum. While we have not seen extensive analyses of these types reported, we would presume that the highly sophisticated analytical techniques now available and in the hands of private institutions have led to extensive additions to information about the composition of petroleum from various fields.

3.3. Experimental Thermochemistry of Pure Hydrocarbons

The availability of so many highly purified hydrocarbons as a result of API Project 6, combined with highly developed calorimetric techniques and instruments already available, presented a unique opportunity to carry out definitive experimental determinations of the energies of combustion of the compounds and to derive enthalpies of formation. An extensive series of investigations was carried out by Rossini and later by Prosen and colleagues, working with Rossini: over one hundred different hydrocarbons were studied in the period 1931-1955. In approximately the same period Jessup, working independently, measured several hydrocarbons from other sources. The hydrocarbons ranged from CH₄ to C₁₆H₃₄ (n-hexadecane). Measurements on n-heptane by Prosen and Rossini [38] may be taken as a typical example. As a result of twenty experiments $\Delta H_c(25\text{ }^\circ\text{C})$ was found to be 4817.14 kJ \cdot mol⁻¹ (4816.35 int kJ \cdot mol⁻¹) with standard deviation of the mean of 0.004 percent and an estimated uncertainty (95 percent confidence limits) of 0.018 percent. Typical uncertainties in enthalpies of formation were \sim 1 kJ \cdot mol⁻¹.

The necessary techniques for carrying out the accurate experimental calorimetric studies were developed at NBS. Dickinson in a classical paper [39] described an accurate bomb calorimeter and how it had been tested for possible sources of error. This calorimeter design, with minor modifications over the years, was used for all of the studies described above. The Dickinson calorimeter is pictured in cross section in figure 4. One of the calorimeters identified by inventory number in [39] is in the possession of the NBS Museum. The calorimeter was used in the very earliest work for certification of standard substances for calibrating bomb calorimeters. The calorimeter itself consisted simply of a stirred water container in which a reaction vessel was immersed; the assembly was surrounded by and isolated from a constant temperature (± 0.001 K) jacket.

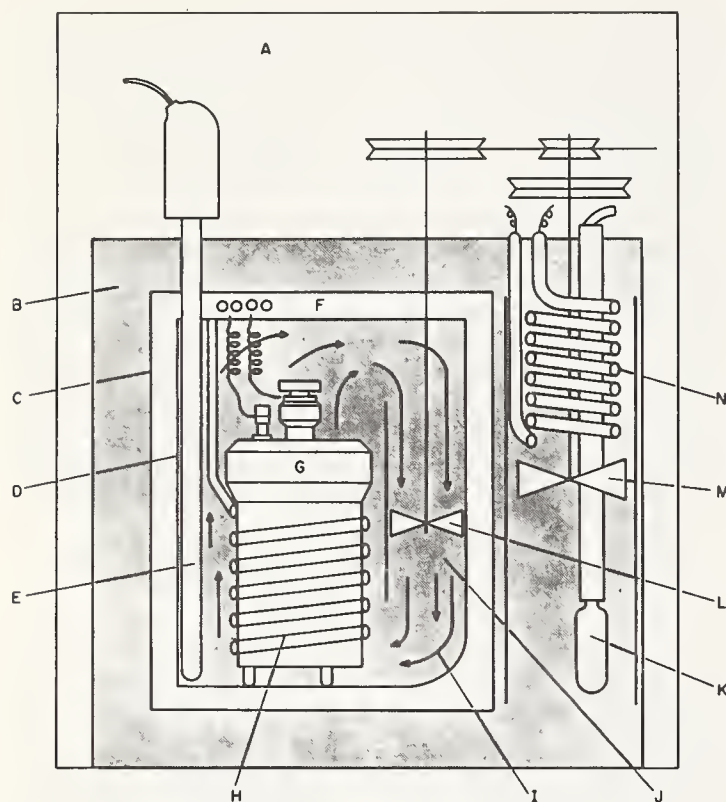


FIGURE 4. Dickinson Calorimeter Cross Section.

Parts of the calorimeter are lettered as follows: A, thermostated air-box (optional); B, stirred water jacket; C, inner wall of jacket; D, outer wall of calorimeter vessel; E, platinum-resistance thermometer; F, air space; G, calorimeter bomb; H, electrical calibration heater; I, arrows showing direction of water circulation; J, stirring well of calorimeter vessel; K, jacket temperature sensor; L, calorimeter-vessel stirrer; M, jacket stirrer; N, jacket heater.

