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CALORIMETRIC DETERMINATION OF THE HEATS OF COMBUSTION OF ETHANE, PROPANE, NORMAL BUTANE, AND NORMAL PENTANE

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ABSTRACT

The present investigation on the calorimetric determination of the heats of combustion of ethane, propane, normal butane, and normal pentane was undertaken because of the dearth of information concerning these thermochemical constants for which there is pressing need in industry and in the sciences.

The data of the present investigation give for the heats evolved in the combustion in oxygen, at a temperature of 25 C and a constant pressure of 1 atmosphere, of gaseous ethane, gaseous propane, gaseous normal butane, and gaseous normal pentane, respectively, to form gaseous carbon dioxide and liquid water, the following values, in international kilojoules per mole: Ethane, 1,559.57 ± 0.44; propane, 2,219.57 ± 0.51; normal butane, 2,877.88 ± 0.63; normal pentane, 3,536.00 ± 0.88. Converted to k-cal$_{15}$ by means of the factor 1.00040/4.1850, these values become, in k-cal$_{15}$ per mole: Ethane, 372.81 ± 0.11; propane, 530.57 ± 0.12; normal butane, 687.94 ± 0.15; normal pentane, 845.27 ± 0.21.

The hitherto "best" values for the heats of combustion of these gases differ from the values obtained in the present investigation by the following amounts Ethane, −1.23 percent; propane, −0.87 percent; normal butane, no existing data; normal pentane, −0.86 percent. These differences are from 30 to 50 times the estimated uncertainties in the values from the present investigation.

CONTENTS

I. INTRODUCTION

Accurate values for the heats of combustion of ethane, propane, normal butane, and normal pentane are needed for the following reasons: First, ethane, propane, and butane are becoming increasingly important as fuel gases in industry and in the home; second, for these substances, values of the free energies of formation, which are needed for computing chemical equilibria in which these gases take part, can be determined accurately only from the relation involving entropies and heats of formation, which latter values are calculated from the heats of combustion; and third, accurate values for the heats of combustion of the normal paraffin hydrocarbon gases will give data from which may be drawn information concerning the energies of the atomic linkages in these molecules.

The existing data on the heats of combustion of ethane, propane, butane, and pentane are very meager and, according to present standards, exceedingly uncertain. For ethane and propane there are the discordant values of Thomsen (1)[1] and Berthelot and Matignon (2), who used the calorimetric equipment available half a century ago and who had not pure gases to work with. For normal butane, there are no data on the heat of combustion recorded in the literature. For normal pentane there exists the value obtained by Roth and Machlett (3), who published no report of their experiments but gave simply the numerical results.

Because of the dearth of information concerning the heats of combustion of these gases and because of the pressing need in industry and in the sciences for accurate values concerning them, the present investigation on the calorimetric determination of the heats of combustion of ethane, propane, normal butane, and normal pentane was undertaken.

II. UNITS, ATOMIC WEIGHTS, ETC.

The fundamental unit of energy employed in the present calorimetric experiments is the international joule based upon standards of emf and resistance maintained at this Bureau (4). Recent experimental work in this Bureau (13) on the relation between the international and the absolute units of current and resistance indicates the relation between the absolute joule and the international joule, derived from standards maintained at this Bureau, to be 1 international (Bureau of Standards) joule = 1.00032 absolute joules. But for the sake of consistency the relation which has heretofore been used for converting the data obtained in the thermochemical laboratory of the Bureau of Standards will be used in the present and succeeding papers, until such time as the relation between the absolute and the international joule will be fixed by international accord. At that time, all the data that will have been obtained in this thermochemical laboratory will be converted to the new basis.

The conversion factors used throughout this paper are:

1 international joule = 1.00040 absolute joules

1 g-cal$_{15}$ = 4.1850 absolute joules

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[1] The numbers in parentheses, here and throughout the text, refer to the references, p. 750.

The atomic weights of oxygen, hydrogen, and carbon are taken from the 1934 report of the International Committee on Atomic Weights (5): Oxygen, 16.0000; hydrogen, 1.0078; carbon, 12.00. As explained in section IV, part 3, of this paper, the thermal data obtained in the present investigation are independent of the atomic weight of carbon, the number of moles of hydrocarbon involved in the calorimetric experiments having been determined from the mass of water formed.

III. METHOD AND APPARATUS

The general calorimetric method employed in the present investigation is the same as that previously used in this laboratory in the determination of the heats of formation of water and hydrogen chloride and the heats of combustion of methane, carbon monoxide, methanol, and ethanol (6); and is, briefly, a substitution method in which the heat evolved by a measured amount of the chemical reaction is found to be equivalent to the heat evolved by a measured amount of electrical energy, the calorimeter serving as the comparator. Unless otherwise stated the procedure and the nomenclature follow the previous investigations (6).

For the combustion of ethane, it was found that the reaction vessel used for the combustion of methane served very well, provided that the proper conditions prevailed with respect to the rates of flow of the ethane and the oxygen. This reaction vessel has already been described (6).

For the combustion of propane, normal butane, and normal pentane a new reaction vessel was designed, in which provision was made for aspirating oxygen into the stream of hydrocarbon gas before it reached the burner tip.[2] A cross section of this new reaction vessel [3] is shown in figure 1. A is the tube through which the oxygen enters the reaction chamber; B is the tube through which the hydrocarbon gas passes to the burner tip F where, having been ignited by sparks across the gap between the ends of the platinum wires D, it burns with a flame; at E is the injector by means of which oxygen is drawn into the stream of hydrocarbon gas; at G is collected as a liquid most of the water formed in the combustion; and the exit gases leave the reaction vessel through the tube C.

