CHEMICAL EQUILIBRIA, FREE ENERGIES, AND HEAT CONTENTS FOR GASEOUS HYDROCARBONS[1]

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Received May 25, 1940

The statistical methods for calculating thermodynamic functions of hydrocarbons are discussed. In addition to the more common methods which are suitable for the simpler molecules, a procedure is described which is especially suited to the complex hydrocarbons and our present incomplete knowledge of their molecular constants. Agreement is obtained with all experimental data for the paraffins on the basis of reasonable rotation-restricting barriers. There appear to be inconsistencies in the data for propylene, which render somewhat uncertain the values for the higher olefins.

Tables are presented which give the heat and free-energy functions for all the paraffins through the heptanes, together with some discussion of estimates for the higher members. The simpler unsaturated hydrocarbons are also included. A few equilibrium constants and heats of reaction are calculated as examples of the use of this data.

I. INTRODUCTION

The first extensive survey of hydrocarbon thermodynamics was included in the monograph by Parks and Huffman (30), whose point of view was almost purely experimental. The point of view of statistical mechanics, which has been so useful for simple molecules, was extended to hydrocarbons by Eidinoff and Aston (9) and by Kassel (20). Their methods were based on the assumption of completely free rotation about single bonds, which led to unsatisfactory results. In 1937 the writer (32) extended their methods to allow for a sinusoidal potential barrier restricting internal rotation. It was then possible to obtain agreement with all experimental data.[2] Furthermore, the potential barriers so obtained varied in a reasonable fashion through any series of similar compounds.

Recently the writer (33) has developed somewhat different statistical

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[1] Presented at the Symposium on Fundamental Chemical Thermodynamics of Hydrocarbons and their Derivatives, which was held at the Ninety-ninth Meeting of the American Chemical Society, in Cincinnati, Ohio, April 10, 1940, under the auspices of the Division of Petroleum Chemistry of the American Chemical Society.

[2] In addition to the paper already mentioned treating several hydrocarbons, the work of Smith and Vaughan (36), of Teller and Topley (39), and of Kemp and Pitzer (22) on ethane alone may be noted.

methods, which are especially suited to long-chain molecules. These have permitted extension of the work through the heptanes and some octanes. These results are included below without change, except that a wider range of temperatures is considered.

In the present paper the calculations for those saturated hydrocarbons which were included in the 1937 paper are completely revised. All of the old results agree within their assigned uncertainties with the values below; however, considerably greater accuracy can now be claimed at certain points. Although some comment will be made on the accuracy of the earlier work on the unsaturated compounds, no changes are made in the values; this arises from the lack of additional experimental evidence. An attempt has also been made to present the data in a form easily used by those not too familiar with thermodynamics.

The treatment presented below may be described essentially as follows: A picture is set up for a given molecule involving atomic masses and the geometry of the equilibrium configuration, i.e., bond angles and distances. Also needed is a knowledge of the potential energy as a function of deviations from this equilibrium position. This is assumed to be given by an expression involving bond stretching and bending force constants, and potential barriers for internal rotation. In terms of this picture it is then possible to calculate the entropy, heat capacity, and related thermodynamic functions. However, certain details of the molecular pictures are not yet known independently, and must then be obtained from experimental entropies or heat capacities with the above calculation reversed. Thus for the present at least, the final result should be regarded as based on the experimental thermodynamic data employed. However, it is possible by these calculations to give reasonably certain values of thermodynamic quantities for temperatures other than those of the measurements, and even to extend the results to other molecules. In addition, valuable information is obtained concerning the forces operating within hydrocarbon molecules.

II. MOLECULAR STRUCTURE DATA

In this section the data taken from non-thermodynamic sources will be discussed. Atomic masses are too well known to require comment. The carbon-to-carbon single-bond distance was taken as 1.54 Å. and the carbon-to-hydrogen distance as 1.09 Å. All angles were assumed to be tetrahedral. The electron diffraction results of Pauling and Brockway (31) support these values.

One of the fundamental assumptions of our treatment involves the separation of the vibration of the hydrogen atoms from the vibration of the carbon skeleton. This assumption has been made very commonly by various workers, and may be regarded for the present as necessary.

The justification is, of course, that the light hydrogen atoms move with much higher frequencies than the heavier carbon atoms, and therefore the former complete several cycles to the latter's one. Actually, certain hydrogen bending motions show about the same frequencies as carbon-to-carbon bond stretching motions. If the geometry is favorable, these motions can interact very considerably. Nevertheless, for our purpose, which is the calculation of thermodynamic functions, an error in a given frequency is not serious, provided a compensating error is made in another. Thus the neglect of interactions which raise one frequency and lower another will be satisfactory here, even though it might be fatal in spectroscopy.

For these calculations, frequencies characteristic of CH_3, CH_2, and CH groups have been selected on the basis of the spectroscopic data from simple molecules. For the methyl group the data on the methyl halides (37) and on ethane (17, 6) were considered; the stretching frequencies were taken as 3 at 3000 $cm.^{-1}$, and the bending frequencies as 3 at 1400 and 2 at 1000 $cm.^{-1}$ For the CH_2 group, the data on methylene chloride (5), formaldehyde (37), and ethylene (37) were considered; the selection was 2 at 3000, 2 at 1400, and 2 at 1000 $cm.^{-1}$ For the CH group, chloroform and bromoform (37) were considered, and the values 1 at 3000 and 2 at 1200 $cm.^{-1}$ chosen.