The measurements were precision measurements requiring the best thermometry available, uniform operating conditions, and extreme care in sample preparation, weighing, characterization of sample, establishment of reaction vessel contents, estimation of amounts and states of reaction products, and reduction of the data. Both constant volume (bomb) and constant pressure (flow) reactions were determined, depending upon the volatility of the combustion sample. The procedures were described in some detail

in accounts scattered through many papers in the literature. Rossini [40b], Coops, Jessup, and Van Nes [40a] and Prosen [40c] summarized the procedures. The elaborate procedure for reducing data for the reaction as observed in the calorimeter to the value for the isothermal process with the substances in their standard thermodynamic states was developed at NBS by E. W. Washburn [41] and is known in practice as "the Washburn Correction."

For some of the combustion work on commercial fuels at NBS (see above), which was done in the same calorimeters, but with somewhat less attention to refinements of the measurements, Jessup [42] prepared a detailed guide to procedures. This is perhaps the most concise guide available for measurements on commercial fuels, and formed the basis of an ASTM Standard [43] suitable for measurements with inaccuracies of 0.1 percent or less.

3.4. Standard Reference Data on Pure Hydrocarbons

Another very important project carried out at NBS was API Project 44. This project was initiated in 1942 to compile tables of selected values of properties of hydrocarbons. The program involved collaboration of scientists at NBS and the University of California. The principal scientists involved were F. D. Rossini, Director, K. S. Pitzer, W. J. Taylor, J. P. Ebert, M. G. Williams, H. G. Werner, C. W. Beckett (Berkeley, CA), J. E. Kilpatrick, B. Epstein, L. Arnett, R. Braun. Regular NBS staff who consulted on the project were C. S. Cragoe, E. J. Prosen, and D. D. Wagman. The results of the investigations appeared periodically as technical articles (many in NBS Journal of Research), as looseleaf tables of data and spectrograms and as bound volumes. All tables prepared as of 1947 appeared in an NBS Monograph [44]. This project continued at NBS until June, 1950, when it was transferred to the Carnegie Institute of Technology, to remain under Rossini's guidance until 1960. The work continues at present (1975) under the leadership of B. J. Zwolinski in the Thermodynamic Research Center at Texas A and M University.

The above group of investigators made a very careful compilation of selected values of physical and thermochemical properties of hydrocarbons. For this work, all pertinent original data in the literature, and all available unpublished data were appraised critically; values of given properties were correlated with temperature, pressure, and molecular structure; original calculations of thermodynamic and physical properties were made as necessary; "best" values of the properties were selected and tabulated in convenient form; and some of the procedures and calculations were published. The properties reviewed are listed in table 3. As of 1947, a total of 347 pages of tables had been prepared. In addition to compilations of the above data, infrared and ultraviolet spectrograms for hydrocarbons and related compounds were collected.

The classes of compounds for which data were tabulated in reference [44] are listed in table 4.

TABLE 3. *Physical properties of hydrocarbons evaluated and tabulated in API Project 44 [44].*

1. boiling point and pressure coefficient of the boiling point
2. refractive index
3. density and specific gravity
4. freezing point
5. molar volume
6. molar refraction and specific refraction
7. specific dispersion
8. refractivity intercept
9. viscosity
10. critical constants
11. P-V-T relations
12. vapor pressures
13. enthalpy and entropy of vaporization
14. enthalpy of combustion
15. enthalpy
16. Gibbs energy function
17. molar heat capacity
18. enthalpy of formation
19. equilibrium constant of formation
20. enthalpy and entropy of fusion
21. cryoscopic constants
22. enthalpy of transition

TABLE 4. *Classes of hydrocarbons and related compounds for which thermodynamic and physical properties data were tabulated in API Project 44 [44].*

