HEATS OF COMBUSTION AND FORMATION OF THE PARAFFIN HYDROCARBONS AT 25　C [1]

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ABSTRACT

Selected "best" values are given for the heats of combustion (in oxygen to form gaseous carbon dioxide and liquid water) and the heats of formation (from the elements solid carbon, graphite, and gaseous hydrogen) for methane and ethane in the gaseous state, and for all the paraffin hydrocarbons from propane through the octanes and the normal paraffins through eicosane, in both the liquid (except for one octane which is solid) and gaseous states, all at 25° C. Equations are given for calculating values for all the normal paraffins above eicosane.

CONTENTS

I. INTRODUCTION

In 1940, values were presented by this Bureau for the heats of formation of the paraffin hydrocarbons from methane through the pentanes, in the gaseous state [1].[2] Since then, a considerable amount of new data has become available, which makes possible the extension of these values to all the isomers of the hexanes, heptanes, and octanes, and to the higher normal paraffins, each in both the liquid and gaseous states. In arriving at the new values given in this paper, cognizance was also taken of slight revisions that have been made in the values of the heats of formation of carbon dioxide and water. This paper also gives values for the increment in energy per CH_2 group for the normal paraffins beyond pentane, for both the heat of combustion and the heat of formation, in both the liquid and gaseous states.

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[1] This investigation was performed at the National Bureau of Standards jointly by the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 on the "Collection and Analysis of Data on the Properties of Hydrocarbon."
[2] Figures in brackets indicate the literature references at the end of the paper.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy upon which the values presented in this paper are based is the international joule determined by standards of resistance (international ohms), electromotive force (international volts), and time (mean solar seconds) maintained at this Bureau. Conversion to the conventional thermochemical calorie is made by means of the relation [16]:

$$4.1833 \text{ international joules (NBS)} = 1 \text{ calorie.}$$

The atomic weights of hydrogen, oxygen, and carbon were taken as 1.0080, 16.0000, and 12.010, respectively, from the 1941 table of International Atomic Weights [17].

The uncertainties assigned to the various quantities dealt with were derived, where possible, by a method previously described [18]. In other cases, reasonable estimates of the uncertainty were made.

III. EXPERIMENTAL DATA CONSIDERED

In arriving at the selected values presented in this paper, consideration was given to experimental values for the following:

Heats of combustion of methane, ethane, propane, n-butane, isobutane, and n-pentane, each in the gaseous state, by Rossini [1, 2, 3, 24].

Heats of combustion of isopentane and neopentane (tetramethyl-methane), in the gaseous state, by Knowlton and Rossini [1, 4].

Heats of combustion of n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane, and n-dodecane, in the liquid state, by Jessup [5].

Heats of combustion of n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-dodecane, and n-hexadecane, in the liquid state, by Prosen and Rossini [6].

Heats of isomerization of the five hexanes, in the liquid state, by Prosen and Rossini [7].

Heats of isomerization of the nine heptanes, in the liquid state, by Prosen and Rossini [8].

Heats of isomerization of the 18 octanes, in the liquid state, by Prosen and Rossini [9].

Standard heats of vaporization at 25° C for the 3 pentanes, 5 hexanes, 9 heptanes, 18 octanes, and the higher normal paraffins, from a correlation by Wagman, Taylor, and Rossini [10] of selected "best" values based largely on the experimental data on the heats of vaporization of n-pentane, 5 hexanes, 7 heptanes, 18 octanes, n-nonane and n-decane, at 25° C, by Osborne and Ginnings [11].

Heat of formation of carbon dioxide, by Prosen, Jessup, and Rossini [12], which is a revision of the previously selected "best" value, by Rossini and Jessup [13].

Heat of formation of water, by Rossini, et. al. [14], which is a slight revision of the previously selected "best" value by Rossini [15].

Consideration of earlier data on the heats of combustion of the paraffin hydrocarbons has already been made [2, 3, 4, 5, 7, 8, 9], except for measurements on n-hexadecane by Richardson and Parks [25]. Corrected to the same unit of energy, their value for n-hexadecane

differs from that of Prosen and Rossini [6] by -0.025 ± 0.032 percent.