The dimensions of the new reaction vessel necessitated the building of a new heating coil to fit it. A thin copper cylinder, 5 cm long and 7.5 cm in diameter, was coated on the outside with a layer of pizein cement; around this cylinder was wound, noninductively, about 65 ohms of enameled constantan wire (no. 30, B. & S. gage); enameled copper leads were soldered to the ends of the constantan wire and insulated with pizein on the cylinder; and the outside of the cylinder was covered with another coating of pizein.

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[2] The author is indebted to Francis A. Smith for valuable advice in the design of the burner.

[3] This reaction vessel was built by E. O. Sperling, and the author is indebted to him for improvements in the design.

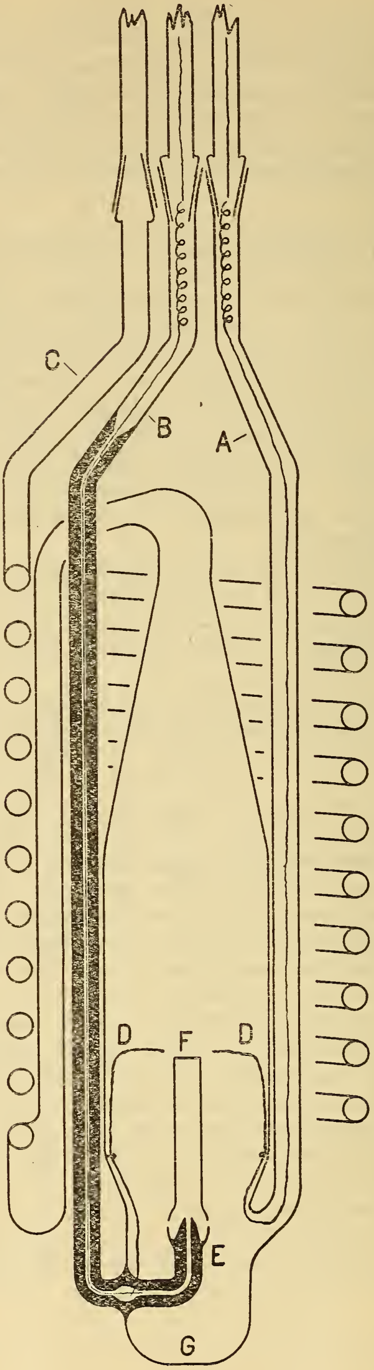

FIGURE 1.—*Crosssection of the reaction vessel used in the combustion of propane, butane, and pentane.*

The description is given in the text. The drawing is made to scale, and the over-all length is 26 cm.

IV. CHEMICAL PROCEDURE

1. PREPARATION AND PURITY OF THE HYDROCARBONS

In the present experiments the amount of reaction was determined from the mass of water formed. Because the heats of combustion of these hydrocarbons per mole of water formed are not greatly different, quite an appreciable amount of a homologous impurity may be contained in a given sample without necessitating any significant correction to the observed heat effect. For example, if a sample of normal butane contains as impurity 0.2 mole percent of propane, the observed heat effect will be less than that for pure normal butane by 0.006 percent. Table 1 gives the amounts of various impurities necessary to cause an error of ± 0.01 percent in the heat of combustion.

TABLE 1.—*The effect of impurities on the heat of combustion*

Substance	Impurity	Amount of impurity necessary to cause an error of 0.01 percent in the heat of combustion	Error in the heat of combustion
		Mole percent	*Percent*
Ethane	Methane	0.10	−0.01
	Propane	.11	+.01
Propane	Ethane	.21	−.01
	Butane	.21	+.01
Normal butane	Propane	.35	−.01
	Pentane	.35	+.01
Normal pentane	Butane	.57	−.01
	Hexane	.57	+.01

The samples of ethane, propane, and normal butane used in the present investigation were prepared to our order by the laboratory of the Linde Air Products Co., Buffalo, N.Y. These saturated hydrocarbons were obtained from natural gas by repeated fractional distillation at low temperatures. The manner of purification was such that each gas was expected to contain less than 0.2 percent by volume of impurity, which impurity would be a homologous substance, as for example, an impurity of ethane or butane in the sample of propane. Subsequent tests made in our laboratory indicated that the amount of impurity in the various samples was, in general, considerably less than 0.2 percent. About 2.4 moles of each gas was placed in highly evacuated steel cylinders, which were fitted with good valves and had internal volumes of about 2.8 liters.

In our laboratory, the ethane, propane, and normal butane were examined for impurities by Martin Shepherd (7), who separated, by isothermal distillation at low pressures, a sample of each gas into three fractions, and measured the difference in the vapor pressures of the middle cut and the initial distillate and of the middle cut and the final residue. The amounts of the initial distillate and the final residue were each less than 1/20 of the entire sample, and the difference in vapor pressures was measured by a differential manometer sensitive to ± 0.02 mm of Hg. The data obtained by Shepherd are given in table 2, where Δp is the difference between the vapor pressures, measured at the temperature t, of the middle cut and the initial distillate or the final residue, and ΔX_B, (see (7) for method of calculation and exact definition of terms), represents approx-

TABLE 2.—*Data on the purity of the ethane, propane, and normal butane, as shown by measurement of the difference in the vapor pressures between the middle cut and the initial distillate and the final residue, respectively*

Initial distillate [1]				Final residue [1]		
Substance	Δp	t	ΔX_B	Δp	t	ΔX_B
	mm Hg	° *C*	*Mole fraction*	*mm* Hg	° *C*	*Mole fraction*
Ethane	0.29	−189.1	0.009 methane	0.01	−150.0	0.005 propane.
Propane	.00	−58.2	0.00001 ethane	.02	−49.3	0.00004 normal or isobutane.
Normal butane	7.82	.0	0.003 propane 0.020 isobutane	.22	.0	0.00035 normal pentane.

