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HEATS OF COMBUSTION OF THE LIQUID NORMAL PARAFFIN HYDROCARBONS FROM HEXANE TO DODECANE

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ABSTRACT

The measurements were made by means of a bomb calorimeter, which was calibrated electrically for some of the measurements, and by burning standard sample benzoic acid for the remainder. The samples of liquid were inclosed in thin-walled glass bulbs which were flattened on opposite sides, and were ignited by an electric fuse of iron wire. No combustible material other than the iron wire was required to ignite the liquids. Combustible impurities and carbon dioxide were removed from the oxygen before admitting it to the bomb. Measurements of carbon dioxide and carbon monoxide formed in the combustion indicated that the liquids contained very little inert impurity, and that combustion was very nearly complete. The Washburn correction was applied to the results of the calorimetric measurements. The empirical equation

$$-\Delta H_{25^\circ\mathrm{C}}=259.28+648.84n+0.2587n^2,$$

where $-\Delta H_{25^\circ\mathrm{C}}$ is the heat of combustion in international kilojoules per mole of liquid normal C_nH_{2n+2} in gaseous oxygen at 25° C and under a constant pressure of 1 atmosphere, the products of combustion being gaseous carbon dioxide and liquid water, also at 25° C, reproduces the mean values within 0.02 percent. The final experimental values are estimated to be accurate within 0.03 or 0.04 percent.

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I. INTRODUCTION

Accurate values of the heats of combustion of organic compounds are of importance in chemical thermodynamics chiefly because such values, together with data on the heats of formation of water and carbon dioxide, may be used to calculate the heats of formation of the compounds; and the heats of formation, together with the entropies of formation derived from specific heat and latent heat data in accordance with the third law of thermodynamics, may be used to calculate the free energies of formation of the compounds. For many organic compounds this is the only feasible method of obtaining the free energies of formation.

Accurate values for the heats of combustion of the gaseous normal paraffin hydrocarbons from methane to pentane have been reported by Rossini [14, 15].[1] Most previous data on the higher members of this series are not sufficiently accurate to permit the calculation of reliable free-energy values. For this reason, and because it is now possible to obtain materials of higher purity than those available to most previous investigators, it was desirable that new measurements of the heats of combustion of the normal paraffins above pentane be undertaken.

II. APPARATUS AND METHOD

The calorimeter and accessory apparatus, experimental procedure, and methods of calculating results have been described in detail previously [3,8].

The only feature of the methods of the present work which requires further description is the method of burning the samples of volatile liquids in the bomb. Samples of 0.5 to 1.0 g of liquid were inclosed in thin-walled glass bulbs which were flattened on opposite sides and filled completely with liquid in the manner described by Richards and Barry [13]. The flexible flat sides of the bulbs yielded sufficiently under the pressure (30 atmospheres) of the oxygen in the bomb, so that the pressure was supported by the inclosed liquid. The empty bulbs without the stems through which they were filled weighed from about 0.02 to 0.09 g each, the usual weight being about 0.03 to 0.04 g. The weights of the bulbs used by Richards and Barry varied from 0.3 to 0.5 g.

The samples were ignited by means of an electric fuse consisting of a 2-cm length of no. 36 AWG iron wire, which was wound in a small helix, attached to platinum leads about 0.2 mm in diameter, and placed in contact with the bulb containing the sample. It was not necessary to use any combustible material other than the iron wire to ignite the samples. The samples were burned in a cylindrical platinum crucible ⅝ inch in height and ¾ inch in diameter.

The glass of the bulbs was fused during combustion, and after opening the bomb at the end of an experiment, was found in the form of one or more small globules on the bottom of the crucible. In some cases these globules were clear and in others they were darkened by some material distributed through the glass. This material was probably iron oxide, although there is a possibility that small amounts of unburned carbon may have been inclosed in the glass. The presence of carbon does not seem very probable, however, in view of the volatility of the liquids. The darkening of the glass globules did not appear to be associated with any systematic lowering of heat of combustion, or of the amount of carbon dioxide plus carbon monoxide formed in the combustion, and consequently if carbon was inclosed in the glass globules the amounts were probably negligible.

The thermal effect of solution of iron oxide and of gases in the molten glass was probably negligible.

The volume of the bomb used was 377 cm^3. One cubic centimeter of water was placed in the bomb before each experiment.

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[1] Numbers in brackets refer to the literature references at the end of this paper.

III. MATERIAL

The samples of normal octane, nonane, decane, undecane, and dodecane used in this work were supplied by Prof. A. L. Henne of Ohio State University. They were prepared by Shepard, Henne, and Midgley [20] by distillation from petroleum. The normal heptane used was separated from petroleum at this Bureau by Hicks-Bruun and Bruun [5], and was further fractionally distilled by S. T. Schicktanz. The normal hexane was synthesized and purified by Mair [11].

