From the deviations between the experimental values for a_1 and those calculated by Equations 1 and 2, it is calculated that the probable error of the equation values for vapor pressure is ±0.008 mm. of mercury, with a 95% confidence limit of 0.025 mm. of mercury.

Three empirical equations are required to represent the viscosities over the range of compositions studied.

$$\eta = \eta_w + 0.223\, m_{AM} + 0.0178\, m^2_{AM} + 0.5\, m_M + 0.05\, m_M m_{AM} + 0.0138\, (m_M m_{AM})^2 \quad (3)$$

$$(m_{AM} = 0.2 \text{ to } 2.7)$$

$$\eta = \eta_w + 0.206\, m_{AM} + 0.0275\, m^2_{AM} - 0.00074\, m^3_{AM} + 0.5\, m_M + 0.05\, m_M m_{AM} + 0.0138\, (m_M m_{AM})^2 \quad (4)$$

$$(m_{AM} = 2.7 \text{ to } 5.5)$$

$$\eta = \eta_w + 0.1891\, m_{AM}^{1.33} + 0.5\, m_M + 0.05\, m_M m_{AM} + 0.0138\, (m_M m_{AM})^2 \quad (5)$$

$$(m_{AM} = 5.5 \text{ to } 18)$$

When m_M is zero, Equations 3, 4, and 5 become identical to equations for the viscosity of pure phosphoric acid solutions (*6*). For the present use, however, the viscosity equations are applied in concentration ranges that differ somewhat from those originally specified, and the empirical constants are rounded to correspond with the experimental data for the three-component system.

The probable error of viscosities calculated by use of Equations 3, 4, and 5, compared to the experimental values, is ±0.05 centipoise, with a 95% confidence limit of ±0.148 centipoise.

The activity of water in the solution has thermodynamic significance and is useful in evaluating the thermodynamics of the three-component system. In this connection, a study of the activity of calcium ions in the calcium oxide–phosphoric oxide–water system is needed.

The viscosity data are useful in engineering calculations on the handling of calcium phosphate solutions. They also are needed in theoretical calculations relating to diffusion of calcium phosphate solutions.

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Net Heat of Combustion of Aviation Gasoline and Its Correlation with Other Properties

GEORGE T. ARMSTRONG, RALPH S. JESSUP, AND THOMAS W. MEARS
National Bureau of Standards, Washington, D. C.

The work described was undertaken to determine the feasibility of finding for 115/145 grade aviation fuels relations between net heat of combustion and aniline-gravity product similar to those found by Jessup and Cragoe (*6*) and Rothberg and Jessup (*11*) for AN-F-28 and AN-F-58 aircraft fuels, and by Jessup and Cogliano (*5*) for JP-4 and JP-5 fuels. The previous work had indicated that it is not possible to make a reliable estimate of the heat of combustion of a petroleum fuel from its aniline-gravity product alone, but that such an estimate can be made for members of a definite class of fuels.

The data at present available show clearly that net heat of combustion of petroleum products is not a function of aniline-gravity product alone, but must depend to some extent upon some other variable or variables; thus, data on many pure hydrocarbons are not in accord with any such relation, the individual fuels of a given type depart from the equation for that type by considerably more than the experimental error of measurement, and different relations between aniline-gravity product and net heat of combustion are obtained for different types of fuels. It appears, therefore, that to develop a satisfactory method of estimating net heat of combustion it will be necessary to investigate the effect of other factors in addition to aniline-gravity product. In particular, it seems desirable to make an approximate determination of composition in terms of hydrocarbon type. The work described in this report, therefore, includes measurements of this type.

FUELS INVESTIGATED

In deriving an equation to represent net heat of combustion as a function of another measured property such as the aniline-gravity product, the fuels selected for measurement can be regarded as a sample from a population of fuels of similar type. To make valid inferences about the population, the fuels selected must constitute a representative sample—i.e., the fuels of the sample should have characteristics typical of the specified population. To ensure a representative sample of any given type of fuel, the following minimum requirements were imposed upon the samples to be used:

That fuels be well distributed over the range of net heat of combustion of interest, and include a number of samples that fail to meet the specified minimum requirements as to net heat of combustion or aniline-gravity product. In all other respects, as far as possible the fuels to be tested comply with specified requirements.

That samples of fuels be obtained from all producers of the type of fuel to be investigated, and the number of samples from each producer be as nearly as possible proportional to the amount of such fuel he produces per year.

That fuels include representatives of all current refinery methods, and be so identified.

That inspection data be supplied for each sample of fuel to be tested, together with other available data, such as data on composition.

Arrangements for selecting samples in accordance with these requirements were made by the Wright Air Development Center. To ensure that the heats of combustion of the samples available should extend below the minimum required by the specifications, a small number of samples of the related aviation fuel, 100/130 grade gasoline, were requested in addition to the 115/145 fuels. A total of 212 fuel samples—26 samples of grade 100/130 and 186 samples of grade 115/145 fuel—were supplied to the National Bureau of Standards by individual refiners, and each was assigned an NBS sample number. The producers of the fuels and the number of samples supplied by each are listed in Table I. From these fuels were selected for detailed study 40 samples, consisting of 7 grade 100/130 and 33 grade 115/145 fuels which, on the basis of data furnished by the suppliers, were considered to constitute a representative sample of the population of interest, and to cover a sufficient range of heats of combustion to permit a test of the possibility of correlating heat of combustion with other properties of the fuels. The study of these 40 fuels forms the basis of the findings reported here. In the selection of the fuels for study, assistance was provided by the Statistical Engineering Laboratory of the National Bureau of Standards.

EXPERIMENTAL MEASUREMENTS

Net Heat of Combustion. Heats of combustion of the 40 gasoline samples were measured in a bomb calorimeter. The calorimeter and accessory apparatus have been described (*7*). In making the measurements, the samples were enclosed in thin-walled glass bulbs of the type used in previous experiments with volatile fuels. The bulbs were filled with a hypodermic needle (No. 27) and syringe. The end of the hypodermic needle was cut off square to permit extraction of air bubbles which occasionally were trapped within or just below the narrow neck of the bulb. The bulbs could be filled much more easily and quickly than by methods used previously, and with very much less chance of change in the sample by evaporation.

The calorimeter was calibrated by burning benzoic acid standard sample 39g. In this calibration the value 26433.8 absolute joules per gram mass (weight in vacuum) (*3, 4, 12*) was taken as the heat of combustion of benzoic acid under the standard conditions of the bomb process. Six calibration measurements exhibited a standard deviation of the mean of 0.017% of the energy equivalent of the calorimeter.

Heats of combustion of the gasolines were made in terms of absolute joules per gram weight of fuel in air against brass weights. They were converted to British thermal units per pound weight using the factor 1 absolute joule per gram = 0.429917 B.t.u. per pound.

A minimum of two acceptable measurements was made on each sample. Measurements were rejected if there was evidence of incomplete combustion, such as an odor of unburned gas, the presence of unburned carbon upon opening the bomb, or other evidence of experimental failure. If two acceptable experiments did not agree within about 0.05%, additional measurements were made.