- 00 O, H, N, C
- 0 O₂, H₂, OH, H₂O, N₂, NO, C, CO, CO₂
- 1 Paraffins, C₁ to C₅ (8 substances)
- 2 Paraffins, C₆ to C₇ (14 substances)
- 3 Paraffins, C₈ (18 substances)
- 4 Paraffins, C₉ (35 substances)
- 5 Alkylbenzenes, C₆ to C₉ (14 substances)
- 6 Alkylcyclopentanes, C₅ to C₇ (8 substances)
- 7 Alkylcyclohexanes, C₆ to C₈ (10 substances)
- 8 Monoolefins, C₂ to C₆ (29 substances)
- 9 Monoolefins, C₇ (36 substances)
- 10 Monoolefins, C₈ (92 substances)
- 11 Diolefins, C₃ to C₆ (32 substances)
- 12 Acetylenes, C₂ to C₅ (7 substances)
- 13 Styrenes, C₈ to C₉ (4 substances)
- 14 Alkylbenzenes, C₁₀ (22 substances)
- 15 Alkylcyclopentanes, C₈ (15 substances)
- 16 Alkylcyclohexanes, C₉
- 17 Paraffins, C₁₀
- 18 Alkylcyclopentenes, C₅ to C₇
- 19 Alkylcyclohexenes, C₆ to C₈
- 20 Normal paraffins, C₁ to C₂₀ (20 substances)
- 21 Normal alkylbenzenes, C₆ to C₂₂ (17 substances)
- 22 Normal alkylcyclopentanes, C₅ to C₂₁ (27 substances)
- 23 Normal alkylcyclohexanes, C₆ to C₂₂ (17 substances)
- 24 Normal monoolefins (1-alkenes), C₂ to C₂₀ (19 substances)
- 25 Normal acetylenes (1-alkynes), C₂ to C₂₀ (19 substances)

The published calculations and correlations included: Gibbs energies and equilibria of isomerization of isomeric hydrocarbons [45], enthalpies, equilibrium constants, and Gibbs energies of formation of selected hydrocarbons as functions of temperature to 1000 or 1500 K [46]; normal coordinate analyses [47] of hydrocarbon molecules. (References are to selected examples.)

The presence of the resulting large amounts of numerical data on homologous series of compounds and compounds showing well defined compositional and structural variations, such as the isomeric forms, the presence of multiple bonds, and cyclization, has encouraged many individual attempts in NBS and

elsewhere to devise correlations. Generally these correlations have as their primary goal sufficient understanding of the effects of these structural and compositional variations to permit estimation of the properties of other substances not measured. Done properly and carefully, such correlations can frequently yield values more reliable than many investigators can measure them. They are sometimes used to screen measured data in a search for errors. The correlations also assist in establishing theoretical models relating the structure and properties of materials.

An example of a correlation derived from measured values is found in Prosen and Rossini [48], [48a]. See also Taylor, Pignocco, and Rossini [48b]. The values for the enthalpies of combustion of the liquid normal paraffins above pentane for reference [44] were obtained by fitting an equation linear in the number of carbon atoms, n , to the experimental data which were available for thirteen substances of which hexadecane has the largest molecule. The resulting equation

$$-\Delta H_c(298.15 \text{ K}) / \text{kcal} \cdot \text{mol}^{-1} = -57.909 + 157.443 n \text{ with an uncertainty of } (0.1647 - 0.03902 n + 0.00268 n^2)^{1/2}, n > 5$$

$$\{ -\Delta H_c(298.15 \text{ K}) / \text{kJ} \cdot \text{mol}^{-1} = -242.291 + 658.741 n \text{ with an uncertainty of } (2.883 - 0.6831 n + 0.0469 n^2)^{1/2}, n > 5 \}$$

was used to calculate the unmeasured values for normal paraffins through n-eicosane. Analogous correlations of other properties were also used in completing the tables of reference [44].

The reason for putting estimated data in the tables is to provide the working technologist with a value selected by an experienced observer rather than leave him to cope alone with unknown values. The scientist interested in testing a new correlation scheme should be wary to seek out only measured data and not base his test on smoothed or other estimated data, as some have done unwittingly.

The configurational analysis of the substituted cyclohexanes by Pitzer and Beckett [49] showed that at ordinary temperatures substantially all the molecules are in the chair configuration of the cyclohexane nucleus, and described in detail the resulting tautomeric forms. One interesting result of this analysis was that among the 1,3-dimethylcyclohexanes, the isomer having the lower energy content must be the "cis" isomer and the isomer having the higher energy content must be the "trans" isomer. This designation [50] reversed the previous labeling of these isomers.

Another interesting illustration of the results of the statistical thermodynamic calculations made on the hydrocarbons is seen in figure 5. This shows the mole fractions of the six methylstyrenes at chemical equilibrium as functions of temperature. There is a significant decrease in alpha-methylstyrene and compensating increases in beta-methylstyrene and ortho-methylstyrene as the temperature rises above 300 K.

