THE FREE ENERGY RELATIONS AMONG THE PARAFFIN AND OLEFIN HYDROCARBONS

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The application of thermodynamics to organic chemistry has been largely a development of the last decade. Up to a few years ago the lack of an adequate body of thermodynamic data pertaining to organic compounds constituted a discouraging factor. Now, however, over three hundred free energy values, representing many different types of substances, have been accumulated; and these results, while in many cases merely preliminary and semi-quantitative, serve as a very promising foundation for what we might term *thermodynamic organic chemistry.* Moreover at the present time new free energies, and more accurate ones, are being added to the literature at an accelerated pace.

One of the fields in which these new data have been recently obtained is that of the aliphatic hydrocarbons. In view of the recent developments in hydrocarbon chemistry, including especially the increasing use of cracking procedures and the utilization of olefins in organic syntheses, such data appear very timely and will undoubtedly aid in establishing thermodynamics as one of the important tools for further advances in aliphatic organic chemistry. The object of the present paper is to review, in the light of these new data, the free energy relations among the paraffins and olefins.

METHODS OF EVALUATING FREE ENERGY CHANGES AMONG THE HYDROCARBONS

In the present connection the term "free energy" of a hydrocarbon is used to denote the change in the free energy function of Lewis and Randall, i.e., the ζ function of Gibbs (14, 7), for the isothermal process in which a mole of the given hydrocarbon, either gaseous at 1 atmosphere pressure or in the liquid state as the case may be, is formed from graphitic carbon and the requisite amount of gaseous hydrogen, initially at 1 atmosphere pressure. For comparative purposes this free energy of formation from the elements has been calculated for the standard temperature of 298.1°K. (25°C.). In terms of the notation of Lewis and Randall, which is used throughout this paper, it is represented by the symbol ΔF^0_{298} in tables 1 and 3, although notice here should be taken of the fact that this symbol is a general one and naturally refers to any standard-state, isothermal process.

There are two methods by which the free energy changes in processes involving the hydrocarbons have been evaluated from experimental data. The first of these depends upon the determination of the equilibrium constant K in a reaction, whereby the free energy change for the standard-state reaction at the particular temperature is given by the equation

$$\Delta F^0_T = -RT \ln K \tag{1}$$

This method has been used in studies of the formation of methane from the elements and of the production of various olefins by dehydrogenation of the corresponding paraffins at more or less elevated temperatures. However, it has its limitations in applicability because often the equilibrium constant cannot be readily determined experimentally and, of course, may be the very thing which one wishes to evaluate from a ΔF^0 value otherwise obtained.

The second method involves the use of the important thermodynamic relation

$$\Delta F^0 = \Delta H^0 - T\Delta S^0 \tag{2}$$

and is quite generally applicable. The quantity ΔH^0, the change in "heat content" for the process, may sometimes be measured directly, as in the hydrogenation of various olefins, and in practically all cases may be evaluated indirectly from suitable combustion data by means of Hess's law. When the process of forming a hydrocarbon from the elements is under consideration, ΔS^0, the increase in entropy, represents the entropy of the hydrocarbon minus that associated with the requisite number of atoms of graphitic carbon and gaseous hydrogen. The entropy of the hydrocarbon may be evaluated from heat capacity data extending down to low temperatures by means of the third law of thermodynamics (16a) or in the simpler cases from spectroscopic data and molecular constants by statistical methods (4, 18). The entropy of graphitic carbon, 1.36 E.U. per gram-atom at 298°K., has been recently evaluated by means of the third law (9); the practical value, $S^0_{298} = 15.615$ E.U., for $\frac{1}{2}H_2$ was obtained by Giauque (5) in 1930 from spectroscopic data after subtraction of the effect for nuclear spin.

FREE ENERGY VALUES FOR SOME PARAFFIN HYDROCARBONS

The normal paraffins

The recent renaissance in thermochemistry has now made it possible to apply equation 2 to calculate fairly accurate values for the free energies of formation of eight members of the normal paraffin series. The results so obtained are given in the last column of table 1 and the essential thermal data involved in obtaining these are tabulated in columns 2, 3, and 4.

The ΔH^0_{298} values for all these paraffins save dodecane have been derived with the aid of the remarkably accurate heats of combustion measured recently by Rossini and his collaborators at the U. S. Bureau of Standards (19). The value for dodecane is based upon the combustion result of Banse and Parks (1), now corrected according to Washburn's method (23) to atmospheric pressure.