Table I. Suppliers of Aviation Gasoline Samples

Producer and Refinery	Samples Supplied 100/130	Samples Supplied 115/145
California Oil Co.,		
Perth Amboy, N. J.	1	....
Cities Service Refining Corp.		
Lake Charles, La.	1	5
Continental Oil Co.		
Westlake, La.	....	10
Ponca City, Okla.	....	7
Cosden Petroleum Corp.		
Big Spring, Tex.	....	1
Eastern States Petroleum Co.		
Houston, Tex.	1	....
Esso Standard Oil Co.		
Baton Rouge, La.	1	....
General Petroleum Corp.		
Los Angeles, Calif.	1	....
Gulf Oil Corp.		
Philadelphia, Pa.	1	....
Port Arthur, Tex.	....	15
Humble Oil and Refining Co.		
Baytown, Tex.	1	4
Magnolia Petroleum Co.		
Beaumont, Tex.	1	4
Phillips Petroleum Co.		
Sweeney, Tex.	2	....
Borger, Tex.	1	12
Richfield Oil Corp.		
Watson Refinery	1	17
Shamrock Oil and Gas Corp.		
Sunray, Tex.	1	....
Shell Oil Co.		
Wood River, Ill.	1	3
Wilmington, Cal.	....	4
Houston, Tex.	....	1
Norco, La.	....	2
Sinclair Refining Co.		
Sinclair, Wyoming	1	....
Corpus Christi, Tex.	....	3
Houston, Tex.	....	9
Sacony-Vacuum Oil Co.		
Paulsboro, N. J.	1	....
Augusta, Kan.	1	....
Standard Oil Co. (Indiana)		
Whiting, Ind.	2	2
Wood River, Ill.	1	....
Neodesha, Kan.	....	2
Standard Oil Co. (Ohio)		
Toledo, Ohio	1	2
Standard Oil Co. of California		
Richmond, Calif.	1	7
El Segundo, Calif.	1	7
Standard Oil Co. of Texas		
El Paso, Tex.	1	....
Sun Oil Co.		
Marcus Hook, Pa.	....	17
Texas City Refining, Inc.		
Texas City, Tex.	....	4
Texas Co.		
Port Arthur, Tex.	....	15
Wilmington, Calif.	....	8
Tide Water Associated Oil Co.		
Avon, Calif.	1	15
Union Oil Co.		
Los Angeles, Calif.	....	7
Utah Oil Refining Co.		
Salt Lake City, Utah	1	3
Total	26	186

The results were obtained as the gross heat of combustion at constant volume, Q_v (gross), the heat liberated when unit weight of fuel is burned in a constant volume bomb, the products of combustion being gaseous carbon dioxide and liquid water. The measurements were made at 28°C. and were adjusted to 25°C. by the procedure outlined by Rothburg and Jessup (*11*). Net heat of combustion at constant pressure, Q_p (net), was calculated from Q_v (gross) using Equation 1 of (*6*)

$$Q_p \text{ (net) (B.t.u./lb.)} = Q_v \text{ (gross)} - 91.23 \text{ (\%H)} \qquad (1)$$

In this relation Q_p (net) is the heat liberated when unit weight of fuel is burned at a constant pressure of 1 atm. to form gaseous carbon dioxide and gaseous water.

Q_v (gross) and Q_p (net) found from each measurement are listed in Table II, in which they are grouped by NBS sample number and fuel grade. The values of Q_p (net) are also shown in Figure 1, plotted as a function of aniline-gravity product, and with fuel grade indicated. The measurements were made in series, designated as a, b, and c. The run numbers in Table II designate the relative sequence of the measurements within each series, but do not form a complete set of numbers, because run numbers were assigned to incomplete or rejected experiments and to a number of measurements on other materials during the same time interval.

For each measurement on a given sample, the deviation from the mean of the measurements on that sample is shown in Table II. An estimated standard deviation of a single measurement of Q_v (gross) was found to be 5.0 B.t.u. per pound, which is about 0.026% of the heat of combustion. The standard deviation of the mean for a single sample is estimated to be 3.4 B.t.u. per pound. An added uncertainty is introduced into the value of Q_p (net) by the uncertainty in the percentage of hydrogen in the fuel, which is required for the conversion. With an estimated standard deviation of 0.1% for the value of hydrogen, the standard deviation in Q_p (net) becomes 9.7 B.t.u. per pound.

Several points may be noted in connection with the combustion measurements. After about half of the measurements had been completed, it became obvious that the heat of combustion found for NBS sample 108, based on runs 12b and 13b, was far out of line with other measurements. Because of this, and because there was some confusion in the labeling of the material set aside for combustion measurements, fresh material was obtained from the original sample container and used for runs 26c and 27c. The resulting value of Q_p (net) is in good agreement with neighboring values in the various correlations that were made. This fact makes it appear that the second series of measurements gave the proper heat of combustion for sample 108. The large discrepancy between the first and second sets may be attributed either to an error in the selection of the combustion material or to partial evaporation of the sample before the measurements were made.

The samples were received from the suppliers in 4- or 5-gallon cans. For convenience in the laboratory a small screw-cap bottle was filled with material to be used for the combustion measurements. Because of the high volatility of the gasolines, the small bottles presented one disadvantage, which is clearly evident from the measurements on NBS sample 174. The measurements obtained from runs 33b, 39b, and 46b were made relatively close together in time. Because of an unsatisfactorily large difference between run 33b and the two following measurements, it was felt advisable to make additional measurements, represented by runs 42c and 43c. The discrepancy between the measurements thus obtained and the previous ones is very striking. The liquid in the bottle had diminished appreciably in volume, apparently by evaporation due to a loosely fitting cap. Repetition of the measurements (runs 45c and 46c) using a freshly filled bottle gave results appreciably higher in net heat of combustion. Because of the loose bottle cap it was felt that the last two measurements were the only reliable ones, and the previous measurements were not used in the final results. This experience indicates a factor which could be of considerable importance in the precise determination of the heat of combustion of so volatile a mixture as gasoline.

A third feature of the measurements becomes apparent only on close examination. Where two consecutive runs were made on the same sample, in a very high proportion of the cases the result of the first measurement is higher than that of the second. Of 39 such pairs of measurements 31 show this trend, seven pairs show the reverse trend, and one pair shows no difference. The irregularity is heightened by the fact that of the seven pairs that were reversed four pairs occurred all together in runs 30 to 39. Data seem to be inadequate to account for these apparently consistent differences between runs. The differences are small; nevertheless, their regularity suggests that, if the cause could be determined, the internal consistency of the measurements could be still further improved. The differences noted here do not appear to be due to a regular change of the gasoline sample with time, for additional measurements made at later dates do not continue the trend.