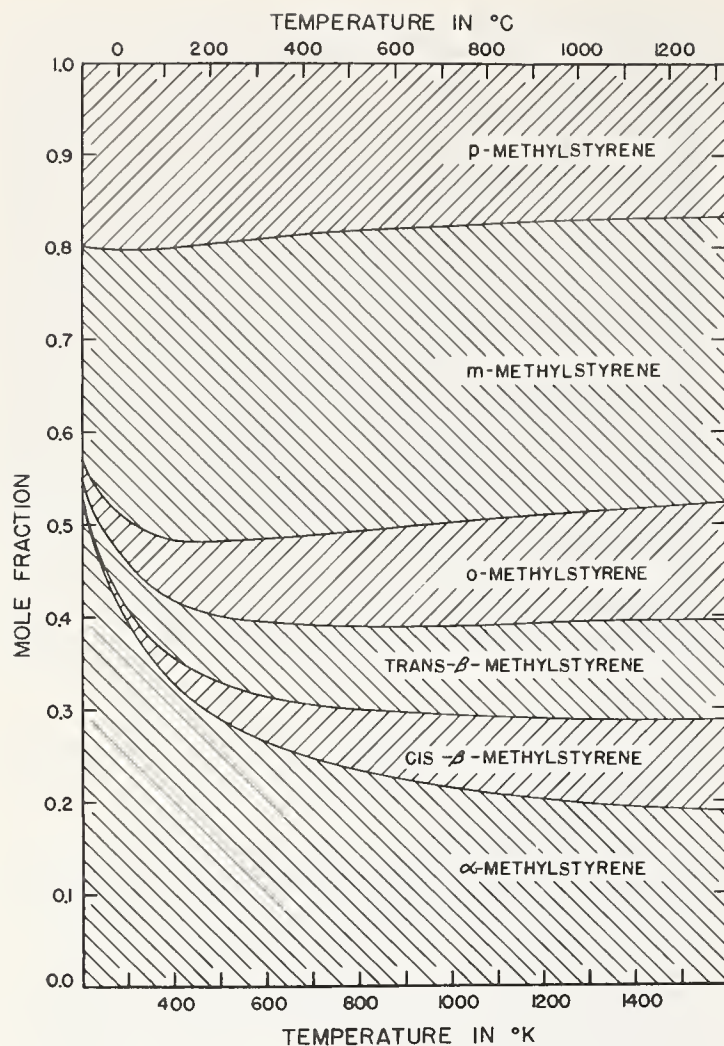


FIGURE 5. *Equilibrium concentrations of the six methylstyrenes.*

The scale of ordinates measures the relative amount (mole fraction) and the scale of abscissas gives the temperature in kelvins, and degrees Celsius. The vertical width of a band at a given temperature measures the mole fraction of the given isomer present at equilibrium with all of its other isomers in the gaseous state.

3.5. Other Work on Petroleum Fuels

In addition to the work on petroleum and petroleum components as materials, there was a long substantial program on engine fuels, which was primarily carried out by F. L. Howard and his colleagues in the Automotive Section (Heat and Power Division). The work of this section was complex and dealt with much more than the fuels themselves, including also the interactions of the fuels with the automobile engine.

Topics with which they dealt included: knock ratings of gasolines, cetane ratings of diesel fuels; fouling of spark plugs; kinetics and mechanisms of the combustion process in flames and in detonations of hydrocarbons; synthesis and characterization of special hydrocarbons; analysis and testing of hydrocarbon mixtures.

A major and somewhat analogous study of the lubricant fractions of petroleum were studied by O. C. Bridgeman, S. A. McKee and their associates in the Heat and Power Division. Rheology of petroleum and viscosity standards were intensively studied.

Other work which may be mentioned was done dur-

ing World War I. Studies were made of aviation gasoline and substitute or mixed fuels [61a], and of the recovery of toluene from natural gas [61c].

4. Solid Fuels — Thermodynamic Studies on Coal, Coke, Graphite, Diamond, and Substances Related to Their Combustion

Coal as a mineral hydrocarbonaceous fuel and its component compounds have received comparatively little attention at NBS as compared to gaseous and liquid fuels.

In addition to the reference materials for coal discussed later, however, one subject closely related to coal will be mentioned here. This is the studies of the thermodynamic properties of graphite and diamond. Coal as a hydrocarbonaceous material is, of course, clearly distinguishable from graphite. Nevertheless, coal itself has structural features similar to graphite; and when coal is carbonized by coking or other charring processes these similarities are enhanced.

For this reason the thermodynamic properties of graphite are important particularly for the future uses of coal, in which its chemical transformation to gaseous and liquid fuels on a large scale is contemplated. The thermochemical equilibria involved may have to refer to differences of coal from graphite as a reasonable baseline, because of the variable character of coal and its chars.