The references cited contain data on the freezing points and boiling points of these compounds. These data indicate that the compounds were of a high degree of purity. Hick-Bruun and Bruun estimated the purity of the *n*-heptane to be better than 99 mole percent. Mair stated that the differences between the freezing points of the compounds synthesized by him and those separated from petroleum by Shepard, Henne, and Midgley indicate differences in purity of much less than 1 mole percent. The impurities most likely to be present in all the compounds are isomers, the heats of combustion of which probably do not differ from those of the normal compounds by more than a few tenths of 1 percent. The presence of 1 mole percent of isomers in a given normal compound would therefore affect the heat of combustion by only a few thousandths of 1 percent.

In the present work tests for inert impurities, such as dissolved water or air, were made by burning weighed samples of the liquids in the bomb under the same conditions as in the calorimetric measurements, and determining the amounts of carbon dioxide and carbon monoxide formed in the combustion. The carbon dioxide was determined by allowing the gaseous products of combustion to flow from the bomb through a drying tube containing Dehydrite ($Mg(ClO_4)_2 \cdot 3H_2O$) and P_2O_5, and then through a weighed glass-stoppered U-tube containing successively Ascarite (a sodium hydroxide-asbestos mixture) to absorb the CO_2, and Dehydrite and P_2O_5 to prevent loss of water vapor coming from the Ascarite. After the pressure in the bomb had been reduced to that of the atmosphere, hydrogen was admitted to the bomb to a pressure of about 10 atmospheres, and then released through the absorbing tubes mentioned above. This procedure was repeated several times until the residual mass of CO_2 in the bomb was negligibly small. The U-tube containing the Ascarite was then weighed and its increase in weight, corrected to vacuum, was taken as the mass of CO_2 formed in the combustion. The U-tube was filled with hydrogen in both the initial and final weighings, so that errors due to uncertainty in the value used for the change in volume of the Ascarite on absorption of CO_2 were negligible [14].

In the measurements on the normal paraffins from octane to dodecane, CO in the products of combustion was determined by C. Creitz of this Bureau, by the iodine pentoxide method described by Eiseman, Weaver, and Smith [4]. The amounts of CO found in the products of combustion of *n*-dodecane, *n*-undecane, *n*-decane, and *n*-octane were negligible. For *n*-nonane the carbon determined as CO amounted to 0.051 percent of the total carbon. Measurements of CO by the iodine pentoxide method were also made for one lot of *n*-heptane and for three measurements on *n*-hexane. The carbon determined as CO by this method in the products of combustion of the *n*-heptane amounted to 0.064 percent of the total carbon, and the total carbon found was higher by about 0.06 percent than that calculated from the mass of *n*-heptane burned, on the assumption that it was pure. The carbon determined as CO in the products of combustion of the *n*-hexane amounted to about 2 percent of the total carbon, and the total carbon was higher by about 2 percent than that calculated from the mass of the samples burned. These data indicated that some trouble had developed in the iodine pentoxide apparatus, and as a result of this trouble the values obtained for CO in the products of combustion were too high. Hence, in the remaining measurements on *n*-hexane, CO was determined by another method. This method consisted in passing the products of combustion, after removal of the CO_2, through a copper tube heated to about 700° C, absorbing the CO_2 formed in Ascarite, and weighing it. These measurements gave for the carbon determined as CO, 0.032 percent of the total carbon. Tests by the iodine pentoxide method indicated no CO in the gas from the bomb after passing through the hot copper tube. Later another lot of *n*-heptane was obtained, and measurements of CO by the second method indicated that only 0.004 percent of the total carbon was present in the products of combustion as CO. The results on *n*-heptane reported in this paper are for this second sample.

Since nitric acid is formed from the nitrogen and water in the bomb, it is possible that some nitric acid may be carried out in the gaseous products of combustion, and be absorbed by the Ascarite. Calculations based on the partial pressure of nitric acid in the gas phase over aqueous solutions [6] indicate that the amount of nitric acid carried out in this manner is entirely negligible. In these calculations it was assumed that the gas in the bomb was at all times in equilibrium with that part of the solution which was condensed on the top and sides of the bomb where the concentration of nitric acid was greatest. The value for the concentration of the solution at these points was obtained in experiments in which the air initially in the bomb was not washed out prior to filling the bomb with oxygen, and consequently the total amount of nitric acid formed was about three times that normally formed.

In connection with the question as to whether nitric acid was carried out of the bomb in the gaseous products of combustion the following experiment was performed: A 1.5-g sample of benzoic acid was burned in the bomb, which had been filled with oxygen without washing out the air initially in it. The products of combustion were allowed to bubble slowly through about 10 cm^3 of distilled water in a glass U-tube which was filled with small glass beads and was immersed in an ice bath. After the pressure in the bomb had been reduced to 1 atmosphere, the bomb was filled several times with hydrogen to a pressure of about 10 atmospheres, and the hydrogen was allowed to bubble through the water in the U-tube. The total volume of gas bubbled through the water was about 40 liters. The water was then removed from the tube and titrated against a 0.01N solution of KOH, using phenolphthalein as an indicator. An approximately equal volume of distilled water was titrated against the same solution of KOH under the same conditions. No difference was detected between the distilled water and the water through which the products of combustion had been bubbled. The method was sufficiently sensitive to detect about 0.1 mg of nitric acid in the water. Even if only one-third of the nitric acid vapor was absorbed in the water, the total mass of nitric acid vapor carried out of the bomb could hardly have exceeded 0.01 percent of the mass of carbon dioxide formed in the combustion.