[1] The amounts of the initial distillate and the final residue were respectively less than 1/20 of the entire sample. The value of ΔX_B gives approximately the mole fraction of the given impurity in the initial distillate or the final residue, not in the entire sample. The values of Δp were read to ±0.02 mm Hg.

imately the mole fraction of a possible impurity, B, present in the initial distillate or the final residue. The mole fraction of the impurity B in the entire sample would be about 1/20 of the value of ΔX_B given in table 2, were it not for the fact that the isothermal distillation does not isolate all of the impurity in the initial distillate or the final residue. Assuming, as a probable case, that one half of the impurity is obtained in the initial distillate or the final residue, then the mole fraction of the impurity B in the entire sample would be about 1/10 the value of ΔX_B.

The normal pentane used in the present experiments was from the lot prepared synthetically by Mair (8), who gave a complete report of its preparation and properties. The following are some of the physical constants of the normal pentane: boiling point at 760 mm Hg, 36.06 degrees C; freezing point in air, −129.73 degrees C; freezing range of the sample, 0.026° C; refractive index, N_D^{25}, 1.35470.

TABLE 3.—*Results of the analytical experiments for determining the ratio of carbon to hydrogen in the ethane, propane, normal butane, and normal pentane*

Substance	Number of experiments	Average amount of hydrocarbon used in each experiment	Ratio	Average value of the ratio	Average deviation from the mean	Maximum deviation from the mean
		Mole				
Ethane	5	0.049	6C/2H	0.99992	±0.00018	0.00039
Propane	7	.034	8C/3H	1.00016	±.00019	.00034
Normal butane	6	.025	10C/4H	1.00014	±.00012	.00028
Normal pentane	6	.019	12C/5H	.99994	±.00022	.00041

In table 3 are given the results of experiments on the determination of the ratio of carbon to hydrogen in the ethane, propane, normal butane, and normal pentane. In these experiments the combustion was carried out in the calorimetric reaction vessel and the analytical procedure was the same as that used for methane (6). The amount of carbon dioxide collected in these experiments was corrected, when necessary, for the small amounts of carbon monoxide formed. (See p. 741.)

From the foregoing data, it appears that the purity of the ethane, propane, normal butane, and normal pentane used in the present investigation was such that, per mole of water formed, the heats of combustion of these samples would differ from the heats of combustion of the absolutely pure hydrocarbons by less than 0.01 percent.

2. PURITY OF THE COMBUSTION REACTION

The purity of the combustion reaction was examined as reported in previous papers.

A new supply of oxygen, prepared commercially from liquid air, was obtained for the present experiments. This oxygen, like that previously used, was low in inert gases (0.6 mole percent) and was similarly purified. A flow of oxygen considerably in excess of the stoichiometric requirements for complete combustion was used in all the experiments.

The combustion of ethane was carried out in the reaction vessel used for methane and other gases (6). It was necessary to use such a rate of flow of the ethane as would give a flame with a blue mantle, a sign of practically complete combustion, and which was sufficiently removed from the burner tip to prevent decomposition (with consequent deposition of carbon on the quartz tip) of the ethane before it reached the flame proper. The desired ethane flame was about 1.5 cm long. In the combustion of the ethane under these conditions, it was found that, on the average, 0.008 percent of the carbon in the sample was burned to carbon monoxide instead of carbon dioxide. This necessitated a correction of + 0.003 percent to the observed heat effect in the calorimetric reaction experiments, and of + 0.008 percent to the observed mass of carbon dioxide in the analytical experiments on the ratio of carbon to hydrogen in the ethane.

For the combustion of the propane and normal butane, the reaction vessel shown in figure 1 was used. The aspiration of oxygen into the stream of hydrocarbon gas before it reached the flame made possible the combustion of these hydrocarbons without deposition of carbon on the burner tip. The amount of oxygen aspirated into the stream of hydrocarbon gas was kept below that amount which would cause the flame to flash back to the capillary jet, by governing the size of the injector holes and the rate of flow of the hydrocarbon gas. In the combustion experiments with propane and normal butane burned in this manner, with a blue flame about 1.5 cm long, no carbon monoxide was detected in the exit gases.

The combustion of the normal pentane, which was carried as a gas into the reaction vessel by means of a stream of nitrogen, was performed in the same reaction vessel that was used for propane and butane. The composition of the gaseous mixture of nitrogen and pentane was about 0.65 mole of normal pentane to 0.35 mole of nitrogen. The nitrogen was bubbled through the liquid normal pentane at a temperature of 24 C and then the mixture passed through ascarite, magnesium perchlorate, and phosphorus pentoxide before arriving at the calorimeter. The pentane flame was blue and about the same size as for the other gases. The amount of carbon monoxide[4] formed in the combustion of the normal pentane in this manner was found to be 0.00020 mole per mole of carbon dioxide, which necessitated a correction of + 0.008 percent to the observed heat effect in the calorimetric reaction experiments, and a correction of + 0.020 percent to the observed mass of carbon dioxide in the analytical experiments on the ratio of carbon to hydrogen. The amount of nitrogen oxides in the exit gases from the combustion of pentane

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[4] The tests for carbon monoxide were made in the gas section by Carroll Creitz.

was found to be 0.00004 mole per mole of carbon dioxide,[5] which necessitated no significant correction.