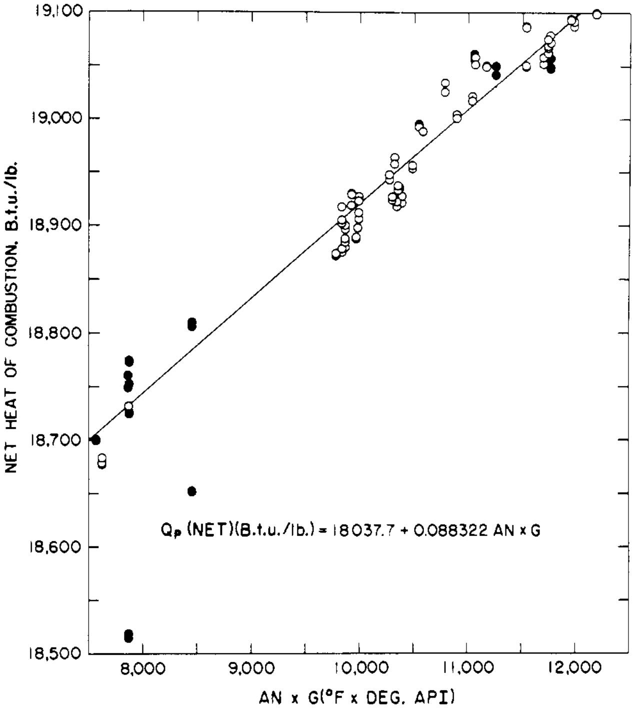

Figure 1. Aniline-gravity product and net heat of combustion of 40 aviation gasoline samples

Individual experimental values

● 100/130 fuels

○ 115/145 fuels

Aniline Point, API Gravity, and Composition. Aniline points of the 40 aviation gasoline samples were determined by ASTM method D 611-53T (*2*). The value so obtained is the temperature (degrees Fahrenheit) at which a clear solution of equal parts of aniline and hydrocarbons becomes cloudy when cooling. The API gravity for each sample was determined by ASTM method D 287 (*2*). Here the density is measured by hydrometer and corrected to 60° F. by means of the ASTM-IP petroleum tables (*1*). Hydrogen and carbon contents of the samples were determined by microcombustion analysis. The results of the measurements of percentage of hydrogen, aniline point, API gravity, and the calculated value of the aniline-gravity product are listed for each sample in Table III, together with the mean value of the net heat of combustion for comparison.

Each fuel was also analyzed into hydrocarbon types—paraffins (alkanes), naphthenes (cycloalkanes), olefins (alkenes), and aromatics. The analysis was carried out in two steps: The gasoline was first separated into saturates, unsaturates, and aromatics; then the saturates were further divided into paraffins and naphthenes.

Determination of saturate, unsaturate, and aromatic was carried out by ASTM method D 1319-54T (*2*). A small quantity of gasoline, to which a fluorescent dye has been

Table II. Heat of Combustion Measurements

NBS Sample No.	Run No.	Q_v (Gross), 25 °C., B.t.u./Lb.	Q_p (Net) 25 °C., B.t.u./Lb.	Dev. from Mean
100/130 Grade				
12	15 b	20,482.4	19,050.1	+ 3.4
	16 b	20,475.5	19,043.2	− 3.5
17	17 b	20,000.9	18,687.2	+0.6
	18 b	19,999.6	18,685.9	−0.7
29	21 b	20,501.7	19,060.3	+ 3.0
	22 b	20,495.7	19,054.3	− 3.0
57	12 a	20,499.7	19.049.1	− 2.5
	13 a	20,498.6	19,048.0	− 3.6
	1 b	20,508.4	19,057.8	+ 6.2
66	10 a	20,074.2	18,760.5	+ 5.6
	11 a	20,063.0	18,749.3	− 5.6
115/145 Grade				
2	4 b	20,569.6	19,091.7	+ 2.0
	5 b	20,565.6	19,087.7	− 2.0
9	55 b	20,510.6	19,050.9	+0.6
	56 b	20,509.4	19,049.7	−0.6
43	7 b	20,568.5	19,099.7	+0.5
	8 b	20,567.4	19,098.6	−0.6
45	57 b	20,331.2	18,935.4	+0.7
	58 b	20,329.7	18,933.9	−0.8
54	9 b	20,269.8	18,874.0	−1.7
	10 b	20,274.1	18,878.3	+ 2.6
	11 b	20,270.6	18,874.8	−0.9
68	59 b	20,400.2	18,995.3	+ 1.3
	61 b	20,397.3	18,992.4	−1.6
	34 c	20,399.2	18,994.3	+ 0.3
80	62 b	20,500.7	19,050.1	+0.2
	63 b	20,500.2	19,049.6	−0.3
88	64 b	20,499.6	19,058.2	+ 3.3
	40 c	20,492.9	19,051.5	−3.4
102	66 b	20,240.1	18,871.7	− 1.1
	67 b	20,242.2	18,873.8	+1.0
104	3 c	20,274.1	18,887.4	−0.9
	5 c	20,275.8	18,889.1	+0.8
111	1 c	20,285.5	18,917.1	+9.2
	2 c	20,273.4	18,905.0	−2.9
	44 c	20,270.1	18,901.7	−6.2
113	4 c	20,457.8	19,025.5	− 4.5
	41 c	20,466.7	19,034.4	+ 4.4
119	24 c	20,316.6	18,929.9	+ 4.2
	25 c	20,305.2	18,918.5	−7.2
	29 c	20,315.4	18,928.7	+ 3.0
122	11 c	20,547.3	19,087.6	+0.7
	12 c	20,545.9	19,086.2	−0.7
130	13 c	20,563.2	19,094.4	+0.4
	14 c	20,562.3	19,093.5	−0.5
136	18 c	20,293.6	18,897.8	+0.2
	19 c	20,293.2	18,897.4	−0.2
142	23 b	20,343.8	18,938.9	+ 3.5
	24 b	20,336.8	18,931.9	− 3.5
147	42 b	20,315.8	18,929.1	+ 6.0
	43 b	20,307.2	18,920.5	− 2.6
	44 b	20,306.5	18,919.8	− 3.3