The results of the measurements of carbon dioxide and carbon monoxide formed in combustion of the various compounds are summarized in table 1. In the third column of this table are given the ratios of the masses of carbon found to those calculated from the masses of the samples on the assumption that the compounds were pure. The values of atomic weights used in the calculations are C=12.009, H=1.0081, and O=16.000. All weights were corrected for the effect of the buoyancy of the air.

There is considerable evidence [2] that the values used for the atomic weights of carbon and hydrogen are more nearly correct than the present international values. The value 12.009 for carbon is believed to be accurate to ±0.002, while the value 1.0081 for hydrogen is believed to be accurate to ±0.0001.

It is very probably that organic liquids exposed to the air contain small amounts of inert impurities, such as dissolved air and water, and consequently it would be expected that the values $C_{found}/C_{calc.}$ given in table 1 would be slightly less than unity. This is seen to be the case for all the compounds listed in table 1 except *n*-nonane and *n*-dodecane. The high value of the carbon found for *n*-nonane is probably due to an error in the determination of CO by the iodine pentoxide method, which, as mentioned previously, gave too high results in some cases. If it were assumed that no CO was present in the products of combustion of this compound, the value of $C_{found}/C_{calc.}$ would be 0.999 68 instead of 1.000 19 as given in table 1, and the heat of combustion per gram of liquid would be lower by 0.021 percent than that given later, if no correction for unburned CO had been applied. Then if the departure from unity of the ratio $C_{found}/C_{calc.}$ were attributed to inert impurities and the value for heat of combustion corrected accordingly, the corrected value for heat of combustion of *n*-nonane would be higher by 0.011 percent than that given later. As some CO was probably present in the products of combustion, the error in the value given for the heat of combustion of *n*-nonane due to error in determining CO is probably less than 0.011 percent.

TABLE 1.—*Results of determinations of carbon dioxide and carbon monoxide in products of combustion of normal paraffin hydrocarbons*

Compound	Number of observations	$\frac{C_{found}}{C_{calc}}$	Deviation from mean	
			Average	Maximum
n-Hexane	5	0.999 89	±0.000 27	0.000 59
n-Heptane	5	.999 82	±.000 08	.000 13
n-Octane	5	.999 97	±.000 30	.000 70
n-Nonane	3	1.000 19	±.000 24	.000 36
n-Decane	3	.999 92	±.000 07	.000 10
n-Undecane	5	.999 97	±.000 13	.000 18
n-Dodecane	4	1.000 01	±.000 38	.000 76

It seems very unlikely that the high value of the carbon found for *n*-nonane could have been caused by the presence of higher members of the paraffin series as impurities, on account of the large amount of such impurities which would be required to explain the high value. For example, a mixture of nonane and decane containing 0.019 percent more carbon per gram than pure nonane would contain about 12 percent of decane.

The oxygen used was ordinary commercial oxygen, and contained some combustible impurities which were removed by passing the oxygen through a porcelain tube containing copper oxide heated to about 700° C. After this treatment the oxygen was passed through a tube containing Ascarite before being admitted to the bomb, in order to remove any CO_2 which might be present.

IV. CALIBRATION OF CALORIMETER

For the measurements on *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, and *n*-dodecane, the energy equivalent, or effective heat capacity, of the calorimeter was the same as in the measurements on benzoic acid [8], namely, 13 $587._2$ international joules per degree centigrade at 28.8° C, a value which was the result of a large number of electrical calibrations of the calorimeter.

Prior to the measurements on *n*-hexane a new resistance thermometer was constructed to replace the original thermometer which had not been entirely satisfactory, also some changes were made in the bomb which increased its heat capacity to some extent. It was therefore necessary to redetermine the energy equivalent of the calorimeter. This was done by burning 10 samples of "standard sample" benzoic acid in the calorimeter, using as the heat of combustion of this material the value recently determined at this Bureau [8], 26 414 international joules per gram mass when the charge is burned under the following standard conditions.

Temperature to which reaction is referred	30° C.
Initial oxygen pressure at 30° C	30 atm.
Mass of benzoic acid burned per unit of bomb volume	3 g/liter.
Mass of water placed in bomb per unit of bomb volume	3 g/liter.

The results of this calibration are given in table 2.