3. DETERMINATION OF THE AMOUNT OF REACTION

The amount of reaction in each calorimetric combustion experiment was computed from the mass of water formed, which was determined according to our usual procedure (6). In this connection it should be emphasized that for work of the highest precision the U-tube absorbers should be filled with hydrogen at the times of weighing, in order to make negligible any errors in corrections due to changes in the room temperature or the barometric pressure, and to make more certain the correction for the change in the volume of the solid absorbent.

In the present experiments 1 mole (18.0156 g) of H_2O was taken as equivalent to 1/3 mole of C_2H_6, to 1/4 mole of C_3H_8, to 1/5 mole of C_4H_{10}, or to 1/6 mole of C_5H_{12}. In this manner the values of the heats of combustion obtained in the present investigation are independent of the atomic weight of carbon.

In an auxiliary experiment an amount of the gaseous mixture of normal pentane and nitrogen containing 0.17 g of pentane was passed through a carefully weighed U-tube containing dehydrite (magnesium perchlorate trihydrate) and phosphorus pentoxide, and the change in mass of the U-tube was found to be zero ± 0.00005 g. This determination was necessary because, at the extinction of the pentane flame, there was always several mg of unburned pentane in the inlet tube, which pentane was later to be swept out through the U-tube.

V. CALORIMETRIC PROCEDURE

1. ELECTRICAL ENERGY EXPERIMENTS

The data of the experiments made to determine the electrical energy equivalent of the calorimeter system used for the combustion of ethane are given in table 4. (See (6) for nomenclature.) The "error" of the mean value of these experiments is

$$\pm\ 2\sqrt{\Sigma\Delta^2/n(n-1)} = \pm\ 0.012 \text{ percent,}$$

where $\Sigma\ \Delta^2$ is the sum of the squares of the percentage deviations and n is the number of experiments.[6]

The data of the experiments made to determine the electrical energy equivalent of the calorimeter system used in the combustion of propane, normal butane, and normal pentane are given in table 5. The "error" of the mean value of these experiments is

$$\pm\ 2\sqrt{\Sigma\Delta^2/n(n-1)} = \pm\ 0.008 \text{ percent}$$

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[5] The test for nitrogen oxides was made in the reagents and platinum metals section by F. W. Schwab.

[6] This formula gives an "error" that is three times as large as that obtained with the usual formula for the "probable error" of the mean.

TABLE 4.—*Calorimetric results of the electrical energy experiments* [1] *for ethane*

Experiment no.	ΔR	k	K	U	$\Delta t_{corr.}$	Average temperature	Electrical energy [2]	Mass of calorimeter water	Electrical energy equivalent of calorimeter system [3]	Deviation from mean
	Ohm	*Min*$^{-1}$	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*	*Int. joules*	*g*	*Int. joules per degree C*	*Joules per degree C*
1	0. 298843	0. 001969	0. 005401	0. 000254	2. 90636	25. 10	44, 944. 5	3, 625. 40	15, 441. 8	1. 5
2	. 289622	. 001943	. 005885	. 000110	2. 81156	25. 06	43, 464. 2	3, 624. 30	15, 441. 2	. 9
3	. 289200	. 001937	. 005867	. 000046	2. 80819	25. 06	43, 392. 7	3, 623. 14	15, 439. 2	−1. 1
4	. 294777	. 001948	. 005835	−. 000140	2. 86566	25. 09	44, 257. 4	3, 621. 44	15, 438. 3	−2. 0
5	. 296576	. 001933	. 005938	. 000012	2. 88097	25. 09	44, 539. 5	3, 624. 94	15, 439. 4	−. 9
6	. 299513	. 001946	. 005366	−. 000014	2. 91601	25. 10	45, 038. 2	3, 620. 49	15, 443. 2	2. 9
7	. 297286	. 001942	. 005430	. 000007	2. 89309	25. 09	44, 673. 9	3, 620. 69	15, 438. 8	−1. 5
8	. 297230	. 001935	. 005355	. 000048	2. 89287	25. 10	44, 655. 2	3, 617. 93	15, 445. 1	4. 8
9	. 296837	. 001931	. 005367	. 000226	2. 88709	25. 10	44, 563. 2	3, 619. 94	15, 435. 7	−4. 6
Mean									15, 440. 3	±2. 2

[1] These experiments were performed in January 1933.

[2] The time of electrical energy input was 17 or 18 minutes, the current 0.78 to 0.83 ampere.

[3] Corrected to 3,620.00 g of water and an average temperature of 25.00 C.

TABLE 5.—*Calorimetric results of the electrical energy experiments* [1] *for propane, butane, and pentane*