NBS Sample No.	Run No.	Q_v (Gross) 25 °C., B.t.u./Lb.	Q_p (Net) 25 °C., B.t.u./Lb.	Dev. from Mean
100/130 Grade				
108	12 b	19,975.3	18,652.5[a]	
	13 b	19,974.5	18,651.7[a]	
	26 c	20,133.0	18,810.2	+ 1.7
	27 c	20,129.6	18,806.8	− 1.7
174	33 b	20,072.8	18,750.0[a]	
	39 b	20,034.6	18,711.8[a]	
	46 b	20,036.1	18,713.3[a]	
	42 c	19,841.2	18,518.4[a]	
	43 c	19,837.5	18,514.7[a]	
	45 c	20,096.9	18,774.1	+0.4
	46 c	20,096.0	18,773.2	−0.5
115/145 Grade				
152	21 c	20,384.1	18,988.3	−0.3
	28 c	20,384.6	18,988.8	+0.2
155	15 c	20,333.0	18,937.2	+ 2.2
	17 c	20,328.5	18,932.7	−2.3
161	20 c	20,453.8	19,021.5	+ 2.0
	21 c	20,449.7	19,017.4	−2.1
176	27 a	20,283.2	18,896.5	+ 6.8
	28 a	20,265.9	18,879.2	− 10.5
	34 a	20,271.4	18,884.7	−5.0
	47 c	20,287.1	18,900.4	+10.7
	48 c	20,274.3	18,887.6	−2.1
180	45 b	20,294.1	18,907.4	−8.6
	47 b	20,310.6	18,923.9	+7.9
	52 b	20,286.0	18,899.3	−16.7
	50 c	20,313.4	18,926.7	+10.7
	51 c	20,309.6	18,922.9	+6.9
181	26 b	20,308.9	18,922.2	+ 3.3
	30 b	20,302.3	18,915.6	− 3.3
182	30 c	20,328.4	18,923.5	−1.6
	31 c	20,331.6	18,926.7	+ 1.6
183	7 a	20,027.1	18,731.6	0.0
	8 a	20,027.1	18,731.6	0.0
186	1 a	20,531.6	19,071.9	− 3.6
	2 a	20,538.7	19,079.0	+ 3.5
191	5 a	19,964.5	18,678.2	− 1.0
	6 a	19,964.2	18,677.9	− 1.3
	9 a	19,969.6	18,683.3	+ 4.1
	33 a	19,963.8	18,677.5	− 1.7
193	3 a	20,528.8	19,069.1	−0.5
	4 a	20,527.1	19,067.4	−1.2
	31 a	20,535.0	19,075.3	+ 6.7
	32 a	20,522.3	19,062.6	−6.0
199	53 b	20,498.6	19,048.0	+ 4.7
	54 b	20,489.2	19,038.6	−4.7
200	36 c	20,367.3	18,953.2	− 1.4
	37 c	20,370.1	18,956.0	+ 1.4
203	32 c	20,344.3	18,957.6	−2.9
	33 c	20,350.1	18,963.4	+ 2.9
208	38 c	20,424.0	19,000.8	− 1.7
	39 c	20,427.3	19,004.1	+ 1.6

[a] Values not considered in average.

added, is forced through a carefully prepared silica gel column. The components are preferentially adsorbed in the gel in the order aromatic, olefin, and paraffin. The dyes, which are individually adsorbed in the same degree as the various classes of hydrocarbons, are made visible by ultraviolet light and the relative lengths of the respective bands are measured. From these lengths are computed the volume percentages of the hydrocarbon types.

The relative amounts of paraffin and naphthene in the saturate fraction were determined by the method of Kurtz, Mills, Martin, Harvey, and Lipkin (*8*), which is based on an empirical relationship between the volume percentage of the paraffin and naphthene and the density and refractivity intercept (refractive index − density/2). The original paper provides a method for cross-checking the results. using the boiling temperatures when 50% of the sample is distilled. However, in a few cases this cross check was in error by a few degrees. When this occurred, the samples were distilled carefully and the several fractions analyzed individually. In each case the summation of the percentage in the various fractions gave the same value as for the unfractionated sample. All fractions containing more than a few tenths of 1% of olefin or aromatic were passed through a large silica gel column to remove these easily adsorbed

Table III. Aniline Point, API Gravity, and Per Cent Hydrogen

NBS Sample No.	Grade	Aniline Point, °F.	Gravity, ° API	$A \times G$	% H.	Q_p (Net) 25 °C., B.t.u./Lb.
12	100/130	161.7	69.6	11,254	15.7	19,046.7
17		120.1	63.0	7,566	14.4	18,686.6
29		161.4	68.5	11,056	15.8	19,057.3
57		166.6	70.6	11,762	15.9	19,051.6
66		121.1	64.9	7,859	14.4	18,754.9
108		126.9	66.6	8,452	14.5	18,808.5
174		122.4	64.3	7,870	14.5	18,773.7
2	115/145	164.3	72.9	11,977	16.2	19,089.7
9		163.8	70.4	11,532	16.0	19,050.3
43		164.4	74.1	12,182	16.1	19,099.2
45		150.2	69.0	10,364	15.3	18,934.7
54		146.8	67.0	9,836	15.3	18,875.7
68		153.3	68.8	10,547	15.4	18,994.0
80		160.2	69.7	11,166	15.9	19,049.9
88		156.2	71.1	11,106	15.8	19,054.9
102		145.3	67.3	9,779	15.0	18,872.8
104		145.9	68.3	9,965	15.2	18,888.3
111		143.3	67.9	9,730	15.0	18,907.9
113		155.2	69.5	10,786	15.7	19,030.0
119		144.8	68.5	9,919	15.2	18,925.7
122		164.3	70.2	11,534	16.0	19,086.9
130		163.0	73.3	11,948	16.1	19,094.0
136		145.9	68.4	9,980	15.3	18,897.6
142		149.3	68.8	10,272	15.4	18,935.4
147		148.2	70.1	10,389	15.2	18,923.1
152		151.8	69.7	10,580	15.3	18,988.6
155		149.8	69.1	10,351	15.3	18,935.0
161		154.6	71.4	11,038	15.7	19,019.4
176		144.2	68.4	9,863	15.2	18,889.7
180		146.0	68.4	9,986	15.2	18,916.0
181		149.2	69.3	10,340	15.2	18,918.9
182		149.9	68.7	10,298	15.4	18,925.1
183		119.9	65.6	7,865	14.2	18,731.6
186		159.7	73.6	11,754	16.0	19,075.5
191		117.0	65.1	7,617	14.1	18,679.2
193		159.0	73.8	11,734	16.0	19,068.6
199		162.4	72.0	11,693	15.9	19,043.3
200		152.6	68.7	10,484	15.5	18,954.6
203		149.1	69.2	10,318	15.2	18,960.5
208		155.9	69.9	10,897	15.6	19,002.5

materials. Only the olefin- and aromatic-free samples were used for refractive index and density determinations.

For the determination of volume percentages ASTM method D 1319-54T gives a reported precision to 2% for olefins and aromatics and 1.5% for paraffins. Kurtz and others (*8*) also claim precision to 2% for their method.

Volume percentages were converted to weight and mole percentages by a series of calculated values for densities and molecular weights of the hydrocarbon types. These values were derived from analytical data obtained on petroleum, gasoline, and alkylate by API Project 6 and summarized by Rossini, Mair, and Streiff (*10*). Also considered were various manufacturers' recipes. All calculations were made on the basis of hydrocarbons in the C_5 to C_8 range.

For purposes of calculation it was assumed that if no naphthene was found, there were no straight-run fractions in the gasoline. Therefore the paraffin hydrocarbons were considered entirely alkylate types. Rossini and others have shown that typical straight runs contain an average of 38% naphthene in the C_5 to C_8 region. This was used as a basis for deciding how much of the paraffin should be considered as alkylate and how much as straight run. In addition, 10% by volume of the fuel was considered as isopentane (9% by weight).