TABLE 2.—*Results of calibration of calorimeter for measurements on n-hexane*

Experiment	Observed energy equivalent at 30° C	Deviation from mean	
	*Int.*j/°C.	*Int.*j/°C.	*Percent*
1	13 601.4	+2.7	+0.020
2	13 592.6	−6.1	−.045
3	13 597.8	−0.9	−.007
4	13 594.4	−4.3	−.032
5	13 596.2	−2.5	−.018
6	13 596.5	−2.2	−.016
7	13 606.3	+7.6	+.056
8	13 601.7	+3.0	+.022
9	13 602.5	+3.8	+.028
10	13 597.2	−1.5	−.011
Mean	13 $598._7$	±3.5	±.025

After the measurements on *n*-hexane about a year elapsed before the measurements were made on *n*-heptane. During this time the gold washer in the bomb was replaced, the constants of the thermometer and the corrections to the bridge changed slightly, and a small amount of oil accumulated on the calorimeter heater. The calorimeter was therefore calibrated again by means of benzoic acid, immediately following the measurements on the *n*-heptane. The results of this calibration are shown in table 3.

TABLE 3.—*Results of calibration of calorimeter for measurements on n-heptane*

Experiment	Observed energy equivalent at 30° C	Deviation from mean	
	Int. j/°C	*Int.* j/°C	*Percent*
1	13 591.7	−3.6	−.026
2	13 591.3	−4.0	−.029
3	13 600.9	+5.6	+.041
4	13 594.9	−0.4	−.003
5	13 597.5	+2.2	+.016
Mean	13 595.$_3$	±3.2	±.026

The value of the energy equivalent calculated from the value given in table 2, the change in weight of the gold washer, and the weight of oil which accumulated on the calorimeter heater is 13 597$_6$ international joules per degree centigrade, a value which is 0.017 percent higher than the mean value given in table 3. The value given in table 3 was used in calculating the results of measurements on *n*-heptane.

V. RESULTS OF CALORIMETRIC COMBUSTION EXPERIMENTS

The results of the individual combustion experiments are given in table 4. Each observed value of heat of combustion under the conditions of the bomb process, $-\Delta U_B$, was reduced, by the method given by Washburn [23], to the difference, $-\Delta U_R$, in the internal energies of the initial system, consisting of liquid hydrocarbon and gaseous oxygen at 30° C and under a pressure of 1 atmosphere, and the final system, consisting of gaseous CO_2 and liquid water each separately at 30° C and under a pressure of 1 atmosphere. The reduction to $-\Delta U_R$ was made by Washburn's complete equation, modified so as to apply at 30° C instead of 20° C. The difference between $-\Delta U_B$ and $-\Delta U_R$ is less by about 20 percent at 30° than at 20° C.

The results are summarized in table 5. The observed values of $-\Delta U_R$ in column 2 were taken from table 4. The values of C_{found}/C_{calc} in column 3 were taken from table 1.

TABLE 4.—*Results of combustion experiments*

n-HEXANE

Experiment	Mass of sample (wt. in vacuo)	Initial oxygen pressure at 30° C	Final temperature of calorimeter	Observed heat of combustion	Reduction to p=1 atm	Reduction to 30° C	$-\Delta U_R$ at 30° C	Deviation from mean	
	g	atm	°C	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Percent*
1	0.486 24	30.6	29.45	48 193.0	−7.7	−2.4	48 182.9	+12.3	+0.026
2	.687 42	31.3	30.00	48 171.6	−8.9	.0	48 162.7	−7.9	−.016
3	.704 48	30.5	29.84	48 183.1	−8.7	−.7	48 173.7	+3.1	+.006
4	.694 47	29.6	30.24	48 180.5	−8.6	+1.0	48 172.9	+2.3	+.005
5	.600 51	27.9	29.83	48 160.6	−7.6	−.7	48 152.3	−18.3	−.038
6	.569 63	29.5	30.30	48 185.5	−7.9	+1.3	48 178.9	+8.3	+.017
Mean							48 170.$_6$	±8.7	±.018