The molal entropies for these several hydrocarbons are given in column 3. The values above propane have all been obtained by Parks, Huffman, and collaborators (16b) from low temperature heat capacity data and the third law of thermodynamics. The highly accurate value for methane is that resulting from the statistical calculations of Giauque and coworkers and of Kassel (6, 10). The tabulated S^0_{298} for ethane is a mean based on the three approximate values (53.5, 55.5, and 56.2 E.U.), which have been calculated, respectively, by the third law by Parks and Huffman and by statistical methods by Mayer, Brunauer, and Mayer and by Smith and Vaughan (16b, 15, 21). The parenthetical value for propane is the result of a direct interpolation between ethane and n-butane. The marked regularities found in the entropies in the normal paraffin series would seem to make such an interpolation highly reliable.

TABLE 1

Thermodynamic data for some normal paraffins

SUBSTANCE	ΔH^0_{298}	S^0_{298}	ΔS^0_{298}	ΔF^0_{298}
	15°-calories	*E. U.*	*E. U.*	*15°-calories*
Methane (g)	−18,070	44.46	−19.36	−12,300 (±80)
Ethane (g)	−20,600	55.0	−41.4	−8,260 (±300)
Propane (g)	−25,390	(64.7)	−64.3	−6,220 (±300)
n-Butane (g)	−30,570	74.4	−87.2	−4,580 (±300)
n-Pentane (l)	−42,230	62.0	−132.2	−2,820 (±500)
n-Heptane (l)	−55,410	78.5	−180.9	−1,480 (±500)
n-Octane (l)	−62,260	86.0	−206.0	−850 (±600)
n-Dodecane (l)	−85,910	118.2	−304.1	+3,540 (±1400)

The resulting free energies are subject to maximum fortuitous errors (indicated in parentheses in the last column of table 1) which are the cumulative effects of similar errors in the contributing combustion and entropy data. As Rossini has noted, there is also the possibility of a systematic error, perhaps as great as 100 calories per carbon atom, arising from the use of 94,240 $\text{cal.}_{15°}$ for the combustion of a gram-atom of β-

graphite. To the reader these tabulated possible errors may seem rather large at first glance, especially in view of the extremely small values for the free energies of formation of the hydrocarbons. However, it should be remembered that in the practical use of free energy data the absolute magnitude of the error and not the percentage error is the important factor. For this reason these ΔF^0_{298} values may be considered quite satisfactory.

Before passing, it should be noted that in the case of methane (16b) additional ΔF^0_{298} values of $-12{,}240$ and $-12{,}060$ cal. have been obtained by downward extrapolation of high temperature equilibrium studies on the two reactions.

$$C(\text{graphite}) + 2H_2(g) \rightleftharpoons CH_4(g)$$

and

$$CO_2(g) + 4H_2(g) \rightleftharpoons 2H_2O(g) + CH_4(g)$$

To facilitate comparisons for these several hydrocarbons in the liquid state and to aid in the preparation of figure 1, values of ΔF^0_{298} for liquid methane, ethane, propane, and *n*-butane have been estimated on the assumption of fugacities for these compounds at 25°C. of 160, 21.5, 9.0, and 2.90 atm., respectively. These free energies become, in turn, -9300, -6440, -4940, and -3950 cal. Of course, as the critical temperature of methane is below 298°K., the value in this case is purely hypothetical. Conversely, by utilization of the vapor pressure data in the International Critical Tables (8), hypothetical ΔF^0_{298} values of -2570, $+190$, and $+1520$ cal. have been computed for gaseous *n*-pentane, *n*-heptane, and *n*-octane, respectively.

Effect of a CH_2 *increment*

All these hydrocarbon free energies have been represented graphically in figure 1, where the heavy dots and solid line refer to data for the liquid state and the circles and broken line to data for the compounds as gases. From the plot it is evident that the free energies of the paraffins rise appreciably with increasing length of the hydrocarbon chain and that beginning in the neighborhood of propane the relationships are practically linear. The straight line for the liquid state corresponds to an increase in ΔF^0_{298} of 860 cal. per CH_2 increment; that for the gaseous state to an increase of 1440 cal. per CH_2 increment.

