SOME FREE-ENERGY DATA FOR TYPICAL HYDROCARBONS CONTAINING SIX OR MORE CARBON ATOMS[1]

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The molal free energies of formation (ΔF_f^0) at 25°C. have been calculated for about thirty typical hydrocarbons containing six or more carbon atoms in the molecule. The calculations have been made by means of the third law of thermodynamics and almost entirely with the aid of modern thermochemical data; the results, therefore, are much more accurate than similar, earlier values.

A number of correlations between molal free energy and molecular structure are deduced from the data. In the series of normal paraffins the free energies conform closely to the linear relation, $\Delta F_f^0 = -8912 + 1243\ n$, where n is the number of carbon atoms in the molecule. The isoparaffins have slightly lower free-energy levels than the normal compounds. The introduction of a double bond to yield an olefin elevates the molal free energy by about 20,000 cal. The free energies of cycloparaffins come between those of the corresponding paraffins and olefins, while those of the aromatic hydrocarbons are definitely higher than the olefins. In all cyclic hydrocarbons, breaking the symmetry of the parent ring by the introduction of a paraffinic side chain first lowers the molal free energy by 1000 to 3000 cal., but subsequent increases in the length of this chain produce an increment per CH_2 group similar to that found in the normal paraffin series. The free-energy contribution of the phenyl group (C_6H_5) averages about 31,600 cal.

The third law of thermodynamics in conjunction with the fundamental equation

$$\Delta F = \Delta H - T\Delta S \tag{1}$$

has provided the only generally applicable, independent method for obtaining free-energy data for the hydrocarbons containing six or more carbon atoms. Statistical calculations of entropy and free energy have yielded extremely accurate values for many of the simpler molecules. At the present time, however, such calculations are just being developed

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for some of the more complicated molecules here involved and this development process is dependent to a high degree on accurate entropy determinations made by the third-law method (15). Moreover, equilibrium measurements, while they have yielded excellent results in a few special cases, notably in the study of the cyclohexane–methylcyclopentane isomerization by Glasebrook and Lovell (4), can constitute only an auxiliary tool in the development of a systematic set of free-energy data for the various classes of hydrocarbons.

Hence, the free energies of formation, ΔF_f^0, presented in this paper have been derived entirely through the third law. They represent the changes in the free-energy function[2] for the hypothetical process

$$\frac{m}{2}\,H_2(g) + nC\text{ (graphite)} = C_nH_m\text{ (l or s)}\,^{3}$$

at 1 atm. constant pressure and 25°C. (i.e., 298.16°K.), in which the product is 1 mole of the particular hydrocarbon in the liquid or crystalline solid state, as the case may be. Most of the hydrocarbon entropies have been calculated from specific heat measurements made in the Stanford laboratory by the author and his coworkers over the temperature range from the boiling point of liquid air up to 25°C. The values for the entropies of formation, ΔS_f^0, have been derived by use of 15.615 E.U. and 1.36 E.U. for the atomic entropies of hydrogen and graphitic carbon, respectively (3, 5). The various ΔH_f^0 values have been calculated from the experimentally measured heats of combustion of the several hydrocarbons by use of 68,318 cal. (17) and 94,030 cal. (19) for the heats of combustion of hydrogen and carbon (graphite), respectively. In the past, uncertainties in the heats of combustion of organic compounds have seriously affected the accuracy of such ΔH_f^0 values, but fortunately a number of laboratories are today turning out combustion results reliable to within 0.04 per cent or better. In fact, most of the hydrocarbon combustion values utilized here are such products of this recent renaissance in thermochemistry.

The energy unit used is the *defined* conventional calorie, derived from the international joule by multiplying by the factor 1.0004/4.185. All molecular weights have been based on the 1939 table of atomic weights (1).

In connection with the tabulated free-energy data an attempt has been made to indicate roughly the reliability of the various values, at least for comparative purposes. The letter "a" after a value indicates that in the

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[2] In general, the nomenclature and symbols used in this paper are those of Lewis and Randall (10).

[3] The abbreviations used to indicate phases are as follows: g = gaseous; l = liquid; s = crystalline.

writer's judgment the maximum uncertainty is thus under 500 cal., "b" that it is under 750 cal., "c" under 1000 cal., "d" under 1500 cal., and "e" under 2000 cal.