Experiment no.	ΔR	k	K	U	$\Delta t_{corr.}$	Average temperature	Electrical energy [2]	Mass of calorimeter water	Electrical energy equivalent of calorimeter system [3]	Deviation from mean
	Ohm	*Min*$^{-1}$	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*	*Int. joules*	*g*	*Int. joules per degree C*	*Joules per degree C*
1	0. 410460	0. 001932	0. 007159	0. 000156	3. 99628	25. 01	60, 887. 8	3, 561. 77	15, 228. 7	−1. 4
2	. 408615	. 001934	. 007255	. 000166	3. 97695	25. 00	60, 962. 0	3, 583. 62	15, 230. 2	. 1
3	. 412305	. 001904	. 007074	−. 000034	4. 01730	25. 01	61, 097. 8	3, 554. 76	15, 230. 6	. 5
4	. 411657	. 001940	. 007156	. 000084	4. 00893	25. 03	60, 991. 1	3, 555. 93	15, 230. 8	. 7
5	. 411322	. 001930	. 007245	. 000075	4. 00479	25. 01	60, 950. 2	3, 557. 44	15, 230. 0	−. 1
6	. 413270	. 001925	. 007277	. 000053	4. 02400	25. 02	61, 236. 0	3, 557. 87	15, 226. 6	−3. 5
7	. 409501	. 001934	. 006995	−. 000046	3. 99040	25. 00	60, 814. 1	3, 563. 15	15, 226. 9	−3. 2
8	. 410563	. 001934	. 006721	−. 000223	4. 00540	25. 00	60, 880. 0	3, 552. 02	15, 232. 8	2. 7
9	. 409252	. 001926	. 006818	. 000000	3. 98923	25. 00	60, 705. 9	3, 556. 92	15, 230. 3	. 2
10	. 408933	. 001941	. 007053	−. 000093	3. 98466	25. 00	60, 673. 4	3, 559. 35	15, 229. 4	−. 7
11	. 410085	. 001941	. 006848	−. 000055	3. 99774	25. 00	60, 830. 3	3, 555. 97	15, 233. 0	2. 9
12	. 407731	. 001943	. 006930	−. 000190	3. 97493	25. 00	60, 454. 7	3, 554. 44	15, 232. 2	2. 1
Mean									15, 230. 1	±1. 5

[1] Experiments 1 to 6 were performed in September 1933, and experiments 7 to 12 in January 1934.

[2] The time of electrical energy input was 16 or 17 minutes, the current 0.95 to 1.00 ampere.

[3] Corrected to 3,560.00 g of water and an average temperature of 25.00 C.

2. CORRECTION EXPERIMENTS

The "spark" energy was determined calorimetrically to be 1.43 ± 0.06 joules per second for the experiments on ethane and 1.31 ± 0.06 joules per second for the experiments on propane, normal butane, and normal pentane.

The "gas" energy and the "vaporization" energy were determined as in the previous investigations (6).

As before (6), calorimetric experiments were performed in which a number of ignitions and extinctions of the flame occurred, the purpose being to subordinate, relatively, the heat evolved in the combustion of the hydrocarbon to the "spark", "gas", and "vaporization" energies. In each of these experiments thermal balance was obtained within the limits of error of the measurements.

3. REACTION EXPERIMENTS

The calorimetric data of the combustion experiments with ethane, propane, normal butane, and normal pentane are given in tables 6, 7, 8, and 9, respectively. The "errors" of the mean values of the combustion experiments on the various gases, computed as $\pm 2\sqrt{\Sigma\Delta^2/n(n-1)}$, are, respectively: Ethane, ± 0.023 percent; propane, ± 0.019 percent; normal butane, ± 0.018 percent; and normal pentane, ± 0.021 percent.

TABLE 6.—*Calorimetric results of the reaction experiments for ethane*

Experiment no.	ΔR	k	K	U	$\Delta t_{corr.}$	Average temperature
	Ohm	*Min^{-1}*	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*
1	0.290372	0.001898	0.006838	−0.000069	2.81135	25.09
2	.294673	.001942	.005332	.000137	2.86687	25.08
3	.296344	.001923	.005790	.000020	2.88005	25.08
4	.298509	.001933	.005946	−.000156	2.90171	25.09
5	.295834	.001980	.006425	.000091	2.86800	25.08
6	.296406	.001957	.006635	−.000075	2.87323	25.08
7	.294781	.001945	.005662	−.000050	2.86652	25.08
Mean						

Experiment no.	Electrical energy equivalent of calorimeter system [1]	"Gas" energy	"Spark" energy	"Vaporization" energy	Mass of ethane	Heat [2] of combustion at 25 degrees C	Deviation from mean
	Int. joules per degree C	*Joules*	*Joules*	*Joules*	*Mole*	*Int. kilojoules per mole*	*Kilojoule per mole*
1	15,442.1	4.6	17.2	375.8	0.0280855	1558.74	−0.83
2	15,459.3	13.9	14.3	342.9	.0286407	1559.46	−.11
3	15,451.1	8.6	14.3	303.4	.0287294	1559.35	−.22
4	15,455.0	13.9	15.0	298.0	.0289423	1559.81	.24
5	15,456.9	5.9	22.9	331.7	.0286226	1559.84	.27
6	15,455.0	12.4	32.9	326.8	.0286718	1559.51	−.06
7	15,430.7	13.1	15.7	261.9	.0285167	1560.26	.69
Mean						1559.57	±.35

[1] Includes the heat capacity of ½ the mass of liquid water formed in the reaction.

[2] Includes a correction of +0.003 percent for the carbon monoxide formed.

TABLE 7.—*Calorimetric results of the reaction experiments for propane*

Experiment no.	ΔR	k	K	U	Δ $t_{corr.}$	Average temperature
	Ohm	*Min^{-1}*	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*
1	0. 403093	0. 001956	0. 011899	−0. 000179	3. 87955	24. 97
2	. 412941	. 001940	. 015120	−. 000008	3. 94359	25. 02
3	. 411032	. 001922	. 007486	−. 000011	4. 00037	25. 01
4	. 413092	. 001935	. 008225	−. 000008	4. 01343	25. 02
5	. 409675	. 001947	. 007578	−. 000081	3. 98670	25. 01
6	. 406890	. 001936	. 007383	. 000098	3. 95925	24. 99
7	. 412252	. 001948	. 010572	. 000027	3. 98149	25. 01
8	. 409171	. 001945	. 008632	. 000059	3. 96987	25. 00
Mean						