For another reason, graphite is important not only for coal but for liquid and gaseous hydrocarbon fuels as well. The process of combustion of all of these fuels leads to carbon dioxide as a principal product, and the energies of formation and molecular binding energies of all the hydrocarbons depend upon the combustion energy of graphite which is the reference state of the element carbon.

The experimental studies on elemental carbon at NBS include: (1) the heat capacity of graphite from about 1200 K to about 2600 K [51a] (West and Ishihara) and 1500 K to 3000 K [51b] (Cezairliyan); (2) the energy of combustion of diamond [52] (Jessup); (3) the energy of combustion of graphite [52] (Jessup, also Prosen and Rossini).

The experimental studies on the energy of combustion of graphite were carried out in an informal joint experimental program with the Coal Research Laboratory of the Carnegie Institute of Technology. In this program the NBS work was complemented by a careful study of the combustion energies of anthracite cokes and of artificial and natural graphites, by Dewey and Harper [53] of the Coal Research Laboratory. Jessup also measured the combustion energy of diamond at this time.

Prior to this research, because of the variability of the data on graphite, the thermodynamic reference state for carbon had been taken as diamond (Bichowski and Rossini) [59]. However, the work of Dewey and Harper and of Jessup showed that, by a simple purification, either natural or artificial graphite can be produced in a thermodynamically reproducible

form. Because of its greater accessibility, ease of handling, and lower cost, graphite was then chosen as the reference state for carbon. As a result of the work mentioned above and of the measurements on graphite a few years later by Prosen and Rossini, the enthalpy of formation of $\text{CO}_2(\text{g})$ from graphite has been taken to be $393.513 \text{ kJ} \cdot \text{mol}^{-1}$ ($-94.0518 \text{ kcal/mol}$) [54]. See for instance Wagman, et al. [55, 56] and Sunner [57].

Using data largely obtained from NBS experimental work, Wagman, et al. [55] calculated enthalpies, Gibbs energies and equilibrium constants of some of the most important reactions in fuel combustion: those involving O_2 , H_2 , H_2O , C , CO , CO_2 , and CH_4 . Eight reactions were treated in the reference cited.

Of considerable interest still today is the extensive work on anthracite coke by Dewey and Harper. Among other information they derived was the variation of energy of combustion with hydrogen content. The variations in hydrogen content were created by different coke formation temperatures ranging from 900 to 1300 °C. The absorptive capacities for carbon dioxide were also determined. An essentially linear relationship is observed between heating value and hydrogen content, but no credible relationship was found between heating value and absorptive capacity.

One final mention can be made of the NBS work on graphite. For some years a study was made of the energetic effects of radiation damage in graphite exposed to nuclear radiation, under arrangements initiated by F. D. Rossini of NBS with Farrington Daniels of the Manhattan Project at the University of Chicago. This work (unpublished) was carried out by E. J. Prosen, W. A. Fraser, J. I. Minor, Jr., W. H. Johnson, and others. The measurements were made by combustion calorimetry. The results are of interest to coal and coke technology because of the fact that radiation damage results in rupturing the regular graphite structure and introduces changes in the direction of the much disordered structures of coal, coke, and char. The effects observed in some cases amounted to as much as $1.75 \text{ kJ} \cdot \text{g}^{-1}$ ($21 \text{ kJ} \cdot \text{mol}^{-1}$).

5. Standard Reference Materials for Hydrocarbon Fuels

Over the years there have been developed a number of hydrocarbons or materials needed for testing fuels.

5.1. Hydrocarbon Blends

Eight mixtures (SRM 592–599) of pure hydrocarbons representative of those occurring in hydrocarbon fuels and blending stocks are available. These blends are primarily for use in calibrating mass spectrometers. However, they may be useful in other spectrometric instruments or gas chromatographic techniques. They each typify either a virgin naphtha or a catalytically cracked naphtha, and each is made up of measured amounts by volume of five to nine hydrocarbons selected from the NBS Standard Samples of Hydrocarbons of one of the following types: C_7

paraffins, C_8 paraffins, C_7 cycloparaffins, C_8 cycloparaffins.

5.2. Reference Fuels

Two reference fuels, n-heptane and 2,2,4-trimethylpentane (isooctane) are issued as SRM 1815 and 1816, respectively. They are intended for use by manufacturers of reference fuels for maintaining the integrity of standards for knock testing of motor and aviation fuels. They are certified as to density, refractive index, freezing point, distillation (50 percent recovery temperature and temperature range of 80 percent minus 20 percent recovery), and zero lead content. The purities were estimated on the basis of freezing points and chromatographic analysis.