I. FREE-ENERGY VALUES FOR SOME PARAFFIN HYDROCARBONS

A. The normal paraffins

The normal paraffins have been studied most thoroughly and the thermodynamic functions for the members of this series are now established with reasonable accuracy up through dotriacontane ($C_{32}H_{66}$).

The molal entropies for the liquid state at 25°C. increase in linear fashion with n, the number of carbon atoms in the molecule. This fact is illustrated graphically in figure 1, where the points represent experimental values and the line corresponds to the equation

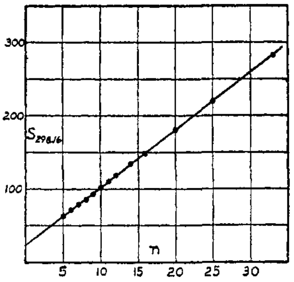

FIG. 1

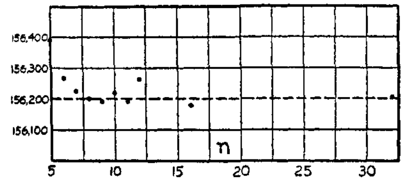

FIG. 2

FIG. 1. The molal entropies of some liquid normal paraffins plotted against n, the number of carbon atoms in the molecule.

FIG. 2. The combustion function $(-\Delta H_R - 57{,}250)/n$ for some liquid normal paraffins plotted against the number of carbon atoms in the molecule.

$$S_{298.16} = 24.0 + 7.8n \tag{2}$$

The heats of combustion for the liquids from n-hexane to n-dodecane, inclusive, have recently been measured with great accuracy by Jessup (6), and a comparable value for n-hexadecane has been reported by Richardson and Parks (16). Beckers (2) has also reported a result for crystalline dotriacontane, which should be fairly reliable. This last, subjected to our present standards for benzoic acid (7), to the Washburn (20) correction, and to conversion to combustion at 25°C., yields a value of 5,029,400 cal. for the solid state. The corresponding value in table 1 for the hypothetical liquid dotriacontane has then been derived by the addition of 26,400 cal., an estimate for the molal heat of fusion at 25°C. These molal heats of combustion for the liquid hydrocarbons containing six to thirty-two carbon atoms, inclusive, conform closely to the equation

$$-\Delta H_R = 57{,}250 + 156{,}200n \qquad (3)$$

This situation is illustrated graphically in figure 2.

In table 1 are tabulated complete thermodynamic data for nine normal paraffins. Column 2 contains the molal heats of combustion and column 3 the values for the ΔH of formation calculated therefrom. The molal entropies (S^0),—experimental values for the first eight compounds and a fairly reliable estimate in the case of dotriacontane,—and the corresponding entropies of formation appear in the succeeding two columns. Finally, the experimental values for ΔF_f^0 are given in the sixth column, and corresponding values per carbon atom in the final column. These last are of especial interest in making comparisons of thermodynamic stability in a group of compounds involving different numbers of carbon atoms.

TABLE 1

Thermodynamic data for some normal paraffins at 25°C.

SUBSTANCE	HEAT OF COMBUSTION AT CONSTANT P	ΔH_f^0	S^0	ΔS_f^0	ΔF_f^0	$\Delta F_f^0/n$
	calories	*calories*	*E.U.*	*E.U.*	*calories*	*calories*
Hexane (l)	994,850	−47,560	70.9	−155.9	−1,080(a)	−180
Heptane (l)	1,150,840	−53,910	78.6	−180.8	000(a)	000
Octane (l)	1,306,850	−60,250	86.2	−205.8	+1,110(a)	+139
Nonane (l)	1,463,000	−66,450	94.0	−230.5	+2,280(b)	+253
Decane (l)	1,619,440	−72,360	102.7	−254.4	+3,490(b)	+349
Undecane (l)	1,775,360	−78,790	111.0	−278.7	+4,310(b)	+392
Dodecane (l)	1,932,380	−84,110	118.3	−304.0	+6,530(c)	+544
Hexadecane (l)	2,556,110	−109,780	148.6	−404.1	+10,710(d)	+668
Dotriacontane (l)	5,055,800	−207,650	272.7	−801.4	+31,300	+978

Since the heats of combustion and the molal entropies follow linear relations, the ΔF_f^0 values calculated from these by equation 1 should follow also the linear relation

$$\Delta F_f^0 = -8912 + 1243n \qquad (4)$$

This equation is represented by the line in figure 3, while the dots portray the actual experimental values.