TABLE 4.—*Results of combustion experiments*—Continued

Experiment	Mass of sample (wt. in vacuo)	Initial oxygen pressure at 30° C	Final temperature of calorimeter	Observed heat of combustion	Reduction to $p=1$ atm.	Reduction to 30° C	$-\Delta U_R$ at 30° C	Deviation from mean	
	g	atm	°C	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Percent*
n-HEPTANE									
1	1.018 85	31.1	29.92	47 926.4	−11.2	−0.3	47 914.9	−6.3	−0.013
2	.921 18	30.7	29.38	47 948.4	−10.6	−2.0	47 935.8	+14.6	+.030
3	.896 79	30.6	30.01	47 935.6	−10.5	.0	47 925.1	+3.9	+.008
4	1.017 79	31.1	29.88	47 929.9	−11.1	−.4	47 918.4	−2.8	−.006
5	.903 58	30.5	30.28	47 909.8	−10.5	+.9	47 900.2	−21.0	−.044
6	1.011 96	30.9	30.29	47 943.3	−11.2	+.9	47 933.0	+11.8	+.025
Mean							47 921.$_2$	±10.1	±.021
n-OCTANE									
1	0.592 92	29.8	28.77	47 751.9	−8.8	−5.2	47 737.9	−6.8	−0.014
2	.546 31	30.1	29.77	47 738.2	−8.8	−1.0	47 728.4	−16.3	−.034
3	.493 43	29.8	30.04	47 750.6	−8.5	+.2	47 742.3	−2.4	−.005
4	.638 15	29.4	29.31	47 769.6	−9.1	−2.9	47 757.6	+12.9	+.027
5	.639 98	29.4	30.17	47 752.2	−9.2	+.7	47 743.7	−1.0	−.002
6	.543 23	29.1	29.68	47 768.2	−8.6	−1.3	47 758.3	+13.6	+.028
Mean							47 744.$_7$	±8.8	±.019
n-NONANE									
1	0.997 76	29.8	30.11	47 615.2	−11.4	+0.4	47 604.2	−1.7	−0.004
2	.967 18	29.8	30.16	47 604.4	−11.0	+.6	47 594.0	−11.9	−.025
3	.578 20	29.8	30.12	47 611.3	−9.0	+.5	47 602.8	−3.1	−.007
4	.655 62	30.1	29.93	47 597.4	−9.5	−.3	47 587.6	−18.3	−.038
5	.621 80	30.1	29.30	47 640.9	−9.5	−2.9	47 628.5	+22.6	+.047
6	.700 36	29.8	30.17	47 627.2	−9.5	+.7	47 618.4	+12.5	+.026
Mean							47 605.$_9$	±11.7	±.025
n-DECANE									
1	0.824 62	30.1	29.52	47 509.7	−10.4	−1.9	47 497.4	−0.9	−0.002
2	.820 19	30.1	30.09	47 508.1	−10.4	+.4	47 498.1	−.2	.000
3	.723 75	30.1	29.64	47 511.1	−9.5	−1.5	47 500.1	+1.8	+.004
4	.707 15	30.1	29.75	47 506.0	−10.0	−1.0	47 495.0	−3.3	−.007
5	.733 20	30.1	30.18	47 506.1	−10.0	+.7	47 496.8	−1.5	−.003
6	.789 18	30.1	30.26	47 511.5	−10.0	+1.1	47 502.6	+4.3	+.009
Mean							47 498.$_3$	±2.0	±.004
n-UNDECANE									
1	0.574 00	21.6	29.76	47 391.5	−7.6	−1.0	47 382.9	−18.9	−0.040
2	.850 56	28.8	29.81	47 408.1	−10.4	−.8	47 396.9	−4.9	−.010
3	.676 60	28.4	29.55	47 441.8	−9.5	−1.8	47 430.5	+28.7	+.061
4	.535 67	28.4	29.71	47 420.7	−9.0	−1.2	47 410.5	+8.7	+.018
5	.934 76	28.4	29.72	47 414.9	−10.9	−1.1	47 402.9	+1.1	+.002
6	.767 13	28.4	29.85	47 397.4	−9.9	−.6	47 386.9	+14.9	−.031
Mean							47 401.$_8$	±12.9	±.027
n-DODECANE									
1	0.483 37	29.8	29.91	47 348.4	−9.0	−0.4	47 339.0	−8.2	−0.017
2	.425 50	29.8	29.95	47 352.3	−8.5	−.2	47 343.6	−3.6	−.008
3	.576 51	29.1	29.84	47 359.7	−9.5	−.6	47 349.6	+2.4	+.005
4	.544 64	28.8	29.83	47 326.5	−9.0	−0.7	47 316.8	−30.4	−.064
5	.670 21	22.2	29.97	47 387.0	−8.0	−.1	47 378.9	+31.7	+.067
6	.429 34	21.6	30.06	47 362.3	−6.6	+.2	47 355.5	+8.3	+.018
Mean							47 347.$_2$	±14.1	±.030

TABLE 5.—*Summary of results*

Substance	$-\Delta U_R$ observed at 30° C	$C_{found}/C_{calc.}$	$-\Delta U_R$ corrected at 30° C		$-\Delta H_{30°\,C}$ observed	$-\Delta H_{25°\,C}$		Obs.−Calc.
						Observed	Calculated	
	Int. j/g (*mass*)		*Int.* j/g	*Int.* kj/*mole*	*Int.* kj/*mole*	*Int.* kj/*mole*	*Int.* kj/*mole*	*Percent*
n-Hexane	48 170.6	0.999 89	48 175.9	4 151.19	4 160.$_1$	4 161.$_5$	4 161.$_6$	−0.002
n-Heptane	47 921.2	.999 82	47 929.8	4 802.22	4 812.$_4$	4 814.$_0$	4 813.$_8$	+.004
n-Octane	47 744.7	.999 97	47 746.1	5 453.46	5 464.$_8$	5 466.$_6$	5 466.$_6$	+.000
n-Nonane	47 605.9	1.000 19	47 605.9	6 105.12	6 117.$_8$	6 119.$_8$	6 119.$_8$	+.000
n-Decane	47 498.3	.999 92	47 502.1	6 758.04	6 772.$_0$	6 774.$_2$	6 773.$_5$	+.010
n-Undecane	47 401.8	.999 97	47 403.2	7 408.82	7 424.$_0$	7 426.$_4$	7 427.$_8$	−.019
n-Dodecane	47 347.2	1.000 01	47 347.2	8 064.04	8 080.$_6$	8 083.$_2$	8 082.$_6$	+.007