5.3. Lead in Reference Fuels

Three reference fuels (SRM 1636, 1637, 1638) are intended for use in calibration of instruments and techniques for the analysis of lead in gasoline. The samples consist of 12 ampoules of a material with accurately measured lead concentration in one of the nominal ranges of lead content, 0.03, 0.05, 0.07, and 2.0 $\text{g} \cdot \text{gal}^{-1}$ (about 8, 13, 18, and 53 $\text{mg} \cdot \text{dm}^{-3}$ respectively). The three reference materials differ in the distribution of ampoules containing the four lead concentrations.

5.4. Sulfur in Fuel Oil

Four reference materials are intended as analytical standards in the determination of sulfur in fuel oils. They are commercially available oils containing sulfur in varying amounts. The sulfur contents are certified. The sulfur was determined as sulfate after combustion in an oxygen bomb reaction. Three of the samples (SRM 1621, 1622, 1623) are residual fuel oils, containing sulfur/wt percent, 1.05 ± 0.02 ; 2.15 ± 0.01 , and 0.268 ± 0.004 , respectively. One of the samples (SRM 1624) is a distillate fuel oil containing sulfur/wt percent, 0.211 ± 0.004 .

5.5. Heating Values of Hydrocarbon Fuels

(1) *Methane*. A special sample of pure methane was analyzed for the Institute of Gas Technology for use in maintaining the integrity of standards for heating value of natural gas. The sample contains methane; the impurities in mole percent are: ethane, 0.04 ± 0.02 ; nitrogen, 0.0017 ± 0.0004 ; oxygen, 0.0002 ± 0.0002 ; carbon dioxide, 0.006 ± 0.002 . Impurities were determined by mass spectrometry and gas chromatographic techniques. The heating value, in Btu per standard cubic foot, is certified for the real gas as 1014.9 ($37.814 \text{ MJ} \cdot \text{m}^{-3}$) on a dry basis and 997.2 ($37.155 \text{ MJ} \cdot \text{m}^{-3}$) on a water saturated basis, with an uncertainty of 0.4 ($0.014 \text{ MJ} \cdot \text{m}^{-3}$).

(2) *Benzoic acid*. Not a hydrocarbon, benzoic acid is specified in standard methods of test for liquid and solid fuels as the test substance for calibrating the bomb calorimeter used in the test. The benzoic acid reference material (SRM 39i) is a highly purified material having a certified energy of combustion in

the standard bomb process (prescribed conditions), $\Delta U_{\text{B}}^\circ/\text{kJ} \cdot \text{g}^{-1}$ is 26.434 ± 0.003 . It is recommended, not only for tests of commercial fuels but also for research on the combustion energies of pure substances.

(3) *2,2,4-trimethylpentane*. Commonly called iso-octane, this reference material (SRM 217b) is certified as to energy of combustion in the standard bomb process (prescribed conditions), $\Delta U_{\text{B}}^\circ/\text{kJ} \cdot \text{g}^{-1}$ is 47.712 ± 0.005 . It is intended for use in petroleum fuel testing to verify procedures for handling volatile fuels.

6. Coal Reference Materials

Four reference coals are provided as standard samples for use in analysis of elements which create pollution problems when coal is burned.

6.1. Trace Mercury in Coal

Trace mercury in coal (SRM 1630) is a suitably prepared commercially available coal, provisionally certified to contain mercury/parts per million by weight, 0.13. This value was obtained by neutron activation analysis, and verified by flameless atomic absorption spectrometry. Selenium content is also given.

6.2. Sulfur in Coal

Sulfur in coal (SRM 1631) is three samples of low-volatile bituminous coals suitable prepared and certified to contain sulfur/percent by weight; 0.546 ± 0.003 ; 2.016 ± 0.014 ; 3.020 ± 0.008 ; and ash/percent by weight; 5.00 ± 0.02 ; 14.59 ± 0.09 ; 6.17 ± 0.02 . The sulfur and ash tests were supported by tests carried out in five other laboratories. Moisture was also determined but lack of homogeneity in the determinations prevented certification.

6.3. Trace Elements in Coal

Trace elements in coal (SRM 1632) is certified for iron, manganese, zinc, vanadium, lead, chromium, copper, nickel, arsenic, selenium, uranium, thallium, cadmium, mercury, based on at least two methods of analysis for each element. The elements are listed above in the order of relative abundance. The abundances/ $\mu\text{g} \cdot \text{g}^{-1}$ range from manganese, 40, to mercury, 0.12. For iron, abundance/ $\mu\text{g} \cdot \text{g}^{-1}$ is 8700. Other elements tested but not certified were: titanium, cobalt, silicon, thorium, beryllium, silver, tellurium.