In the calculations on the simpler molecules the observed skeletal vibration frequencies were used (26). For the more complex hydrocarbons the force constants were employed. These were calculated from the simpler molecules, care being taken to assume consistently that the hydrogen and carbon vibrations do not interact. On this basis the value 4.1×10^5 dynes per centimeter was obtained for the carbon bond stretching constant. The bending constant was taken as 3.6×10^4 dynes per centimeter at the end of one bond length.

III. THERMODYNAMIC FUNCTIONS FOR THE SIMPLER HYDROCARBONS

By using the same methods as in the earlier papers (32), but the constants just given, thermodynamic functions were calculated for the molecules derivable from methane by substituting only methyl groups. The carbon skeleton of any of these involves no internal rotations, such rotations moving only the hydrogens of a methyl group. The formulas used for the rigid molecule are as follows:

$$(H_0^0 - F_T^0)/T = R[3/2 \ln M + 4 \ln T - \ln P + \frac{1}{2}\ln (I_1I_2I_3 \times 10^{117}) - \ln \sigma] - 10.237$$

$$(H_T^0 - H_0^0)/T = C_p = 4R = 7.948$$

$$S_T^0 = (H_0^0 - F_T^0)/T + (H_T^0 - H_0^0)/T$$

The symbols are the usual ones, I representing a moment of inertia and σ the symmetry number. The formulas and tables for internal rotation contributions were given in the 1937 paper (32). The vibrational contributions for harmonic oscillators are given in many places (27), usually under the name "Einstein functions" which are for three degrees of freedom.

The one remaining constant needed in these calculations is the height of the potential barrier (assumed to be sinusoidal in shape) restricting internal rotation. These values were selected to fit the known entropies and heat capacities of ethane (41, 24), propane (21, 23), and tetramethylmethane (2). In the latter cases the barriers for each methyl group were assumed to be equal and independent. No assumption is needed as to which is the equilibrium position. Lacking experimental data, the potential barrier must be estimated for isobutane. Since the value 3600 cal. per mole was adopted for all internal rotations in more complex molecules, it is used here even though a comparison of other molecules indicates a slightly higher value. The error from this source in the thermodynamic functions should not be greater than a few tenths of a calorie per degree. Table 1 contains the various parameters appearing in the calculations, and the entropies at 298.1°K.

TABLE 1

The various parameters appearing in the calculations, and the entropies at 298.1°K.

SUBSTANCE	CH_3CH_3	$CH_2(CH_3)_2$	$CH(CH_3)_3$	$C(CH_3)_4$
$I_1I_2I_3 \times 10^{117}$ g.^{3} cm.^{6}	18.2	336	1965	6570
$I_r \times 10^{40}$ g. cm.^{2}	2.63	4.4	5.0	5.1
V_0, in calories per mole	2800	3300	(3600)	4700
Skeletal vibration frequencies (26) in cm.$^{-1}$	993	1053	962(2)	921(3)
		867	794	732
		373	438(2)	416(3)
			370	332(2)
Symmetry number	6	2	3	12
$S^0_{298.1}$, in calories per degree mole	54.86	64.7	70.5	73.2

IV. THERMODYNAMIC FUNCTIONS FOR THE MORE COMPLEX HYDROCARBONS

When internal rotation appears in the carbon skeleton, the method of calculation commonly used ceases to be very suitable. This is because the assumption of that method, that the molecule is essentially rigid, is no longer even approximately correct. The harmonic oscillations of ordinary molecules do not change the moments of inertia much on the average, but the possible gyrations of a long-chain hydrocarbon might have considerable effect. In the 1937 paper the writer treated *n*-butane by considering the molecule in each potential minimum with respect to rotation. Such a method becomes very laborious, however, in even slightly more complex cases. A different scheme of calculation has been developed recently by the writer (33), which is more suitable for the complex hydrocarbons. The general principles of this scheme will be reviewed briefly, without pretending to repeat the derivation.

This method is based on the integral or classical form of the partition function which is approached at high temperatures (10). This equation involves only the masses of the particles and a knowledge of the potential energy as a function of their positions. It does not require knowledge of the normal coördinates of vibration and their frequencies. Actually some corrections must be made at the lower temperatures, as will be explained below. The molecules are treated first on the basis of the carbon atoms alone, assigning an effective mass. Then contributions from the hydrogen atoms of the CH_3, CH_2, and CH groups are added on.

The potential energy of the molecule is assumed to be given by an expression including the usual terms for bond stretching and bending, with the force constants given above, and a threefold sinusoidal potential barrier for each internal rotation. In addition, the potential energy of certain configurations is raised to account for steric repulsions.