The corrected values of $-\Delta U_R$ in column 4 were obtained from the observed values on the assumption that the departures from unity of the ratios $C_{found}/C_{calc.}$, where these ratios are less than unity, are due to inert impurities. The conversion to international kilojoules per mole was made using the atomic weights C=12.009 and H=1.0081. This method of calculation is equivalent to determining the mass of hydrocarbon burned from the mass of CO_2 formed in the complete combustion of the sample. Hence an error of 0.001 in the value used for the atomic weight of carbon would cause an error of only 1 in 44 000 in the heat of combustion per mole of hydrocarbon. Where the observed ratio $C_{found}/C_{calc.}$ is greater than unity, as in the case of *n*-nonane, an error of 0.001 in the atomic weight of carbon would cause an error of about 0.007 percent in the heat of combustion per mole of hydrocarbon.

The observed values of $-\Delta H_{30°\,C}$ for the reaction:

$$C_nH_{2n+2}(\text{liq})+\frac{3n+1}{2}O_2(\text{gas})$$
$$=nCO_2(\text{gas})+(n+1)H_2O(\text{liq})\ (30°\ C,p=1\ \text{atm})$$

which are given in column 6 of table 5 were obtained by adding to the values of $-\Delta U_R$ in column 5 the values of $-\Delta(pV)$ for the above reaction. The reduction to 25° C was made using the specific heat data taken from International Critical Tables [7]. These data are given in table 6.

TABLE 6.—*Specific heat data used in calculating temperature coefficients of heats of combustion*

Substance	C_p (p=1 atm)	Temperature	Substance	C_p (p=1 atm)	Temperature
	j/*mole* °C	°C		j/*mole* °C	°C
Oxygen (gas)	29.18	28	*n*-Octane (liquid)	241.3	0 to 50
Carbon dioxide (gas)	36.90	28	Nonane (liquid)	269.9	0 to 50
Water (liquid)	75.23	28	Decane (liquid)	298.9	0 to 50
n-Hexane (liquid)	190.0	0 to 50	Undecane (liquid)	327.7	0 to 50
n-Heptane (liquid)	212.6	0 to 50	Dodecane (liquid)	356.5	0 to 50

The values of $-\Delta H_{25°\,C}$ in column 8 of table 5 were calculated by means of the following empirical equation, which was derived by the method of least squares:

$$-\Delta H_{25°\,C}=259.28+648.84n+0.2587n^2,$$

where n is the number of carbon atoms per molecule. As shown in the last column of table 5 the average difference between observed and calculated results is about 0.01 percent, and the maximum difference about 0.02 percent. This agreement is somewhat better than would be expected from the precision of the various measurements, and may be partly fortuitous. It is believed, however, that the experimental results are accurate within about 0.03 to 0.04 percent.

If $n=5$ is substituted in the preceding equation, the calculated value 3 509.95 international kilojoules per mole is obtained for the heat of combustion of liquid *n*-pentane at 25° C and a constant pressure of 1 atmosphere. Rossini [15] has reported the value 3 536.00 ±0.88 international kilojoules per mole for the heat of combustion of gaseous *n*-pentane at 25° C and at constant pressure, and from a review of existing data [16] has selected 6.3 kilocalories per mole, or 26.35 international kilojoules per mole, as the most probable value for the heat of vaporization of *n*-pentane at 25° C. Subtracting this value for heat of vaporization from Rossini's value for the heat of combustion of gaseous *n*-pentane gives 3 509.65 international kilojoules per mole for the heat of combustion of liquid *n*-pentane, a value which is in agreement within 0.01 percent with that obtained by extrapolation of the data of the present work.

Values obtained by substituting 2, 3, and 4 for *n* in the preceding equation are higher, by amounts greater than the experimental uncertainties, than the heats of combustion of liquid ethane, propane, and normal butane, respectively, obtained by combining Rossini's data on heats of combustion of gaseous ethane, propane, and normal butane with values for the heats of vaporization of these compounds. This is to be expected, for Rossini has shown [17] that although there is a linear relation between heat of combustion and the number of carbon atoms in the molecule for the gaseous normal paraffin hydrocarbons above *n*-pentane, this relation does not hold for the gaseous normal paraffins below *n*-pentane.

VI. PREVIOUS WORK

Values of the heats of combustion of liquid normal paraffin hydrocarbons deduced from data reported by previous investigators are compared in table 7 with the results of the present work.

TABLE 7.—*Results deduced from data of previous investigators compared with results of present work*

[Values of $-\Delta U_R$ at 30° C are given in international joules per gram mass. Figures in parentheses represent percentage differences from results of present work.]