A summary of the NBS data on the heats of combustion of the normal paraffin hydrocarbons is given in table 1, in which the values represent the decrement in heat content for the reaction

$$C_nH_{2n+2} \text{ (gas)} + \frac{3n+1}{2} O_2 \text{ (gas)} = nCO_2 \text{ (gas)} + (n+1)H_2O \text{ (liq)}$$
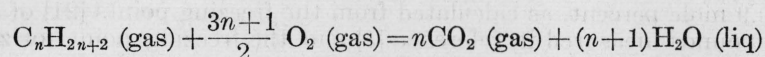
as deduced from several investigations made at this Bureau within the past 15 years. Where appropriate, data obtained for the liquid hydrocarbon have been converted to the gaseous state with selected values of the standard heat of vaporization at 25° C [10, 11].

TABLE 1.—*Summary of the NBS data on the heats of combustion of the normal paraffin hydrocarbons*

Compound	Value of the heat of combustion at 25°C, $-\Delta Hc°_{298.16}$, of the gaseous hydrocarbon, to form gaseous carbon dioxide and liquid water, from the data of—		
	[1, 2, 3]	[5]	[6]
	kcal/mole	*kcal/mole*	*kcal/mole*
Methane	212.798 ±0.072		
Ethane	372.820 ±0.110		
Propane	530.605 ±0.133		
n-Butane	687.982 ±0.167		
n-Pentane	845.30 ±0.22		845.07 ±0.18
n-Hexane		1002.72 ±0.33	1002.55 ±0.20
n-Heptane		1159.89 ±0.45	1160.07 ±0.21
n-Octane		1317.30 ±0.34	1317.46 ±0.25
n-Nonane		1474.77 ±0.45	1474.99 ±0.27
n-Decane		1632.31 ±0.27	1632.41 ±0.36
n-Undecane		1789.59 ±0.61	
n-Dodecane		1947.86 ±0.75	1947.37 ±0.39
n-Hexadecane			2576.97 ±0.68

The values deduced from references [2, 3] are the same as reported indirectly in reference [1], with a small correction for the molecular weight of water (since in these experiments, the mass of water formed in the combustion was used to determine the amount of reaction) and also with a slight change in conversion to zero pressure.

The values deduced from reference [5] were obtained as a result of the following corrections, in addition to the conversion to the gaseous state: (a) a change in the energy equivalent of the calorimeter system and in the correction for the formation of nitric acid, made by Jessup [19] in accordance with the procedure described on page 262 of reference [20]; (b) a change in the reference states of the gaseous reactants and products to the thermodynamic standard state of unit fugacity (in which the energy content is the same as that of the real real gas at zero pressure); (c) a change in the amount of reaction, the number of moles of hydrocarbon burned being taken as equal to 0.99965 ± 0.00010 times the mass of the sample divided by the molecular weight of the given hydrocarbon. The factor 0.99965 is the average obtained in the experiments on the same compounds described in reference [6], and was there determined as the ratio of the mass of carbon dioxide formed in the combustion to the mass of carbon dioxide calculated stoichiometrically from the mass of the

sample. In connection with the data from reference [5], it may be pointed out that the purities of the normal paraffin hydrocarbons measured in that investigation were lower than of the corresponding compounds described in reference [6] by amounts ranging from zero to 0.9 mole percent, as calculated from the freezing points [21] of the compounds measured in reference [5] and the freezing point for zero impurity [22].

The values attributed to reference [6] are the same as those given in that report, with conversion being made to the gaseous state, as previously described.

IV. SELECTED VALUES

In table 2 are given the selected "best" values for the heats of combustion and formation of methane and ethane in the gaseous state, and of propane, the 2 butanes, the 3 pentanes, the 5 hexanes, the 9 heptanes, the 18 octanes, and all the higher normal paraffins, in both the liquid and gaseous states. Equations are given for calculating values for all the normal paraffins above eicosane.

The values of heats of combustion given in table 2 for methane, ethane, propane, and n-butane, in the gaseous state, are the same as in table 1. The value for gaseous n-pentane is taken as the weighted mean of the values from [3] and [6]. The corresponding values for the liquid state were obtained by applying the standard heat of vaporization.