That increment values of this order actually exist can be demonstrated in another way. Rossini (19) has found for the normal paraffin series that above *n*-butane the heat of combustion in the gaseous state increases regularly by 157,000 (±80) cal. per carbon atom. This means that the ΔH^0_{298} of formation must decrease (algebraically) by 5550 cal. per CH_2 group. On the other hand, Parks and Huffman (16d) from their study of entropy regularities among organic compounds have deduced 10.0 (±0.5) E. U. for the increase in entropy in the gaseous state per CH_2 group. Correspondingly the $T\Delta S$ term in equation 2 decreases by about 6740 cal. and consequently ΔF^0_{298} should increase by approximately 1200 cal. If a similar calculation is carried out for the liquid state where the changes in heat of combustion and molal entropy are, respectively, 156,000 (±200) cal. and 7.7 (±0.2) E.U. per carbon atom, the resulting change in ΔF^0_{298} comes out about 870 cal.

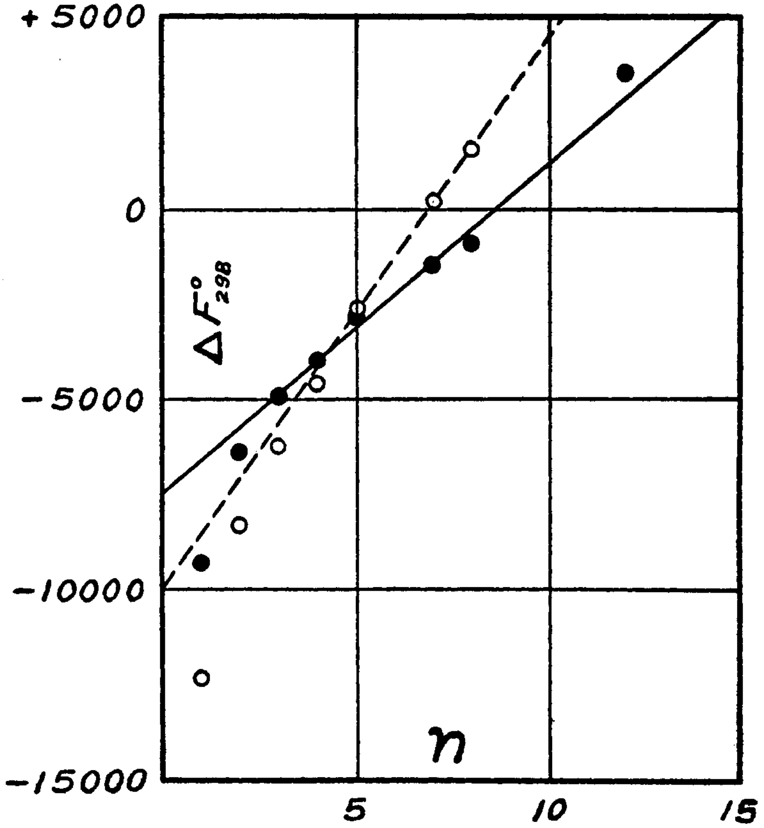

FIG. 1. A plot of the molal free energies of some normal paraffin hydrocarbons against n, the number of carbon atoms in the molecule. The heavy dots and solid line refer to the liquid state; the circles and broken line to the gaseous state.

Effect of branching

Among a group of paraffin isomers the molal free energy generally appears to increase slightly with increased branching in the formula of the hydrocarbon, i.e., the branched isomers become progressively less stable in a thermodynamic sense as compared with the normal compound.

At present the only reasonably satisfactory data available in this field pertain to two groups,—one of seven heptanes (*n*-heptane, 2-methylhexane, 3-ethylpentane, 2,2-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, and 2,2,3-trimethylbutane) and another of three octanes (*n*-octane, 2,2,4-trimethylpentane, and hexamethylethane). Here the U. S. Bureau of Standards (11) in 1928 made the necessary determinations of the heats of combustion and Parks, Huffman, and Thomas (16b) determined the molal entropies with portions of the same materials. Accordingly the resulting free energies should be on a truly comparable basis. The increases in the molal ΔF^0_{298} values for the liquid state over that of the corresponding normal paraffins are given in table 2 in terms of the number of methyl (or ethyl) branches attached on the main chain of the hydrocarbon. While these increases are small and in some cases are not larger than the possible errors in the combustion values, they point in the same direction and yield on the average an effect of +750 cal. per branch.