As the olefins occur only in small quantities, it was assumed that the properties for diisobutylene would sufficiently describe this class,

The aromatics were taken as a 50-50 mixture of toluene and the xylenes. The only benzene present is an insignificant amount in any straight-run fractions added.

From these assumptions the following values were obtained:

	Density	Molecular Weight
Paraffins		
Isopentane	0.620	72
Straight run	0.681	101.6
Alkylate	0.701	111.8
Naphthene	0.759	101.7
Olefin	0.716	114
Aromatic	0.864	99

The maximum error introduced by using this method is considerably less than 1% in converting volume per cent to weight per cent and less than 2% in going from weight per cent to mole per cent. These extremes were found in sample 174, assuming no isopentane present and the aromatic to be all toluene. Generally the calculation errors are much smaller.

The observed volume percentages of hydrocarbon types are given in Table IV, together with the weight percentages calculated from them in the manner shown above. The values of mole per cent were calculated but are not shown.

RELATIONSHIPS BETWEEN EXPERIMENTALLY MEASURED QUANTITIES

The mean net heat of combustion is shown plotted as a function of aniline-gravity product ($AN \times G$), aniline point (AN), API gravity (G), and per cent hydrogen (H) in Figures 2 to 5. An approximately linear relation exists in each case. No significant difference appears to exist between the 100/130 and the 115/145 grade fuel samples. As is evident from Figure 2, the data on these aviation gasolines do not fit the equations found previously for the JP-4 or JP-5 fuels. Equation 2 previously determined for JP-4 fuels

$$Q_p \text{ (net) (B.t.u./lb.)} = 17977 + 0.1056\,(AN \times G) \qquad (2)$$

is shown as line 1. Equation 3 previously determined for JP-5 fuels

$$Q_p \text{ (net) (B.t.u./lb.)} = 17914 + 0.1056\,(AN \times G) \qquad (3)$$

is shown as line 2. Each line is broken in the region in which it is extrapolated beyond the range in which it was fitted. The heats of combustion of the 100/130 and 115/145 grade fuels lie below either of these equations and fit a line with a smaller slope, although the possibility that the 115/145 fuels alone would fit a line of the same slope was not thoroughly investigated. Not shown is Equation 4

$$Q_p \text{ (net) (B.t.u./lb.)} = 17940 + 0.1056\,(AN \times G) \qquad (4)$$

which was previously derived to fit AN-F-28 aircraft fuels. Equation 4 would lie between Equation 2 and Equation 3.

No simple graph has been devised which will represent the net heat of combustion as a function of the three variables required for defining the compositions of the fuels in terms of the four hydrocarbon types. However, the composition suggests itself as a logical property for correlating with the net heat of combustion. It may be assumed that in a fuel having boiling range and other properties limited by specifications such as those required for aircraft fuels, the hydrocarbons of which it is composed are limited to a relatively small group of compounds within each hydrocarbon type. Within such a group of compounds the range of possible values of heat of combustion is much less than for hydrocarbons of this type whose mixtures do not meet fuel specifications. As a consequence, the approximation may be made that mixtures within such a restricted group of compounds have a characteristic heat of combustion per unit weight which does not vary much from one mixture to another. The heat of combustion per unit weight of the fuel will in this case be a linear combination of the percentages by weight of the various hydrocarbon types.

Table IV. Composition of Gasoline Samples

NBS Sample No.	Grade	Hydrocarbon Types							
		Volume Per Cent				Weight Per Cent			
		Paraffin	Naphthene	Olefin	Aromatic	Paraffin	Naphthene	Olefin	Aromatic
12	100/130	91.2	7.2	0.6	1.0	90.3	7.9	0.6	1.2
17		74.8	7.8	1.0	16.4	71.3	7.7	1.0	20.0
29		97.7	0.8	0.6	0.9	97.4	0.9	0.6	1.1
57		94.8	4.7	0.5	...	94.5	5.0	0.5	...
66		84.7	...	0.5	14.8	81.9	...	0.5	17.6
108		87.0	...	0.6	12.4	84.4	...	0.6	15.0
174		72.4	14.2	0.6	12.8	69.0	15.0	0.6	15.4
2	115/145	99.6	...	0.4	...	99.6	...	0.4	...
9		98.7	...	0.5	0.8	98.4	...	0.6	1.0
43		99.7	...	0.3	...	99.7	...	0.3	...
45		93.6	...	0.6	5.8	92.3	...	0.6	7.1
54		89.3	...	3.2	7.5	87.5	...	3.3	9.2
68		95.3	...	0.5	4.2	94.3	...	0.6	5.1
80		99.2	...	0.4	0.4	99.2	...	0.4	0.4
88		89.0	10.0	0.5	0.5	87.9	10.9	0.6	0.6
102		90.4	...	0.6	9.0	88.4	...	0.6	11.0
104		91.8	...	0.5	7.7	89.9	...	0.6	9.5
111		91.8	...	0.6	7.6	90.1	...	0.6	9.3
113		84.1	15.2	0.3	0.4	80.9	18.3	0.3	0.5
119		90.7	2.0	0.5	6.8	88.9	2.1	0.6	8.4
122		99.1	...	0.2	0.7	98.8	...	0.3	0.9
130		99.2	...	0.4	0.4	99.2	...	0.4	0.4
136		92.1	...	1.7	6.2	90.8	...	1.7	7.5
142		92.2	...	2.2	5.6	90.9	...	2.2	6.9
147		91.1	...	2.1	6.8	89.6	...	2.1	8.3
152		94.2	...	0.5	5.3	92.8	...	0.6	6.6
155		91.4	1.2	0.9	6.5	90.5	1.2	0.8	7.5
161		94.6	2.5	0.3	2.6	93.7	2.7	0.3	3.3
176		90.8	0.8	0.6	7.8	89.0	0.8	0.6	9.6
180		92.2	...	0.6	7.2	90.6	...	0.6	8.8
181		93.0	...	0.6	6.4	91.5	...	0.6	7.9
182		91.4	1.2	1.2	6.2	89.9	1.3	1.3	7.5
183		82.9	...	0.4	16.7	79.6	...	0.4	20.0
186		95.2	4.4	0.4	...	94.8	4.8	0.4	...
191		80.6	...	0.5	18.9	77.7	...	0.5	21.8
193		93.3	6.4	0.3	...	92.7	7.0	0.3	...
199		97.8	...	0.6	1.6	97.4	...	0.6	2.0
200		94.9	...	0.7	4.4	93.9	...	0.7	5.4
203		92.7	...	0.5	6.8	91.0	...	0.6	8.4
208		94.3	1.4	0.5	3.8	93.0	1.6	0.6	4.8

Linear equations have been derived to fit the data relating each of the independent variables measured to the net heat of combustion as the dependent variable. For aniline-gravity product, aniline point, API gravity, and per cent hydrogen, an equation of the form

$$U = a + bX$$

was derived, in which U is the calculated net heat of combustion and X represents, respectively, $AN \times G$, AN, G, or H.