Investigator	*n*-Hexane	*n*-Heptane	*n*-Octane	*n*-Decane	*n*-Dodecane
Louguinine		[a] 47 360 (−1.2)			
Stohmann, Kleber, and Langbein	[b] 47 969 (−0.43)				
Zubow	[a] [c] 47 934 (−0.50)		[a] [c] 47 599 (−0.31)	[a] [c] 47 267 (−0.50)	
Richards and Jesse			47 542 (−0.43)		
Jessup (unpublished)		[b] 47 894 (−0.075)	[b] 47 712 (−0.071)		
Roth			[a] 47 777 (+0.065)		
Banse and Parks			[a] 47 761 (+0.031)		[a] 47 349 (+0.004)
Present work	48 176	47 930	47 746	47 502	47 347

[a] Experimental conditions not given in sufficient detail to permit comparison with present work to be made with certainty.

[b] Results are probably too low on account of loss of liquid by evaporation.

[c] The Washburn correction has not been applied to these values.

Measurements of the heat of combustion of liquid *n*-hexane by means of a bomb calorimeter were made by Zubow [24], and by Stohmann, Kleber, and Langbein [21]. Zubow reported the value 11 602.6 calories per gram weighed in air for the heat of combustion at 18° C under the conditions of the bomb process. He also reported the value 9 706 calories per gram weighed in air for the heat of combustion of naphthalene under the same conditions. Using the value 1.5203, based on Dickinson's [3] work, for the ratio of the heats of combustion per gram in air of naphthalene and benzoic acid at about 25° C, and the value reported by Jessup and Green [8] for the heat of combustion of benzoic acid at 25° C and under the standard conditions mentioned previously, 26 440 international joules per gram weighed in air, the heat of combustion of naphthalene at 25° C and under the conditions of the bomb process is calculated to be 40 197 international joules per gram weighed in air. Upon reduction to 18° C the heat of combustion of naphthalene becomes 40 207 international joules per gram weighed in air. Multiplying Zubow's value for *n*-hexane by the ratio 40 207/9 706, reducing to 30° C and correcting for air buoyancy, there is obtained the value 47 934 international joules per gram mass for the heat of combustion under the conditions of the bomb process. Application of the Washburn correction probably would not change the value given above by more than about 0.03 percent.

Stohmann, Kleber, and Langbein [21] made two measurements of the heat of combustion of liquid *n*-hexane at about 15° C and under an initial oxygen pressure of 24 atmospheres. The volume of their bomb was 294 cm^3. Combustible impurities were removed from the oxygen by passing it through a red-hot copper tube. No water was placed in the bomb, but the oxygen was not dried before compressing it, and presumably was saturated with water vapor. In the first experiment the platinum crucible was covered with a thin sheet of collodion to prevent evaporation of the *n*-hexane. In the second experiment the sample was burned in a glass bulb having two necks, one of which was very narrow. The larger neck was closed by a drop of molten stearic acid, and the *n*-hexane was introduced through the smaller neck. It appears doubtful whether either of these devices entirely prevented evaporation. The two results agreed within 0.06 percent, the mean being 11 501.2 calories per gram (in air?) under the conditions of the bomb process. Stohmann, Kleber, and Langbein also measured the heat of combustion of benzoic acid [22] under the conditions mentioned above, and obtained the value 6 322.3 calories per gram (weighed in air?). After application of the Washburn correction, reduction to 30° C, correction for air buoyancy, and reduction to present energy units on the basis of data on the heat of combustion of benzoic acid by Stohmann, Kleber, and Langbein, and by Jessup and Green [8], the data on *n*-hexane by Stohmann, Kleber, and Langbein yield the value 47969 international joules per gram mass for $-\Delta U_B$ at 30° C.

Louguinine [10] reported the value 1 137 450 calories per mole for the heat of combustion of liquid *n*-heptane. The measurement was made at constant pressure, and the mass of sample burned was calculated from the mass of carbon dioxide formed in combustion. The temperature to which the reaction is referred, and the atomic weights of carbon and oxygen are not given, and the relation of the energy unit used to the present units is not known. Using the relation, 1 calorie=4.1833 international joules, Louguinine's value for *n*-heptane becomes 4 758 international kilojoules per mole. The corresponding value of $-\Delta U_R$ is 47 360 international joules per gram.

The present writer in 1927 made two measurements of the heat of combustion of *n*-heptane and two measurements of the heat of combustion of *n*-octane. The data were not published but the values obtained were given by Kharasch [9] in a review of the literature on heats of combustion of organic compounds. The samples were burned in gelatin capsules, which did not entirely prevent loss of liquid by evaporation. The calorimeter was calibrated with benzoic acid. The two results on *n*-heptane agreed within 0.08 percent, while the two results on *n*-octane agreed with 0.02 percent. The mean values of $-\Delta U_R$ at 30° were, expressed in international joules per gram mass, 47 894 for *n*-heptane, and 47 712 for *n*-octane.