Experiment no.	Electrical energy equivalent of calorimeter system [1]	"Gas" energy	"Spark" energy	"Vaporization" energy	Mass of propane	Heat of combustion at 25 degrees C	Deviation from mean
	Int. joules per degree C	*Joules*	*Joules*	*Joules*	*Mole*	*Int. kilojoules per mole*	*Kilojoules per mole*
1	15, 197. 4	−4. 0	57. 6	451. 2	0. 0267306	2220. 25	0. 68
2	15, 235. 8	−8. 3	68. 2	340. 5	. 0271917	2219. 34	−. 23
3	15, 231. 2	4. 8	24. 9	260. 5	. 0275458	2220. 69	1. 12
4	15, 230. 8	6. 9	32. 7	294. 6	. 0276635	2219. 40	−. 17
5	15, 223. 6	−2. 6	13. 1	278. 0	. 0274649	2219. 35	−. 22
6	15, 225. 4	6. 3	23. 6	280. 5	. 0272818	2219. 22	−. 35
7	15, 232. 4	2. 9	35. 4	281. 2	. 0274421	2219. 08	−. 49
8	15, 230. 9	. 6	19. 7	257. 8	. 0273537	2219. 20	−. 37
Mean						2219. 57	±. 45

[1] Includes the heat capacity of ½ the mass of liquid water formed in the reaction.

TABLE 8.—*Calorimetric results of the reaction experiments for normal butane*

Experiment no.	ΔR	k	K	U	Δ$t_{corr.}$	Average temperature
	Ohm	*Min^{-1}*	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*
1	0. 409115	0. 001946	0. 006179	−0. 000048	3. 99469	25. 00
2	. 410905	. 001939	. 006254	−. 000024	4. 01145	25. 00
3	. 409376	. 001940	. 006779	−. 000074	3. 99158	25. 00
4	. 411469	. 001925	. 006667	−. 000053	4. 01323	25. 00
5	. 411537	. 001923	. 006314	−. 000041	4. 01729	25. 00
6	. 409147	. 001927	. 006896	−. 000139	3. 98880	25. 00
7	. 411499	. 001928	. 006312	−. 000170	4. 01821	25. 00
8	. 410687	. 001935	. 006511	−. 000142	4. 00791	25. 00
Mean						

Experiment no.	Electrical energy equivalent of calorimeter system [1]	"Gas" energy	"Spark" energy	"Vaporization" energy	Mass of normal butane	Heat of combustion at 25 degrees C	Deviation from mean
	Int. joules per degree C	*Joules*	*Joules*	*Joules*	*Mole*	*Int. kilojoules per mole*	*Kilojoules per mole*
1	15, 254. 0	6. 9	7. 9	221. 7	0. 0212578	2876. 90	−0. 98
2	15, 260. 4	4. 0	14. 4	207. 3	. 0213428	2877. 49	−. 39
3	15, 208. 5	7. 4	23. 6	236. 3	. 0211713	2877. 80	−. 08
4	15, 224. 6	4. 6	17. 0	221. 9	. 0213016	2878. 17	. 29
5	15, 250. 5	5. 1	15. 7	220. 2	. 0213528	2879 06	1. 18
6	15, 248. 2	1. 9	15. 7	238. 8	. 0212144	2877. 63	−. 25
7	15, 218. 2	2. 4	17. 0	221. 5	. 0213140	2878. 72	. 84
8	15, 222. 1	2. 4	14. 4	216. 6	. 0212752	2877. 23	−. 65
Mean						2877. 88	±. 58

[1] Includes the heat capacity of ½ the mass of liquid water formed in the reaction.

TABLE 9.—*Calorimetric results of the reaction experiments for normal pentane*

Experiment no.	ΔR	k	K	U	$\Delta t_{\text{corr.}}$	Average temperature
	Ohm	*Min*$^{-1}$	*Ohm*	*Ohm*	*Degrees C*	*Degrees C*
1	0.410430	0.001937	0.005964	−0.000108	4.01045	25.00
2	.409639	.001936	.006180	−.000134	4.00072	25.00
3	.407770	.001952	.007482	−.000213	3.97007	25.00
4	.409557	.001950	.006136	−.000106	4.00007	25.00
5	.411967	.001949	.005585	−.000127	4.02963	25.02
6	.409974	.001943	.006808	−.000122	3.99770	25.00
7	.413547	.001925	.006274	−.000046	4.03766	25.01
8	.410295	.001945	.006162	−.000094	4.00701	25.01
Mean						

Experiment no.	Electrical energy equivalent of calorimeter system [1]	"Gas" energy	"Spark" energy	"Vaporization" energy	Mass of normal pentane	Heat [2] of combustion at 25 degrees C	Deviation from mean
	Int. joules per degree C	*Joules*	*Joules*	*Joules*	*Mole*	*Int. kilojoules per mole*	*Kilojoules per mole*
1	15,180.4	4.0	9.8	211.0	0.0172803	3535.25	−0.75
2	15,230.2	2.8	21.6	251.2	.0172938	3537.05	1.05
3	15,229.6	4.0	14.4	350.5	.0172008	3535.15	−.85
4	15,222.7	6.2	17.0	229.0	.0172761	3537.54	1.54
5	15,258.6	−1.1	15.1	256.6	.0174528	3537.07	1.07
6	15,214.3	1.7	24.9	282.7	.0172768	3535.76	−.24
7	15,063.6	−2.5	22.3	255.6	.0172734	3534.76	−1.24
8	15,213.7	1.1	18.3	240.5	.0173076	3535.41	−.59
Mean						3536.00	±.92

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[1] Includes the heat capacity of ½ the mass of liquid water formed in the reaction.