The equations derived were:

$$Q_p \text{ (net)} = 18037.7 + 0.088322\ (AN \times G) \tag{5}$$

$$Q_p \text{ (net)} = 17747.4 + 8.071\ (AN) \tag{6}$$

$$Q_p \text{ (net)} = 16152.4 + 40.477\ (G) \tag{7}$$

$$Q_p \text{ (net)} = 15859.2 + 201.06\ (H) \tag{8}$$

For the composition in terms of hydrocarbon types an equation of the form

$$U = a + bX + cY + dZ$$

in which X, Y, and Z represent the weight per cents of naphthenes, N, olefins, O, and aromatics, Ar, respectively, was derived to fit the data. The equation found was

$$Q_p \text{ (net)} = 19089.2 - 2.09\ (\text{N}) - 14.16\ (\text{O}) - 18.24\ (\text{Ar}) \tag{9}$$

The percentage of paraffins, P, has been omitted from the fitted equation, because for each fuel the sum of the observed P, N, O, and Ar is 100%. That is

$$\text{P} + \text{N} + \text{O} + \text{Ar} = 100 \tag{10}$$

Accordingly, any one of the percentages can be obtained from a knowledge of the rest. All four types may be made to appear in the equation, by adding any multiple of Equation 10 to 9. Thus by adding 190.892 × Equation 10 to Equation 9 one obtains:

$$Q_p \text{ (net)} = 190.892\ (\text{P}) + 188.80\ (\text{N}) + 176.73\ (\text{O}) + 172.65\ (\text{Ar}) \tag{11}$$

Or if it is desired to include P and leave out some other type, this too can be done.

Equations 5 through 9 were fitted to the data by the method of least squares; in each case it was assumed that the independent variables are without error and that all the error is in the net heat of combustion.

The fitting of the data and calculation of deviations were carried out by the Statistical Engineering Section, National Bureau of Standards. An error, later found for some samples, in the conversion from Q_v (gross) to Q_p (net) causes the fitted equations to deviate slightly from a least squares fit. As the error thus introduced is less than 1 B.t.u. per pound, no modification of the equations has been undertaken.

The deviations between observed and calculated values of Q_p (net) on the basis of these equations are shown in Table V. The average scatter of the data points around the fitted line was computed from the usual formula

$$S_U = \sqrt{\frac{\Sigma\ (u - U_c)^2}{N - P}}$$

where U_c is the calculated value of U, N is the number of data points (in the present case $N = 40$), and P is the number of constants to be determined. The u's are the observed values of U, and are the averages of two or more determinations. If the straight line is the true functional form for relating the variables, S_U is an estimate of the

Table V. Correlation of Net Heat of Combustion with Other Properties

NBS Sample No.	Grade	Observed Q_p (Net) 25 °C., B.t.u./Lb.	Deviations (Observed — Calculated) Eq. 6 aniline	Eq. 7 gravity	Eq. 5 $A \times G$	Eq. 8, %H	Eq. 9 composition
12	100/130	19,047	−5	+78	+15	+31	+5
17		18,687	−29	−15	−18	−67	−7
29		19,057	+7	+132	+43	+21	−2
57		19,052	−40	+42	−25	−5	−20
66		18,755	+30	−24	+23	0	−6
108		18,809	+37	−40	+24	+34	+1
174		18,774	+38	+19	+41	−1	+5
2	115/145	19,090	+16	−14	−6	−27	+6
9		19,050	−19	+48	−6	−26	−12
43		19,099	+25	−53	−14	+3	+14
45		18,935	−25	−11	−19	−1	−17
54		18,876	−57	+11	−30	−60	+1
68		18,994	+9	+57	+25	+38	+6
80		19,050	+10	+76	+26	−6	−26
88		19,055	+47	+25	+36	+19	+8
102		18,873	−47	−4	−29	−2	−7
104		18,888	−37	−29	−30	−27	−19
111		18,908	+4	+7	+11	+33	−3
113		19,030	+30	+65	+40	+14	−8
119		18,926	+10	+1	+12	+10	+2
122		19,087	+14	+93	+31	+11	+18
130		19,094	+31	−25	+1	−2	+18
136		18,898	−27	−23	−22	−38	−31
142		18,935	−18	−3	−10	−21	+3
147		18,923	−21	−67	−32	+8	+15
152		18,989	+16	+15	+17	+53	+28
155		18,935	−21	−14	−17	−1	−4
161		19,019	+24	−23	+6	+4	0
176		18,890	−22	−31	−19	−26	−14
180		18,916	−10	−5	−4	+1	+2
181		18,919	−33	−39	−32	+4	−18
182		18,925	−32	−8	−22	−31	−6
183		18,732	+17	−76	−1	+17	+13
186		19,075	+39	−56	0	−1	+2
191		18,679	−12	−108	−31	−15	−5
193		19,069	+38	−71	−6	−8	−2
199		19,043	−15	−23	−27	−13	−1
200		18,955	−24	+22	−9	−21	−26
203		18,961	+9	+7	+12	+45	+33
208		19,002	−3	+21	+2	+7	+13
Standard deviation		5	27	49	23	26	14
Max. deviation		16.7	−57	132	43	−67	33

standard deviation of U. The uncertainties in the estimates of a, b, c and d have also been estimated. If $\hat{a}$, $\hat{b}$, $\hat{c}$, and $\hat{d}$ denote the computed values of a, b, c, and d, their estimated standard deviations may be denoted by $S_{\hat{a}}$, $S_{\hat{b}}$, $S_{\hat{c}}$, and $S_{\hat{d}}$. If the true functional form is a straight line, these estimate the true standard deviations of a, b, c, and d.

The five equations derived in this work are shown in Table VI, together with the three equations from previous work. Also shown are the estimated standard deviations in the values of the net heat of combustion and the standard deviations in the fitted constants. In the last column is shown the maximum deviation of the mean value for any sample from the equation obtained from the samples on which measurements were made.