B. Branched-chain isomers

The free energies of branched-chain paraffins present an interesting problem which should be investigated further. The change from the normal compound to a branched-chain isomer produces a decrease in the molal entropy; and the quantitative aspects of this effect have been worked out fairly well in a preliminary way. However, the corresponding quantitative changes in the heat of combustion with branching must now be measured very accurately in order to evaluate the effect on ΔF^0_f.

Using preliminary combustion data for the isomeric heptanes and three isomeric octanes, Parks and Huffman (13a) in 1932 were led to the conclusion that any branched-chain isomer should be on a higher free-energy level than the normal compound. However, Knowlton and Rossini's (9, 18) recent combustion values for the butane and pentane isomers have indicated that the converse is true. This situation has led to a direct study of the equilibrium in the butane isomerization by Montgomery, McAteer, and Franke (11) and to unpublished determinations of the heat of combustion and entropy of 2-methylnonane by Moore (12). All these results, presented in table 2, point to the conclusion that at room temperature the 2-methyl isoparaffin is definitely more stable (i.e., on a lower free-energy level) than the corresponding straight-chain compound.

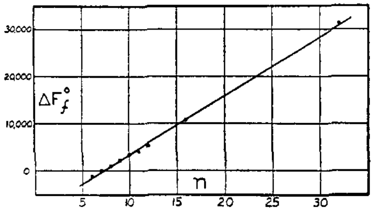

Fig. 3

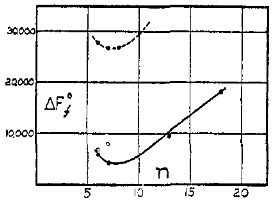

Fig. 4

Fig. 3. The molal free energies of some normal paraffins in the liquid state plotted against the number of carbon atoms in the molecule.

Fig. 4. A plot of the molal free energies of some cyclic hydrocarbons. The lower curve and dots refer to the cyclohexane series, the circles to cyclopentane derivatives, and the upper curve and dots to monophenyl benzenoid hydrocarbons.

TABLE 2

Free energy of isomerization at 25°C.

REACTION	$\Delta F^0_{298.16}$
n-C_4H_{10} (l) → iso-C_4H_{10} (l)	−820 (±100)
n-C_5H_{12} (l) → iso-C_5H_{12} (l)	−1020 (±400)
n-$C_{10}H_{22}$ (l) → iso-$C_{10}H_{22}$ (l)	−1490 (±670)

Similar studies, dealing with the effects of multiple branching, appear very desirable.

II. DIFFERENCES BETWEEN OLEFINS AND PARAFFINS

The withdrawal of a mole of hydrogen from a paraffin to produce an olefin hydrocarbon always raises the molal free energy considerably. In the case of the reaction

$$n\text{-heptane(l)} \rightarrow \text{1-heptene(l)} + H_2\text{(g)}$$

$\Delta F^0_{298.16}$ = 20,620 (±300) cal., according to the calorimetric studies of Kistiakowsky and coworkers (8) and the entropy measurements of Parks, Todd, and Shomate (14). Similar studies for the reaction

$$\text{tetramethylethane (l)} \rightarrow \text{tetramethylethylene (l)} + H_2\text{(g)}$$

yield $\Delta F^0_{298.16}$ = 17,100 (±700) cal. Thus with additional spatial protection to the ethylene group the olefins becomes progressively less unstable with reference to the parent paraffin hydrocarbons.

TABLE 3

Thermodynamic data for some cycloparaffins at 25°C.