[2] Includes a correction of + 0.008 percent for the carbon monoxide formed.

VI. RESULTS OF THE PRESENT INVESTIGATION

The uncertainties in the final values obtained from the present data have been computed by taking the total percentage "error" as equal to $\pm\sqrt{e_1^2+e_2^2+e_3^2}$, where e_1 is the percentage "error" of the mean value of the calorimetric experiments with electrical energy, e_2 is the percentage "error" of the mean value of the calorimetric combustion experiments, and e_3 is an "error" of 0.01 percent assumed in the determination of the amount of reaction, due to impurities and other causes.

The data of the present investigation then yield for the heats of combustion, at a temperature of 25 C and a constant total pressure of 1 atmosphere, of gaseous ethane, gaseous propane, gaseous normal butane, and gaseous normal pentane, respectively, with gaseous oxygen to form gaseous carbon dioxide and liquid water, the following values, in international kilojoules per mole:

Ethane	1,559.57 ± 0.44
Propane	2,219.57 ± .51
Normal butane	2,877.88 ± .63
Normal pentane	3,536.00 ± .88

VII. DATA OF PREVIOUS INVESTIGATIONS

1. ETHANE

The existing data on the heat of combustion of ethane are those of Thomsen (1), and Berthelot and Matignon (2).

Thomsen performed seven experiments on ethane in his flame calorimeter at constant pressure and at an average temperature of 19 C. The first three experiments were made with a sample of ethane having the empirical formula $C_2H_{6.054}$, prepared from zinc ethyl and hydrochloric acid; the last four with a sample having the formula $C_2H_{6.033}$, prepared by the electrolysis of sodium acetate. Thomsen determined the amount of reaction from the mass of carbon dioxide formed. The writer has recomputed Thomsen's data, including a correction for an impurity of methane, and obtains from his work, for the heat of combustion of ethane at a temperature of 25 C and a constant pressure of 1 atmosphere, the value 368.9 ± 1.3 k-cal_{15}, or 1,543.2 ± 5.5 international kilojoules, per mole.

Berthelot and Matignon (2) performed three experiments on the heat of combustion of ethane, using a bomb calorimeter and working at an average temperature of 13 C. The amount of reaction was determined from the mass of carbon dioxide formed. Their recomputed data yield for the heat of combustion of ethane, at a temperature of 25 C and a constant pressure of 1 atmosphere, the value 372.1 ± 0.8 k-cal_{15}, or 1,556.6 ± 3.4 international kilojoules, per mole.

The various data on the heat of combustion of ethane are compared in figure 2. The values from Thomsen (1) and Berthelot and Matignon (2) are lower than the value from the present investigation by 1.05 and 0.19 percent, respectively.

2. PROPANE

The existing data on the heat of combustion of propane are those of Thomsen (1) and Berthelot and Matignon (2).

Thomsen performed seven experiments in his flame calorimeter, at constant pressure and at an average temperature of 17.8 C, on a sample of propane having the empirical formula $C_3H_{7.991}$, prepared from isopropyl iodide, zinc, and hydrochloric acid. The amount of reaction was determined from the mass of carbon dioxide formed. The recomputed data of Thomsen, including a correction for impurity, yield for the heat of combustion of propane, at a temperature of of 25 C and a constant pressure of 1 atmosphere, the value 528.7 ± 1.2 k-cal_{15}, or 2,211.7 ± 5.0 international kilojoules, per mole.

Berthelot and Matignon performed three experiments on propane in their bomb calorimeter at an average temperature of 17 C. The amount of reaction was determined from the mass of carbon dioxide formed. Their recomputed data yield for the heat of combustion of propane, at a temperature of 25 C and a constant pressure of 1 atmosphere, the value of 527.9 ± 1.8 k-cal_{15}, or 2208.4 ± 7.5 international kilojoules, per mole.

The various data on the heat of combustion of propane are compared in figure 2. The values from Thomsen (1), and Berthelot and Matignon (2) are lower than the value from the present investigation by 0.35 and 0.50 percent, respectively.

3. NORMAL BUTANE

There are no data on the heat of combustion of normal butane recorded in the literature.

4. NORMAL PENTANE

The only value for the heat of combustion of normal pentane recorded in the literature is that of Roth and Machlett (3). These authors have not published a report of their experiments, and give only the numerical result. Roth and Machlett found for the heat of combustion of liquid normal pentane, at constant volume in a bomb calorimeter at a temperature of 20 C, the value 11,551 g-cal$_{15}$ per gram of liquid normal pentane, weighed in air. Applying the appropriate corrections, this value becomes 832.8 k-cal$_{15}$ per true mole of liquid normal pentane, at a temperature of 25 C and a constant pressure of 1 atmosphere (lack of information prevents making the Washburn