Equation 5, having aniline-gravity product as the variable, provides a correlation with heat of combustion with about the same degree of fit as was found for the JP-4 and JP-5 fuels, and somewhat better fit than Equations 6 and 8, having aniline point and per cent hydrogen as the variables. Equation 7, having API gravity as the variable, provides a significantly poorer correlation. [Since the publication of (5) it has been found that the data on JP-4 and JP-5 fuels can be represented as linear functions of API gravity with about the same precision as by linear functions of the aniline-gravity product. The data on both JP-4 and JP-5 fuels can be represented to about the same precision by a single linear function of $(AN^{0.6} \times G)$. However, such relations do not satisfactorily represent the available data on other types of hydrocarbon fuels.] Equations 9 and 11,

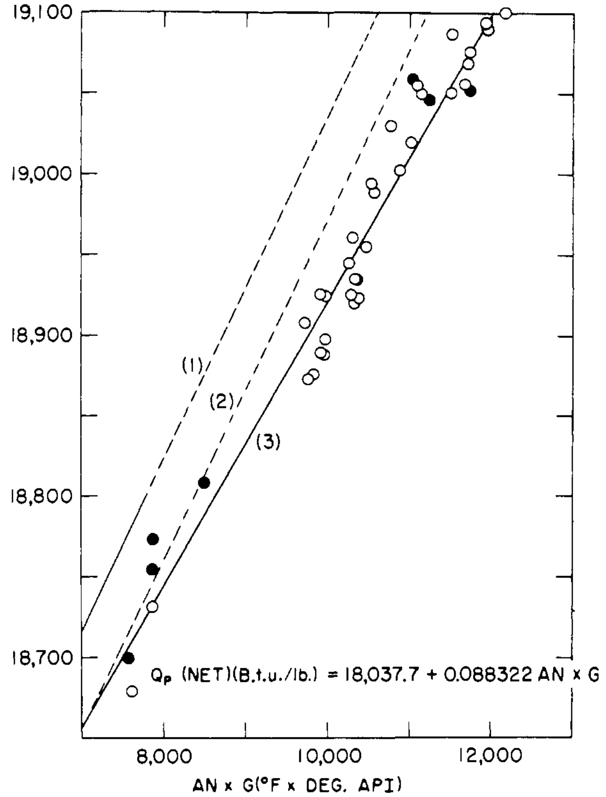

Figure 2. Aniline-gravity product and net heat of combustion of 40 aviation gasoline samples