Richards and Jesse [12] reported the results of two measurements of the heat of combustion of *n*-octane. They give their results in terms of the temperature rise of their calorimeter produced by burning together in the bomb, a known mass of *n*-octane and a known mass of sucrose. They also give the temperature rise produced by the combustion of a known mass of sucrose alone in the bomb. The present writer has applied the Washburn correction and recalculated their results, using the value 1.6027, based on Dickinson's [3] work, for the ratio of the heats of combustion per gram weighed in air of benzoic acid and sucrose, at about 25° C and under an initial oxygen pressure of 30 atmospheres, and the value 26 440 international joules per gram [8] (weighed in air) for the heat of combustion of benzoic acid at 25° C and under the standard conditions mentioned previously. The two recalculated values for the heat of combustion of *n*-octane agree within 0.04 percent, the mean value of $-\Delta U_R$ being 47 542 international joules per gram mass.

Zubow [24] reported the value 11 519.9 calories per gram weighed in air for the heat of combustion of *n*-octane. After recalculation in the manner described for *n*-hexane this value becomes 47 599 international joules per gram mass.

Roth [18] determined the heat of combustion of *n*-octane by means of a bomb calorimeter. The data were not published, but the value 11 449 calories per gram weighed in air is given in the Landolt-Börnstein tables. As the conditions under which this value was obtained and the energy unit used are not known, comparison with the results of the present work cannot be made with certainty. Assuming that the temperature to which the combustion was referred was 20° C, the initial oxygen pressure 35 atmospheres, and the calorie used was equal to 4.184 international joules, the value of $-\Delta U_R$ at 30° C calculated from Roth's value given above is 47 777 international joules per gram mass.

Zubow [24] reported the value 11 438.8 calories per gram weighed in air for the heat of combustion of liquid *n*-decane at 18° C and under the conditions of the bomb process. This value when recalculated in the manner described for *n*-hexane and *n*-octane becomes 47 267 international joules per gram mass.

Banse and Parks [1] in Roth's laboratory made three measurements of the heat of combustion of *n*-octane and four measurements of the heat of combustion of *n*-dodecane. The samples used were prepared by

Shepard, Henne, and Midgley [20], and were therefore probably identical with the samples of *n*-octane and *n*-dodecane used in the present work. The measurements were made at 19° C by means of a bomb calorimeter which was standardized with benzoic acid, using the value 6 324 calories per gram weighed in air for the heat of combustion of this substance. The average deviation from the mean of the individual results was 0.10 percent for *n*-octane, and 0.08 percent for *n*-dodecane. The values reported for the heats of combustion under the conditions of the bomb process are 11 434 calories per gram mass for *n*-octane, and 11 335 calories per gram mass for *n*-dodecane. After reduction to the present energy units, using data on the heat of combustion of benzoic acid by Jessup and Green [8], application of the approximate Washburn correction, and reduction to 30° C, the data of Banse and Parks yield for $-\Delta U_R$ the values 47 761 international joules per gram mass for *n*-octane and 47 349 international joules per gram mass for *n*-dodecane. There is some uncertainty in the application of the Washburn correction to the data of Banse and Parks, as they do not give the volume of their bomb, the mass of the samples burned, or the mass of water placed in the bomb. They refer to Roth's Thermochemie for details of the procedure. On page 78 of this work Roth states that usually 5 cm^3 and occasionally 10 cm^3 of water was placed in the bomb. The approximate Washburn correction which was applied in obtaining the values of $-\Delta U_R$ given above from the data of Banse and Parks was based on the assumption that the bomb volume was ⅓ liter, and the masses of water and sample of combustible were each 3 g per liter of bomb volume. The effect of using a larger amount of water would be partially compensated for if the same mass of water was used in the calibration of the calorimeter with benzoic acid. Assuming the volume of the bomb to be ⅓ liter, and the mass of the samples of benzoic acid to be 1 g, the effect of the heat of solution of carbon dioxide in the water is greater by 0.04 percent of the heat evolved with 5 cm^3 of water in the bomb, than with 1 cm^3. For the hydrocarbons the difference amounts to about 0.03 percent, assuming 1-g samples. Hence, if 5 cm^3 of water was placed in the bomb by Banse and Parks, the values of $-\Delta U_R$ calculated from their data may be too low by about 0.01 percent. The error may not be quite as large as this, however, on account of the fact that with such a large quantity of water in the bomb, the water may not be entirely saturated with carbon dioxide at the end of an experiment. Roth [19] has determined the heat capacity of his calorimeter by means of benzoic acid with 1, 5, and 10 g of water in the bomb, without applying the Washburn correction. The values obtained with 5 and 10 g of water in the bomb were lower by 0.011 and 0.064 percent, respectively, than the value obtained with 1 g of water in the bomb. The corresponding differences calculated by the method given by Washburn [23] are 0.046 and 0.102 percent, respectively. The actually observed effect of the larger amount of water is therefore of the order of half the calculated effect.

No data on the heats of combustion of *n*-nonane and *n*-undecane have been found in the literature.

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