TABLE 2

Free energy effects of branching (in calories per mole)

	NUMBER OF BRANCHES			
	1	2	3	4
Isomeric heptanes	0 +1200	+1200 +1700 +600	+2200	
Isomeric octanes			+2200	+4500
Average effect of a branch				+750 calories

In one case, that of 2-methylhexane, no increase in ΔF^0_{298} over the value for *n*-heptane was found, and this result was at first considered to be due to a fortuitous error which might mask an effect of only a few hundred calories. However, the equality may be real and it is even possible that certain of the simpler isoparaffins, such as isobutane, may have a slightly lower molal free energy than the normal compound. Thus from his recent value for the heat of combustion of isobutane, Rossini (20) has calculated

$$n\text{-}C_4H_{10} \rightarrow iso\text{-}C_4H_{10};\ \Delta H^0_{298} = -1630\ (\pm 150)\ \text{cal.}$$

From the entropy studies of Parks and Huffman (16d) a prediction of −4 to −5 E.U. for the ΔS^0_{298} of this reaction might now be made. However, even the latter figure would yield, by equation 2, $\Delta F^0_{298} = -140\ (\pm 150)$

cal. for the isomerization process; hence the evidence at present must be considered to favor a slightly greater thermodynamic stability for isobutane than for *n*-butane.

FREE ENERGY VALUES FOR SOME OLEFINS

Thermal data recently obtained make possible the calculation, by equation 2, of accurate free energies for seven olefin hydrocarbons. These ΔF^0_{298} values are given in the last column of table 3, and the essential heat content and entropy data appear in columns 2, 3, and 4. The contributing ΔH^0_{298} values, except in the case of diisobutylene, have been derived by combining the highly accurate heats of hydrogenation for these olefins, measured by Kistiakowsky (12, 13) and his collaborators, with the corresponding ΔH^0_{298} values given in table 1. The ΔH^0_{298} for diisobutylene represents the combination of a heat of hydrogenation of 28,460 (±700) cal., obtained by Mr. B. L. Crawford, Jr. (2), with a ΔH^0_{298} value for 2,2,4-trimethylpentane based on the Bureau of Standards combustion work. The tabulated entropy value for ethylene is a weighted mean of the two values (52.55 and 51.91 E.U.) calculated by statistical methods by Smith

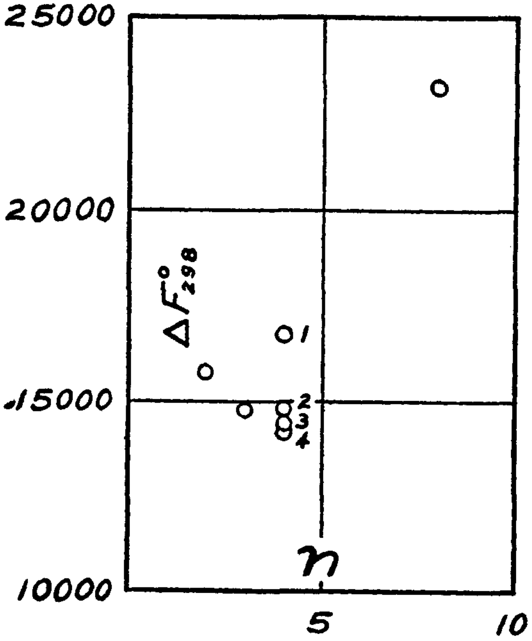

FIG. 2. A plot of the molal free energies of some gaseous olefins against the number of carbon atoms in the molecule. For the butenes the numbers 1, 2, 3, and 4 refer to butene-1, *cis*-butene-2, *trans*-butene-2, and isobutene, respectively.

and Vaughan (21) and by Kassel (10), respectively. The third law values for propylene and diisobutylene are taken from the work of Parks and Huffman (16c); those for the butenes are from a recent investigation of Todd and Parks (22).

These free energy values for the gaseous state are also represented graphically in figure 2. They suffice to delineate fairly well the general free energy relations among the aliphatic olefins, although naturally in view of the great number of possible olefin hydrocarbons and their importance to the chemical industry a larger body of such thermodynamic data is highly desirable. The present values indicate that the effects of increasing the length of the chain and of branching are essentially similar to those among the paraffins if other factors remain unchanged. Thus the free energy increase in going from propylene to butene-1 is within the limits of error the same as that found in going up the paraffin series from propane to *n*-butane. Also, by using the numerical effects derived in the study of the paraffins in conjunction with the tabulated ΔF^0_{298} for *cis*-butene-2, a calculated value of about 22,200 cal. for gaseous diisobutylene is obtainable; this is in fair agreement with the experimental result of 23,150 cal. in table 3.