Mean experimental values

Line 1. Equation 2
Line 2. Equation 3
Line 3. Equation 5

● 100/130 fuels
○ 115/145 fuels

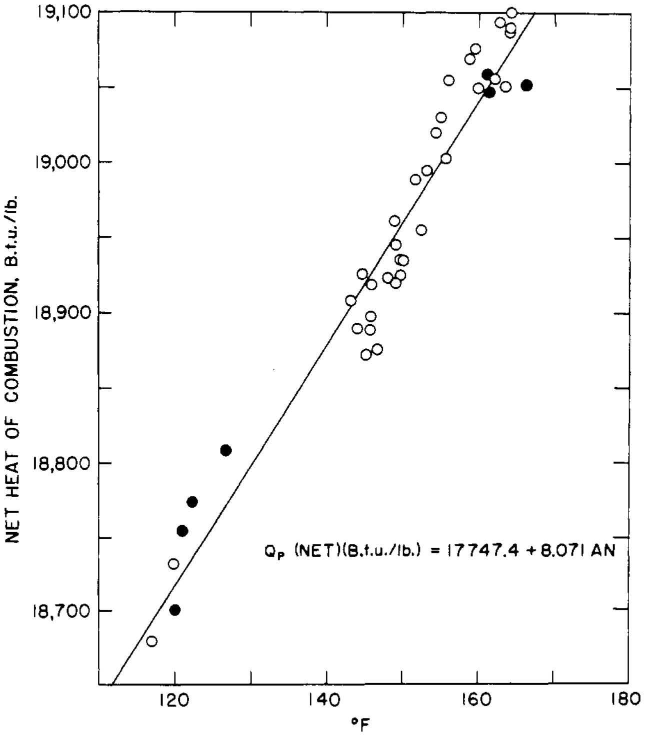

Figure 3. Aniline point and net heat of combustion of 40 aviation gasolines

● 100/130 fuels
○ 115/145 fuels

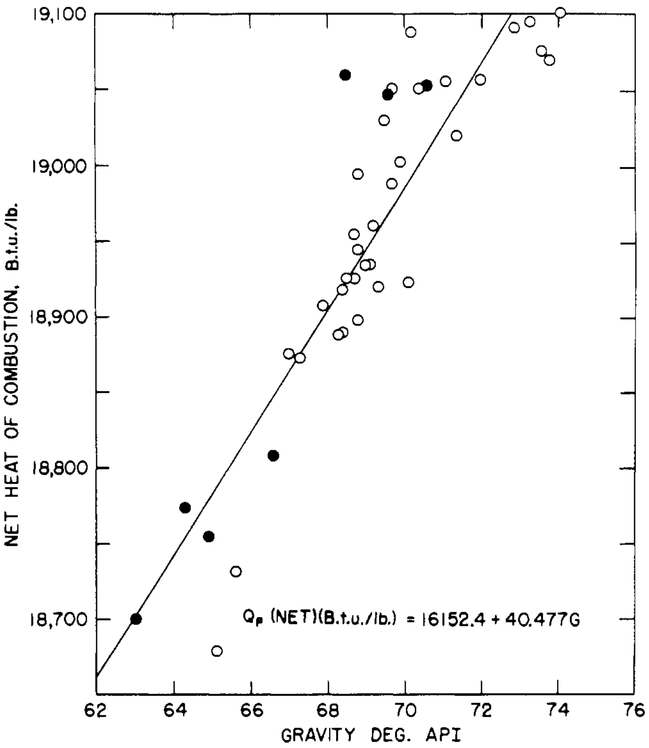

Figure 4. API gravity and net heat of combustion of 40 aviation gasolines

● 100/130 fuels
○ 115/145 fuels

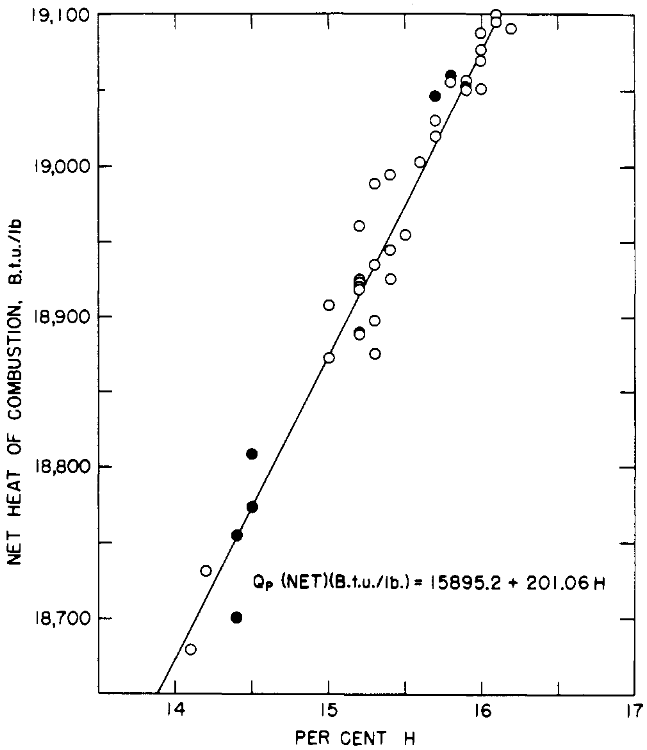

Figure 5. Per cent hydrogen and net heat of combustion of 40 aviation gasolines

● 100/130 fuels
○ 115/145 fuels

Table VI. Equations for Calculating Net Heat of Combustion of Aviation Fuels

Eq.	$U = \hat{a} + \hat{b}X + \hat{c}Y + \hat{d}Z$	S_U	$S_{\hat{a}}$	$S_{\hat{b}}$	$S_{\hat{c}}$	$S_{\hat{d}}$
2	Q_p (net) = 17977 + 0.1056 ($AN \times G$)(JP-4)	19	15	0.0023		
3	Q_p (net) = 17914 + 0.1056 ($AN \times G$)(JP-5)	30	15	0.0023		
4	Q_p (net) = 17940 + 0.1056 ($AN \times G$) (AN-F-28) (AN-F-58)	28	17	0.0023		
5	Q_p (net) = 18037.7 + 0.088322 ($AN \times G$)	23	30	0.002890		
6	Q_p (net) = 17747.4 + 8.071 (AN)	28	47	0.319		
7	Q_p (net) = 16152.4 + 40.477 (G)	49	217	3.126		
8	Q_p (net) = 15859.2 + 201.06 (H)	26	112	7.29		
9	Q_p (net) = 19089.2 − 2.09 (N) − 14.16 (O) − 18.24 (Ar)	14	4.77	0.57	4.13	0.40

giving net heat of combustion in terms of hydrocarbon types, offer a significantly better correlation for the aviation fuels than any other equations that were derived. In this case the estimated standard deviation of the net heat of combustion is 14 B.t.u. per pound, which is 0.08%, and the maximum deviation among the 40 fuel samples studied was 33 B.t.u. per pound, which is about 0.17%. For heats of combustion calculated from the aniline-gravity product, the standard deviation is 23 B.t.u. per pound and the maximum deviation is 45 B.t.u. per pound. These numbers may be compared with the standard deviation of the mean net heat of combustion, previously mentioned, 9.7 B.t.u. per pound.

Equation 11 is related in a logical manner to the properties of the hydrocarbons of which the gasolines are principally composed. It is, therefore, of some interest to compare the values of the constants that gave the best fit to the data, with the constants estimated from the known heats of combustion of pure hydrocarbons. A few hydrocarbons have been selected on the basis of boiling points for the comparison. The boiling point of the 40 gasoline samples averaged 97.2°C. (207°F), at 50% distillation, on the basis of inspection data supplied by the manufacturers. Shown in Table VII are several hydrocarbons having boiling points near this temperature, representing each type contributing to the equation, together with their boiling points (degrees centigrade) and net heat of combustion (B.t.u. per pound of liquid). Shown for comparison is 100 times the coefficient for each type of hydrocarbon taken from Equation 11.

There is general agreement of the calculated coefficients with the net heats of combustion of the pure hydrocarbons of the type they represent, except in the case of the olefins. It is to be presumed that the discrepancy here is due to the fact that olefins were present in the gasolines in only a very small amount, and is not at all surprising in view of the extremely large extrapolation involved. The method used in computing the coefficients would tend to lump together in this term, which contributes least to the total calculated heat of combustion, some uncertainties in the experiment, such as the division into hydrocarbon types. The degree of correspondence of the coefficients, in fact, appears to bear a direct relation to the importance of their contributions to the heat of combustion.

The complete calculation of the heat of combustion of a gasoline mixture by resolution into its molecular com-

Table VII. Heats of Combustion of Representative Pure Hydrocarbons

Hydrocarbon	B.P.(°C.) (9)	Q_p (Net) (9)	100 × Coefficient Eq. 11
Paraffin			
n-Heptane	98.4	19,157	19,089.2
2,2,4-Trimethylpentane	99.2	19,065	
3-Ethylpentane	93.5	19,155	
2,2-Dimethylhexane	106.8	19,055	
Naphthene			
Cyclohexane	80.7	18,676	
Methylcyclohexane	100.9	18,642	
cis-1,2-Dimethylcyclopentane	99.5	18,750	18,880
trans-1,2-Dimethylcyclopentane	91.9	18,724	
cis-1,3-Dimethylcyclopentane	91.9	18,729	
Olefins			
cis-2-Heptene	98.5	19,022	
trans-2-Heptene	98.0	19,004	17,673
cis-3-Heptene	95.8	19,022	
trans-3-Heptene	95.8	19,004	
2-Ethyl-1-pentene	94	18,997	
Aromatics			
Benzene	80.1	17,259	17,265
Toluene	110.6	17,424	

ponents, followed by a summation of the heats of combustion of the components is possible in principle, but beyond present experimental feasibility. The method described, of separating the gasoline into hydrocarbon types and estimating the heat of combustion of the fuel from the proportions of each type found, is within the capacity of most petroleum testing laboratories, and provides a better correlation than has been found for other easily measured physical properties. It is, however, subject to limitations on the fuels to which it can be applied in the same manner, as, for example, the estimation of heat of combustion from aniline-gravity product—that is, the coefficients of the equation used in the calculation may be expected to be sensitive to factors which vary from one fuel type to another, such as the boiling range and mean boiling point of the fuel and perhaps, outside of certain rather wide limits, the proportions of the hydrocarbon types present in the fuel.

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Liquid-Vapor Equilibria of the System Bromine Trifluoride-Bromine Pentafluoride

R. D. LONG,[1] J. J. MARTIN, AND R. C. VOGEL
Chemical Engineering Division, Argonne National Laboratory, Lemont, Ill., and
Department of Chemical and Metallurgical Engineering, University of Michigan, Ann Arbor, Mich.

The purpose of the present investigation was determination and correlation of the liquid-vapor equilibria data on the system bromine pentafluoride–bromine trifluoride. Bromine forms three halogen fluorides. Bromine monofluoride has been reported but never isolated. Bromine trifluoride is stable up to about 180°C. Bromine pentafluoride has been reported to be stable at several hundred degrees centigrade. Both bromine trifluoride and pentafluoride react violently with water and organic compounds. This reactivity makes necessary the use of specialized equipment. The vapor pressures of the two pure components as reported in this work are in general more accurate than those previously available. No previous data are available for the liquid-vapor equilibria of this particular system.

METHODS AND APPARATUS

Equilibrium Still. An all-metal Othmer still of the type used by Barber and Cady (*1*) was modified for this investigation. All-welded nickel construction was used because of the excellent corrosion resistance of nickel to bromine fluorides. A schematic diagram of the equilibrium still is shown in Figure 1. A loading port placed rather high up on the boiling chamber was used to charge the interhalogen into the still. As it was impossible to see the level of interhalogen in the nickel charging pot, the still was first evacuated and then sufficient time was allowed for all the interhalogen to flow into the still. For best operation, approximately 100 mm. of interhalogen of appropriate composition was charged. The still was recharged for each pair of data points.

The still was heated by asbestos-covered Nichrome wire on one side of a loop of $\frac{3}{8}$-inch nickel tubing attached to the bottom of the boiling chamber. This mixed the contents of the boiling chamber by thermal cycling. Mixing was further enhanced by bringing the vapor condensate back to the center of the heating loop rather than directly to the boiling chamber.

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[1] Present address, Standard Oil Co. of Indiana, Whiting, Ind.