SUBSTANCE	HEAT OF COMBUSTION AT CONSTANT P	ΔH^0_f	S^0	ΔS^0_f	ΔF^0_f	$\Delta F^0_f/n$
	calories	*calories*	*E.U.*	*E.U.*	*calories*	*calories*
Methylcyclopentane (l)	940,360	−33,730	59.3	−136.2	6,880 (b)	1,147
Ethylcyclopentane (l)	1,096,440	−40,000	67.1	−161.0	8,000 (c)	1,143
Cyclohexane (l)	936,410	−37,680	49.3	−146.2	5,910 (b)	985
Methylcyclohexane (l)	1,090,420	−46,020	59.4	−168.7	4,280 (c)	611
n-Heptylcyclohexane (l)	2,025,560	−84,960	106.8	−316.9	9,530 (d)	733
n-Dodecylcyclohexane (l)	2,809,630	−112,630	147.5	−439.1	18,290 (d)	1,016

III. FREE ENERGIES OF SOME CYCLOPARAFFINS

The saturated hydrocarbons containing five- or six-membered rings occupy free-energy levels somewhat intermediate between the corresponding aliphatic paraffins and olefins. Thus the ΔF^0_f values for methylcyclopentane and cyclohexane are 7960 cal. and 6990 cal., respectively, above that for *n*-hexane.

In table 3 appear thermodynamic data for two members of the cyclopentane series and four members of the cyclohexane series. These are based on accurate combustion and entropy determinations recently made in the Stanford laboratory by Moore and Renquist (12). The ΔF^0_f results are also plotted in figure 4.

While it is evident that more members of these two series should be studied, two facts stand out in a consideration of the data for the cyclohexane family: (*a*) Breaking the symmetry of the ring in cyclohexane to produce the methyl derivative produces a marked drop in ΔF_f^0. (*b*) Progressive increases in the aliphatic side chain on the ring cause an increase in ΔF_f^0 similar to that found with the normal paraffins. Thus the average increment in free energy per CH_2 group between methylcyclohexane and dodecylcyclohexane is 1270 cal., as against about 1240 cal. in the normal paraffin series.

In passing, it is worth noting that these third-law values yield $\Delta F_{298.16}^0 = 970$ cal. for the isomerization reaction

$$\text{cyclohexane (l)} \rightarrow \text{methylcyclopentane (l)}$$

in excellent agreement with the result, 1150 cal., obtained by Glasebrook and Lovell (4) from their direct equilibrium measurements.

TABLE 4

Thermodynamic data for some aromatic hydrocarbons at 25°C.

SUBSTANCE	ΔH_f^0	S^0	ΔS_f^0	ΔF_f^0	$\Delta F_f^0/n$
	calories	*E.U.*	*E.U.*	*calories*	*calories*
Benzene (l)	11,200	41.9	−59.9	29,060 (c)	4,843
Toluene (l)	3,520	52.4	−82.0	27,970 (c)	3,996
Ethylbenzene (l)	−3,430	61.3	−105.7	28,090 (c)	3,511
n-Butylbenzene (l)	−16,630	76.9	−155.3	29,670 (d)	2,967
Diphenyl (s)	23,250	49.2	−123.3	60,010 (d)	5,001
1,3,5-Triphenylbenzene (s)	52,920	87.9	−225.8	120,240 (e)	5,010
Naphthalene (s)	18,030	39.9	−98.6	47,430 (b)	4,743
β-Methylnaphthalene (s)	7,990	48.8	−122.3	44,450 (b)	4,041
Anthracene (s)	26,740	49.6	−125.6	64,190 (c)	4,584
Phenanthrene (s)	16,940	50.6	−124.6	54,090	3,864
Pyrene (s)	26,900	51.4	−126.5	64,620 (c)	4,039

IV. FREE ENERGIES OF SOME AROMATIC HYDROCARBONS

While entropy determinations have been made for about thirty aromatic hydrocarbons, the corresponding combustion data are in many cases inadequate for an accurate evaluation of ΔF_f^0 by equation 1. In table 4, however, appear thermodynamic (13b, 16) data for eleven compounds, which at least serve to indicate the general trends among the monophenyl and polyphenyl aromatics.

The four ΔF_f^0 values for benzene and its monophenyl derivatives are a revision of the earlier calculations of Parks and Huffman. They indicate that the general free-energy level for this series is about 23,000 cal. above the corresponding cyclohexane compounds. Here, as also in the cases of cyclohexane and naphthalene, a break in the symmetry of the parent molecule to introduce side chains on the ring causes an appreciable initial drop in the molal free energy.

With 27,000 cal. as the approximate *basic* free energy of the benzene molecule in forming derivatives, the free-energy values for diphenyl and triphenylbenzene here yield 33,000 cal. and 3 × 31,100 cal., respectively, for the introduction of additional phenyl groups.