The values for the normal paraffins above pentane were obtained by fitting an equation linear in the number of carbon atoms to the data in table 1 [23]. By the method of least squares, using the data for the normal paraffins from hexane to dodecane, inclusive, and weighting the values inversely as the squares of their assigned uncertainties, the following equation was obtained for the relation between the number of carbon atoms in the molecule and the heat of combustion of the gaseous hydrocarbon at 25° C:

$$C_nH_{2n+2}(\text{gas}) + \frac{3n+1}{2} O_2(\text{gas}) = nCO_2(\text{gas}) + (n+1)H_2O(\text{liq}) \qquad (1)$$
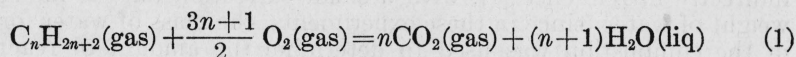
$$-\Delta Hc°_{298\cdot16} = 57.909 + 157.443n \pm (0.1647 - 0.03902n + 0.002684n^2)^{1/2}$$
$$\text{kcal/mole}; n > 5. \qquad (2)$$

The uncertainties attached to the constants in eq 2 represent the over-all uncertainties insofar as they can be estimated [18].

The corresponding equations representing the heat of combustion of the liquid hydrocarbon at 25° C, and applicable to the normal paraffins above pentane, is

$$C_nH_{2n+2}(\text{liq}) + \frac{3n+1}{2} O_2(\text{gas}) = nCO_2(\text{gas}) + (n+1)H_2O(\text{liq}) \qquad (3)$$
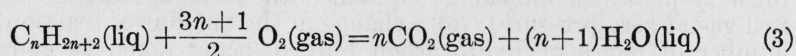
$$-\Delta Hc°_{298\cdot16} = 57.430 + 156.263n \pm (0.1653 - 0.03916n + 0.002694n^2)^{1/2}$$
$$\text{kcal/mole}; n > 5. \qquad (4)$$

TABLE 2.—*Selected "best" values for the heats of combustion and formation of the paraffin hydrocarbons*