6.4. Trace Elements in Coal Fly Ash

Trace elements in coal fly ash (SRM 1633) is certified for manganese, zinc, vanadium, lead, chromium, copper, nickel, arsenic, uranium, selenium, cadmium, mercury, based on at least two methods of analysis for each element. The elements are listed above in order of relative abundance. The relative abundances/ $\mu\text{g} \cdot \text{g}^{-1}$ range from manganese, 493, to mercury, 0.14. Other elements tested but not certified were: potassium, strontium, rubidium, cobalt, thorium, beryllium, thallium.

7. Conclusion

In retrospect, it will be clear that the extensive work done on hydrocarbons at the NBS has not been covered completely in this article. For instances of work not covered adequately in this review, we may refer to the hydrocarbon synthesis work at the NBS in the period 1937–1953 involving F. L. Howard, T. W. Mears, and D. B. Brooks. See, for a few references, Cochrane's history of the National Bureau of Standards [58].

There are other aspects in which the question of scope must be brought in: thus petroleum products are used not only for fuel but for lubrication, and here a whole new class of work may be brought in, as was mentioned only briefly. Similarly the combustion of fuels involves kinetics and reaction mechanisms, whole areas that have had an important impact on hydrocarbon fuels and which are not touched here. Key names of NBS workers in these areas are O. C. Bridgeman, H. S. White, S. A. McKee, J. D. Swindells, W. J. Levedahl, and R. E. Ferguson.

Additional aspects of hydrocarbons used for fuel are the side effects of hydrocarbon usage: atmospheric pollution by hydrocarbons and engine exhaust products, pollution of streams and the oceans by spillage and the associated problems of modeling fate and effect. None of these are touched here. In this area the most recent work at NBS has been done by S. Wasik.

NBS has cooperated with universities, the Bureau of Mines, Army, Navy and Air Force, NASA and industrial laboratories during the past 75 years. As new national programs emerge this cooperation is expected to continue, as for instance in the preparation of a National Academy of Sciences report on needs for thermodynamic data in the national energy program (1974–1975) [60].

This historical review was started as a small part of a review of much broader scope intended to form a short chapter on "Seventy-five years of materials research at NBS." It soon became apparent that if the review was to indicate fairly the scope and complexity of the NBS work on hydrocarbons related to their use as fuels, it would grow considerably beyond the initial length planned.

A concise statement outlining a small portion of the work was prepared and appears elsewhere as originally planned. However, the author felt that the content of the full review was of sufficient general interest, particularly in the light of current related problems in national energy resources, that it should be made public, rather than resting in the technical files. This feeling was strengthened by the realization that the historical path was being gradually dimmed by dispersal of scientists having intimate knowledge of the details. Hence, the review was completed in this form and is published as a separate document. Though not complete in many respects, we hope that it presents a satisfactory broad outline of the NBS work on hydrocarbons and sufficient hints of work not covered

in detail to provide later historians with clues that will enable definitive histories to be written.