In the case of the cyclic series benzene–naphthalene–anthracene the data show increases in ΔF_f^0 of 18,370 cal. and 16,760 cal., respectively, for each C_4H_2 increment involving the successive production of an additional ring within the molecule.

V. CONCLUSION

It is hoped that this brief review of the free energies of formation of some hydrocarbons containing six or more carbon atoms within the molecule has served to indicate the relative free-energy levels at room temperature for the various types and the general trend of the ΔF_f^0 values with structural changes. However, these problems evidently merit much additional study, as do also the problems connected with the application of such free-energy data to reactions at more elevated temperatures.

TABLE 5

Free-energy values for typical hydrocarbons at 25°C.

SUBSTANCE	FORMULA	ΔF_f^0
n-Decane (l)	$C_{10}H_{22}$	+3,490 (b)
2-Methylnonane (l)	$C_{10}H_{22}$	+2,000 (b)
1-Decene (l)	$C_{10}H_{20}$	+24,100 (*estimated*)
n-Butylcyclohexane (l)	$C_{10}H_{20}$	+7,000 (*estimated*)
n-Butylbenzene (l)	$C_{10}H_{14}$	+29,670 (d)
Naphthalene (s)	$C_{10}H_8$	+47,430 (b)

To summarize the present findings on a comparative basis, table 5 has been prepared, partly from actual experimental values and partly from estimates made with the aid of the observed regularities, for typical compounds containing ten carbon atoms in the molecule.

REFERENCES

(1) Baxter, G. P., Guichard, M., Hönigschmid, O., and Whytlaw-Gray, R.: J. Am. Chem. Soc. **61,** 223 (1939).
(2) Beckers, M.: Bull. soc. chim. Belg. **40,** 518 (1931).
(3) Giauque, W. F.: J. Am. Chem. Soc. **52,** 4825 (1930).
(4) Glasebrook, A. L., and Lovell, W. G.: J. Am. Chem. Soc. **61,** 1717 (1939).
(5) Jacobs, C. J., Jr., and Parks, G. S.: J. Am. Chem. Soc. **56,** 1513 (1934).

(6) JESSUP, R. S.: J. Research Natl. Bur. Standards **18,** 115 (1937).

(7) JESSUP, R. S., AND GREEN, C. B.: J. Research Natl. Bur. Standards **13,** 469 (1934).

(8) KISTIAKOWSKY, G. B., RUHOFF, J. R., SMITH, H. A., AND VAUGHAN, W. E.: J. Am. Chem. Soc. **58,** 137 (1936).

(9) KNOWLTON, J. W., AND ROSSINI, F. D.: J. Research Natl. Bur. Standards **22,** 415 (1939).

(10) LEWIS, G. N., AND RANDALL, M.: *Thermodynamics and the Free Energy of Chemical Substances.* McGraw-Hill Book Company, Inc., New York (1923).

(11) MONTGOMERY, C. W., MCATEER, J. H., AND FRANKE, N. W.: J. Am. Chem. Soc. **59,** 1768 (1937).

(12) MOORE, G. E., AND RENQUIST, M. L.: Private communication to the author.

(13) PARKS, G. S., AND HUFFMAN, H. M.: *The Free Energies of Some Organic Compounds,* (a) pp. 69–72; (b) pp. 87–90. The Chemical Catalog Company, Inc., New York (1932).

(14) PARKS, G. S., TODD, S. S., AND SHOMATE, C. H.: J. Am. Chem. Soc. **58,** 2505 (1936).

(15) PITZER, K. S.: Preceding paper in this symposium.

(16) RICHARDSON, J. W., AND PARKS, G. S.: J. Am. Chem. Soc. **61,** 3543 (1939).

(17) ROSSINI, F. D.: J. Research Natl. Bur. Standards **22,** 407 (1939).

(18) ROSSINI, F. D.: J. Chem. Phys. **3,** 438 (1935).

(19) ROSSINI, F. D., AND JESSUP, R. S.: J. Research Natl. Bur. Standards **21,** 491 (1938).

(20) WASHBURN, E. W.: Bur. Standards J. Research **10,** 525 (1933).