| Compound	Formula	Heat of combustion [a] at 25° C, $-\Delta Hc°$		Heat of formation [b] at 25° C, $\Delta Hf°$	
		Liquid	Gas	Liquid	Gas
		kcal/mole	*kcal/mole*	*kcal/mole*	*kcal/mole*
Methane	CH_4		212.798±0.072		−17.889±0.075
Ethane	C_2H_6		372.820±0.110		−20.236±0.116
Propane	C_3H_8	526.782[c] ±0.133	530.605±0.133	−28.643[c] ±0.142	−24.820±0.142
n-Butane	C_4H_{10}	682.844[c] ±0.167	687.982±0.167	−34.950[c] ±0.179	−29.812±0.179
2-Methylpropane	C_4H_{10}	681.625[c] ±0.151	686.342±0.151	−36.169[c] ±0.164	−31.452±0.164
n-Pentane	C_5H_{12}	838.80 ±0.14	845.16 ±0.14	−41.36 ±0.16	−35.00 ±0.16
2-Methylbutane	C_5H_{12}	837.30 ±0.18	843.24 ±0.18	−42.86 ±0.20	−36.92 ±0.20
2,2-Dimethylpropane	C_5H_{12}	835.18[c] ±0.24	840.49 ±0.24	−44.98[c] ±0.25	−39.67 ±0.25
n-Hexane	C_6H_{14}	995.01 ±0.17	1002.57 ±0.17	−47.52 ±0.19	−39.96 ±0.19
2-Methylpentane	C_6H_{14}	993.71 ±0.23	1000.87 ±0.23	−48.82 ±0.25	−41.66 ±0.25
3-Methylpentane	C_6H_{14}	994.25 ±0.21	1001.51 ±0.21	−48.28 ±0.23	−41.02 ±0.23
2,2-Dimethylbutane	C_6H_{14}	991.52 ±0.21	998.18 ±0.21	−51.01 ±0.23	−44.35 ±0.23
2,3-Dimethylbutane	C_6H_{14}	993.05 ±0.22	1000.04 ±0.22	−49.48 ±0.24	−42.49 ±0.24
n-Heptane	C_7H_{16}	1151.27 ±0.15	1160.01 ±0.15	−53.63 ±0.19	−44.89 ±0.19
2-Methylhexane	C_7H_{16}	1149.97 ±0.28	1158.30 ±0.28	−54.93 ±0.30	−46.60 ±0.30
3-Methylhexane	C_7H_{16}	1150.55 ±0.28	1158.94 ±0.28	−54.35 ±0.30	−45.96 ±0.30
3-Ethylpentane	C_7H_{16}	1151.13 ±0.26	1159.56 ±0.26	−53.77 ±0.28	−45.34 ±0.28
2,2-Dimethylpentane	C_7H_{16}	1147.85 ±0.30	1155.61 ±0.30	−57.05 ±0.32	−49.29 ±0.32
2,3-Dimethylpentane	C_7H_{16}	1149.09 ±0.28	1157.28 ±0.28	−55.81 ±0.30	−47.62 ±0.30
2,4-Dimethylpentane	C_7H_{16}	1148.73 ±0.20	1156.60 ±0.20	−56.17 ±0.23	−48.30 ±0.23
3,3-Dimethylpentane	C_7H_{16}	1148.83 ±0.19	1156.73 ±0.19	−56.07 ±0.22	−48.17 ±0.22
2,2,3-Trimethylbutane	C_7H_{16}	1148.27 ±0.25	1155.94 ±0.25	−56.63 ±0.27	−48.96 ±0.27
n-Octane	C_8H_{18}	1307.53 ±0.16	1317.45 ±0.16	−59.74 ±0.20	−49.82 ±0.20
2-Methylheptane	C_8H_{18}	1306.28 ±0.28	1315.77 ±0.28	−60.99 ±0.31	−51.50 ±0.31
3-Methylheptane	C_8H_{18}	1306.92 ±0.24	1316.45 ±0.24	−60.35 ±0.27	−50.82 ±0.27
4-Methylheptane	C_8H_{18}	1307.09 ±0.25	1316.58 ±0.25	−60.18 ±0.28	−50.69 ±0.28
3-Ethylhexane	C_8H_{18}	1307.39 ±0.23	1316.87 ±0.23	−59.88 ±0.26	−50.40 ±0.26
2,2-Dimethylhexane	C_8H_{18}	1304.64 ±0.21	1313.56 ±0.21	−62.63 ±0.24	−53.71 ±0.24
2,3-Dimethylhexane	C_8H_{18}	1306.86 ±0.34	1316.14 ±0.34	−60.41 ±0.36	−51.13 ±0.36
2,4-Dimethylhexane	C_8H_{18}	1305.80 ±0.24	1314.83 ±0.24	−61.47 ±0.27	−52.44 ±0.27
2,5-Dimethylhexane	C_8H_{18}	1305.00 ±0.34	1314.06 ±0.34	−62.27 ±0.36	−53.21 ±0.36
3,3-Dimethylhexane	C_8H_{18}	1305.68 ±0.23	1314.66 ±0.23	−61.59 ±0.26	−52.61 ±0.26
3,4-Dimethylhexane	C_8H_{18}	1307.04 ±0.35	1316.36 ±0.35	−60.23 ±0.37	−50.91 ±0.37
2-Methyl-3-ethylpentane	C_8H_{18}	1307.58 ±0.28	1316.79 ±0.28	−59.69 ±0.31	−50.48 ±0.31
3-Methyl-3-ethylpentane	C_8H_{18}	1306.80 ±0.27	1315.89 ±0.27	−60.47 ±0.30	−51.38 ±0.30
2,2,3-Trimethylpentane	C_8H_{18}	1305.83 ±0.34	1314.66 ±0.34	−61.44 ±0.36	−52.61 ±0.36
2,2,4-Trimethylpentane	C_8H_{18}	1305.29 ±0.30	1313.70 ±0.30	−61.98 ±0.32	−53.57 ±0.32
2,3,3-Trimethylpentane	C_8H_{18}	1306.64 ±0.31	1315.54 ±0.31	−60.63 ±0.33	−51.73 ±0.33
2,3,4-Trimethylpentane	C_8H_{18}	1306.28 ±0.38	1315.30 ±0.38	−60.99 ±0.40	−51.97 ±0.40
2,2,3,3-Tetramethylbutane	C_8H_{18}	1303.03[d] ±0.44	1313.28 ±0.44	−64.24[d] ±0.46	−53.99 ±0.46
n-Nonane	C_9H_{20}	1463.80 ±0.18	1474.90 ±0.18	−65.84 ±0.22	−54.74 ±0.22
n-Decane	$C_{10}H_{22}$	1620.06 ±0.21	1632.34 ±0.21	−71.95 ±0.26	−59.67 ±0.26
n-Undecane	$C_{11}H_{24}$	1776.32 ±0.25	1789.78 ±0.25	−78.06 ±0.30	−64.60 ±0.30
n-Dodecane	$C_{12}H_{26}$	1932.59 ±0.29	1947.23 ±0.29	−84.16 ±0.34	−69.52 ±0.34
n-Tridecane	$C_{13}H_{28}$	2088.85 ±0.33	2104.67 ±0.33	−90.27 ±0.39	−74.45 ±0.39
n-Tetradecane	$C_{14}H_{30}$	2245.11 ±0.38	2262.11 ±0.38	−96.38 ±0.43	−79.38 ±0.43
n-Pentadecane	$C_{15}H_{32}$	2401.37 ±0.43	2419.55 ±0.43	−102.49 ±0.48	−84.31 ±0.48
n-Hexadecane	$C_{16}H_{34}$	2557.64 ±0.48	2577.00 ±0.48	−108.59 ±0.53	−89.23 ±0.53
n-Heptadecane	$C_{17}H_{36}$	2713.90 ±0.53	2734.44 ±0.53	−114.69 ±0.58	−94.15 ±0.58
n-Octadecane	$C_{18}H_{38}$	2870.16 ±0.58	2891.88 ±0.58	−120.80 ±0.64	−99.08 ±0.64
n-Nonadecane	$C_{19}H_{40}$	3026.43 ±0.63	3049.33 ±0.63	−126.90 ±0.69	−104.00 ±0.69
n-Eicosane	$C_{20}H_{42}$	3182.69 ±0.68	3206.77 ±0.68	−133.01 ±0.74	−108.93 ±0.74
Δ per CH_2		156.263	157.443	−6.106	−4.926