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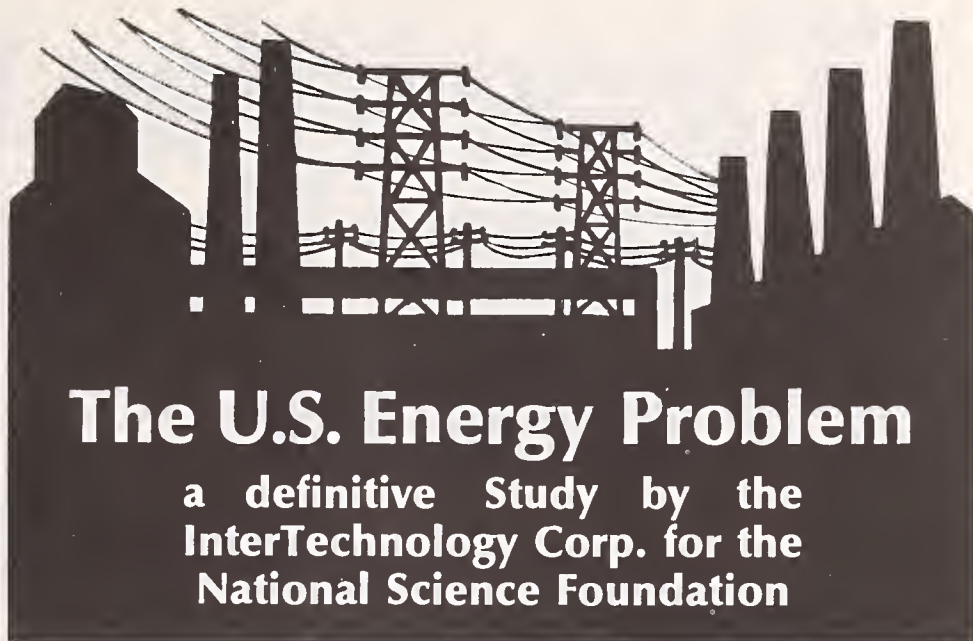
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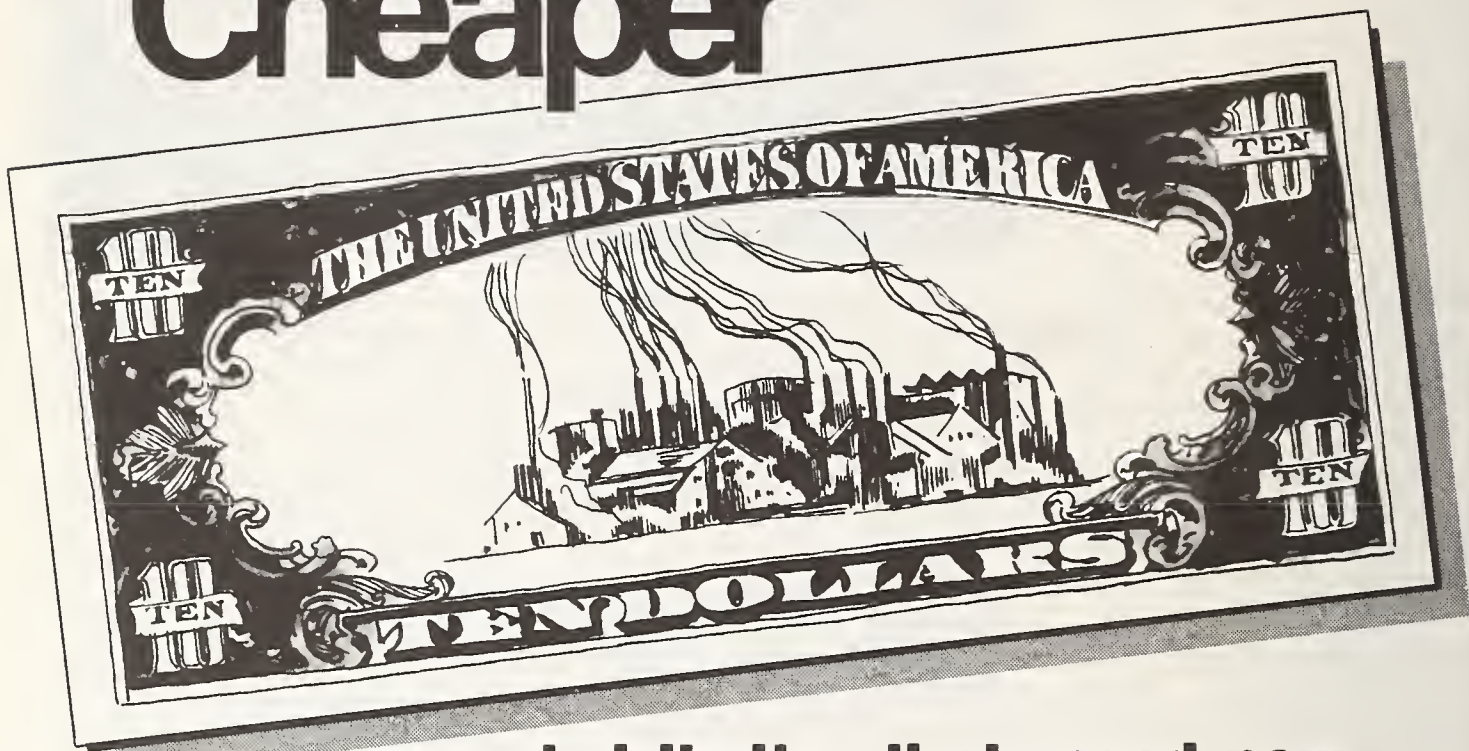
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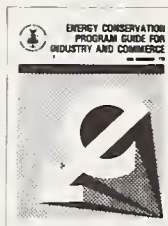
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