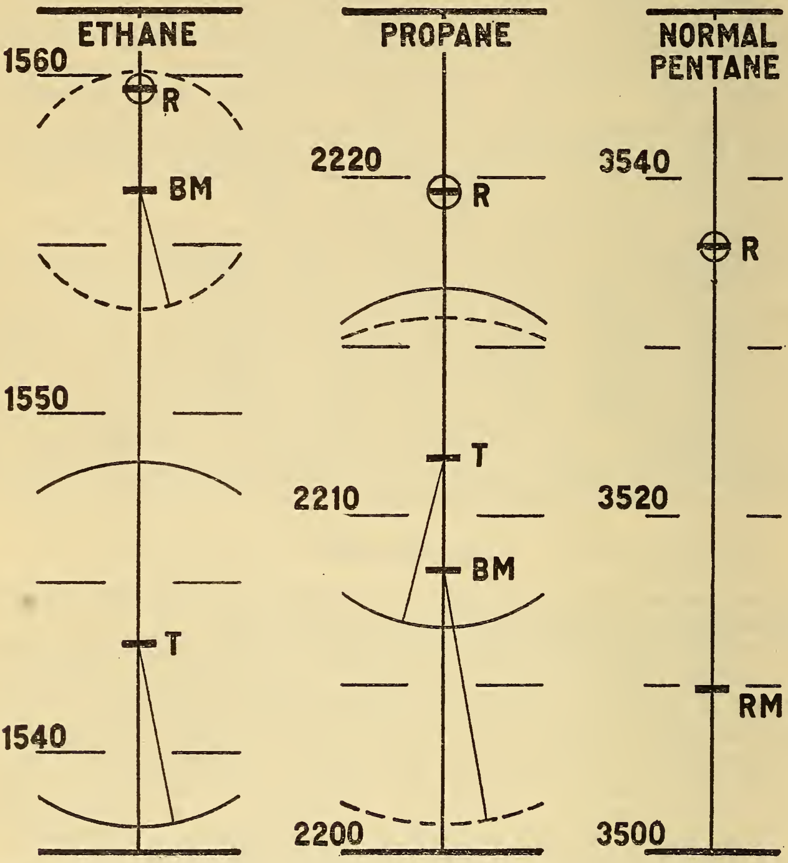

FIGURE 2.—*Plot of the various data on the heats of combustion of ethane, propane, and normal pentane.*

The ordinate scale gives the heat of combustion at a temperature of 25 C and a constant total pressure of 1 atmosphere in international kilojoules per mole. The average values of each investigation, together with the estimated uncertainties, are indicated as follows: T, Thomsen; BM, Berthelot and Matignon; RM, Roth and Machlett; R, Rossini.

correction). Roth and Machlett give for the heat of vaporization of liquid normal pentane at 20 degrees C the value 4.9 k-cal per mole. This value is apparently too low, as the calorimetric data of Griffiths and Awbery (9) yield 6.2 k-cal per mole for the heat of vaporization at 25 degrees C, and the data on the variation of the vapor pressure with temperature (10) yield 6.6 k-cal per mole. Taking the directly measured value of 6.2, the data of Roth and Machlett yield for the heat of combustion of gaseous normal pentane, at a temperature of 25 C and a constant total pressure of 1 atmosphere, the value 839.0 k-cal_{15}, or 3509.8 international kilojoules, per mole. If the value for the heat of vaporization given by Roth and Machlett were used, the above value would be lowered by 1.3 k-cal, or 5.4 kilojoules.

The data on the heat of combustion of gaseous normal pentane are compared in figure 2. The value from Roth and Machlett (3) is lower than that from the present investigation by 0.74 percent.

VIII. SUMMARY

The results of the present investigation confirm the suspected existence of exceedingly large uncertainties in the hitherto existing "best" values for the heats of combustion of ethane, propane, normal butane, and normal pentane. The values from the previous investigations given in the preceding section of the present paper were computed from the original data by this writer; while the values which have mostly been used for the heats of combustion of these gases are those given in the International Critical Tables (11). These latter values were taken from the compilation by Kharasch (12), and, when corrected to a temperature of 25 C, are all lower than those from the present investigation by the following respective amounts: Ethane, 1.23 percent; propane, 0.87 percent; normal butane, no existing data; normal pentane, 0.86 percent. These differences are from 30 to 50 times the estimated uncertainties in the values obtained from the present investigation.

The data of the present investigation give, for the heat involved in the reaction, C_nH_{2n+2} (gas) $+\frac{3n+1}{2}$ O_2 (gas) $= nCO_2$ (gas) $+ (n+1)H_2O$ (liquid) at a temperature of 25 C and a constant total pressure of 1 atmosphere, the following values for ethane, propane, normal butane, and normal pentane:

TABLE 10.—*Results of the present investigation*

Substance	Formula	State	Heat of combustion [a] at 25 degrees C and a constant pressure of 1 atmosphere	
			International kilojoules per mole (fundamental unit)	k-cal_{15} per mole (defined unit)
Ethane	C_2H_6	Gas	1559.57±0.44	372.81±0.11
Propane	C_3H_8	Gas	2219.57± .51	530.57± .12
Normal butane	n–C_4H_{10}	Gas	2877.88± .63	687.94± .15
Normal pentane	n–C_5H_{12}	Gas	3536.00± .88	845.27± .21

[a] As explained in sec. II, p. 736, the fundamental unit of energy in the present investigation is the international joule based upon standards maintained at this Bureau, while the k-cal_{15} is a defined unit, 1 k-cal_{15} being taken equivalent to 4.1850/1.00040 international kilojoules. One mole (18.0156 g, true mass) of H_2O is taken as equivalent to ⅓ mole of C_2H_6, to ¼ mole of C_3H_8, to ⅕ mole of C_4H_{10}, and to ⅙ mole of C_5H_{12}.

Data have now been obtained in this laboratory on the heats of combustion of all the normal paraffin hydrocarbons in the gaseous state from methane to pentane, inclusive. In a subsequent paper, these data will be utilized: First, in the calculation of the heats of formation of these molecules; second, in the accurate prediction of the heats of combustion and of formation of the gaseous normal paraffin hydrocarbons containing more than five carbon atoms in the molecule; and third, in drawing conclusions concerning the energies of the atomic linkages in these molecules.

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