[a] $-\Delta Hc°_{298.16}$ represents the heat evolved in the combustion of the given hydrocarbon in the state indicated, in gaseous oxygen to form gaseous carbon dioxide and liquid water, at 25° C and constant pressure, with all reactants and products in their appropriate standard reference states, unless otherwise indicated.

[b] $\Delta Hf°_{298.16}$ represents the increment in the heat content of the process of forming the given hydrocarbon in the state indicated, from its elements, at 25° C, with all reactants and products in their appropriate standard reference states, unless otherwise indicated.

[c] At saturation pressure.

[d] For the solid state.

Similarly, the heats of formation of the normal paraffins above pentane, for the gaseous state at 25° C, are given by the equations

$$nC(c, \text{graphite}) + (n+1)H_2(\text{gas}) = C_nH_{2n+2}(\text{gas}) \qquad (5)$$
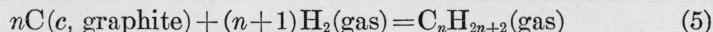
$$\Delta Hf°_{298\cdot16} = -10.408 - 4.926n \pm (0.1648 - 0.03884n + 0.002893n^2)^{1/2}$$
$$\text{kcal/mole}; n>5. \qquad (6)$$

The corresponding equations for the formation of the normal paraffins above pentane in the liquid state at 25° C are

$$nC(c, \text{graphite}) + (n+1)H_2(\text{gas}) = C_nH_{2n+2}(\text{liq}) \qquad (7)$$
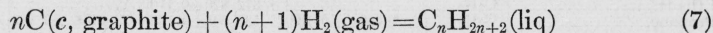
$$\Delta Hf°_{298\cdot16} = -10.887 - 6.106n \pm (0.1654 - 0.03898n + 0.002903n^2)^{1/2}$$
$$\text{kcal/mole}; n>5. \qquad (8)$$

The values given in table 2 for the heats of combustion of the normal paraffins above pentane were calculated from eq 2 and 4, and the values for the heats of formation of the same compounds were calculated from eq 6 to 8.

The values for isobutane, 2-methylbutane (isopentane), and 2,2-dimethylpropane (neopentane), in the gaseous state, were calculated, using the heats of isomerization from the appropriate normal paraffin hydrocarbon given in reference [1]. The corresponding values for the liquid state were obtained by applying the heat of vaporization [10].

The values for the 4 branched-chain hexanes, the 8 branched-chain heptanes, and the 17 branched-chain octanes, in the liquid state for all except 1 octane, which is solid at 25° C, were calculated, using the heats of isomerization from the appropriate normal paraffin hydrocarbon given in references [7, 8, 9]. The corresponding values for the gaseous state were obtained by applying the heats of vaporization [10].

The over-all uncertainties on many of the values given in table 2 have arbitrarily been made somewhat larger than would be calculated from the known uncertainties of the components of the calculation.

The values for the heats of combustion and formation of all the paraffin hydrocarbons through the octanes presented in table 2, which are based on experimental measurements, are being utilized to estimate the corresponding values for the 34 branched-chain nonanes, the 74 branched-chain decanes, etc. Deviations from linearity for the normal paraffins below pentane will be discussed in a later report covering several homologous series.

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