TABLE 3

Thermodynamic data for some olefins

SUBSTANCE	ΔH^0_{298}	S^0_{298}	ΔS^0_{298}	ΔF^0_{298}
	15°-calories	*E. U.*	*E. U.*	*15°-calories*
Ethylene (g)	11,975	52.3	−12.9	15,820 (±300)
Propylene (g)	4,475	63.1	−34.7	14,820 (±300)
Butene-1 (g)	−480	72.5	−57.9	16,780 (±600)
cis-Butene-2 (g)	−2,250	73.0	−57.4	14,860 (±500)
trans-Butene-2 (g)	−3,200	71.2	−59.2	14,450 (±500)
Isobutene (g)	−4,060	69.0	−61.4	14,240 (±500)
Diisobutylene (l)	−34,890	71.4	−189.3	21,550 (±1500)
Diisobutylene (g)				23,150 (±1500)

Undoubtedly the position of the double bond and geometrical isomerism are other very important factors in determining the magnitude of ΔF^0_{298}. These influences are quite evident in the data for the isomeric butenes, where the order of increasing thermodynamic stability is: butene-1, *cis*-butene-2, *trans*-butene-2, and isobutene. In this connection it should also be noted that merely the addition of one methyl group to the ethylene molecule to yield propylene causes a lowering in molal free energy of 1000 cal., although we have previously seen in the paraffin series that the normal effect of a CH_2 increment is an increase of about 1400 cal. Thus the addition of one or more radicals, such as methyl groups, to the carbon atoms adjacent to the double bond exerts a progressively protective action on the double bond and by a sort of spatial screening tends to render the olefin more like a paraffin hydrocarbon. As yet, however, the available data are too meager for a quantitative evaluation of this screening effect on the molal free energy.

FREE ENERGY DIFFERENCES BETWEEN OLEFINS AND PARAFFINS

The differences in ΔF^0_{298} between the olefins and the corresponding paraffins, with the exception of the ethylene–ethane combination, are approximately 20,000 cal. These differences really represent ΔF^0_{298} for the dehydrogenation reaction

TABLE 4

ΔF^0_{298} *for dehydrogenation reactions*

SUBSTANCE FORMED	BY EQUATION 2	FROM EQUILIBRIUM MEASUREMENTS
Ethylene	24,080	23,330
Propylene	21,040	20,540
Butene-1	21,360	20,710
cis-Butene-2	19,440	19,620
trans-Butene-2	19,030	18,850
Isobutene		18,730
Diisobutylene	20,350	

$$\textit{paraffin hydrocarbon} \rightarrow \textit{olefin hydrocarbon} + H_2$$

and may be readily evaluated in six cases from the free energy values in the preceding tables. The values so obtained have been incorporated in table 4 under the heading "By equation 2."

The dehydrogenation equilibria for ethane have been studied experimentally by Pease and Durgan (17) from 600° to 700°C. and by Frey and Huppke (3) between 400° and 500°C. Their results have been discussed recently in an interesting theoretical paper by Smith and Vaughan (21). The dehydrogenation equilibria for propane, for isobutane, and for *n*-butane to yield a mixture of butene-1, *cis*-butene-2, and *trans*-butene-2 have also been measured experimentally by Frey and Huppke at temperatures of 350°, 400° and 450°C. While the free energy changes for these dehydrogenation processes at the various temperatures are readily obtainable by equation 1, the extrapolation downward to 25°C. provides some uncertainty. The author, however, has attempted this extrapolation on the assumption that ΔC_p for the dehydrogenation is uniformly 4.0 cal. and constant with changing temperature. Tables 3 and 1 provided the necessary data for obtaining the ΔH of the several reactions. In this manner the values of ΔF^0_{298} "from equilibrium measurements" in table 4 were arrived at. While they are undoubtedly more uncertain than the corresponding values by equation 2, there is only an average discrepancy of 2 per cent in the five cases where parallel data exist.

SUMMARY

The conclusions of this review may be briefly summarized as follows:

1. Among the paraffin hydrocarbons the free energy increases with increasing length of chain in the series of normal compounds and in a group of isomers with increased branching.

2. Among the olefin hydrocarbons the effects of increasing the length of the chain and of branching are roughly similar to those among the paraffins, but the position of the double bond and geometrical isomerism are also important factors.

3. The free energy level of the olefins averages about 20,000 cal. above that of the corresponding paraffins.

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