With this potential energy, the expression for a thermodynamic function takes the form:

$$Th.F. = F_{0(T)} + N_1\,[\text{C—C str.}] + N_2\,[\text{C—C bend.}] + N_3\,[\text{I.Rot.}] + F_{(\text{steric})} + F_{(\sigma)} + N_4\,[\text{CH}_3] + N_5\,[\text{CH}_2] + N_6\,[\text{CH}]$$

where *Th.F.* represents the thermodynamic function; $F_{0(T)}$ is a function of T not depending on the molecule; [C—C str.] is a function of the C—C bond stretching constant, and N_1 is the number of such bonds in the molecule; [C—C bend.] is similarly for C—C bond bending, and N_2 is the number of such degrees of freedom; [I.Rot] is similarly for internal rotation, and N_3 the number of skeletal rotations. $F_{(\text{steric})}$ is a function of energy assigned various positions on the basis of steric repulsions, and $F_{(\sigma)}$ adjusts for the symmetry number σ in the usual manner; N_4, N_5, and N_6 are the numbers of CH_3, CH_2, and CH groups in the molecule, and [CH_3], [CH_2], and [CH] represent their contributions to the thermodynamic function in question. All terms may depend on the temperature except $F_{(\sigma)}$, and are, of course, different for the various thermodynamic functions. Values for the various terms are tabulated in the paper (33) wherein this method is developed.

In the simpler hydrocarbons the potential barriers were determined from experimental data in three cases and estimated in the fourth. The sparsity of accurate experimental data for the more complex molecules makes a different procedure desirable. Here the potential barriers and other constants will be given the same values for all molecules, and these values will be selected on the basis of the constants for the simpler molecules and the available thermodynamic data on the more complex ones. On this basis it is hoped that calculations for other molecules will have some validity.

The potential barrier expected for the rotation of a methyl group at the end of a long chain would be the same as in propane, 3300 cal. For rotations within the chain a somewhat higher value might be expected. As a simplifying compromise 3600 cal. per mole is used throughout.

For the carbon skeleton rotations it becomes necessary to decide which position is the stable one. Let us define as the *cis*-position that corresponding to a symmetry of D_{3h} in ethane. Here each hydrogen is as near as possible to one at the other end of the molecule. The *trans*-position then corresponds to an ethane symmetry D_{3d}, or a rotation of 60° from the *cis*-position. This puts a hydrogen at one end half-way between two at the other. Conn, Kistiakowsky, and Smith (4) have considered the evidence favoring either position. They consider the reasonableness of either case through a large body of thermochemical data, and conclude "unreservedly" in favor of the *trans*-position as the stable one. Somewhat different conclusions have been reached by Gorin, Walter, and Eyring (14), and for ethane alone by Karweil and Schafer (17). The range of facts considered by these authors does not compare, in the writer's opinion, with that considered by Conn, Kistiakowsky, and Smith, at least for the case of the multi-carbon systems. Consequently we shall assume the *trans*-position to be stable, yet realizing that this conclusion is not absolutely certain. The thermodynamic functions would not be greatly affected by changing this assumption.

As compared to methyl group rotations which have by symmetry a potential barrier with three equal peaks and minima, the internal rotation of a carbon skeleton is not usually symmetrical and may have peaks and minima of different heights. Thus in *n*-butane there is one planar position with the methyl groups far apart and two positions derived by 120° rotation in either direction. In these latter positions the methyl groups are a bit closer than allowed by their ordinary van der Waals or kinetic theory radii. These two positions are probably somewhat higher in energy than the planar one, because of these steric repulsions.

With the addition of more bonds the number of such positions increases rapidly. However, in the normal paraffins they can be easily classified as follows: (*1*) The planar, zigzag configuration which is presumably most stable. (*2*) Positions which involve one or more interactions of the type met in n-butane. They are assigned an energy na, where n is the number of interactions and a is the energy factor to be fixed from the available data. (*3*) Positions which involve such close approach of non-bonded atoms as to be of very high energy, and consequently excluded.

In the branched-chain compounds different situations arise. However, in order to avoid additional constants, each position was assigned an energy in terms of a. This somewhat arbitrary procedure was carried out with the aid of the "Fisher–Hirschfelder" models, which approximate proportional atomic sizes. Fortunately the number of different positions is less in the branched-chain isomers, because of the increased number of symmetrical methyl groups and occasional tertiary butyl groups which are likewise symmetrical. On the other hand, it was impossible to assemble a model completely in a few cases, most notably that of 2,2,4-trimethylpentane. In such cases the energy assignments are little better than a guess.

TABLE 2

Molal entropies of the normal paraffins, together with data used in their calculation
($\sigma = 2$ and $N_4 = 2$ throughout)

SUBSTANCE	N_1	N_2	N_3	N_5	NUMBER OF POSITIONS WITH ENERGY 0	a	$2a$	$3a$	$4a$	$5a$	∞	$S^0_{298.1}$ Calculated	$S^0_{298.1}$ Observed*
												cal. per degree	*cal. per degree*
Butane	3	2	1	2	1	2	0	0	0	0	0	74.17	73.7
Pentane	4	3	2	3	1	4	2	0	0	0	2	83.27	82.2[3]
Hexane	5	4	3	4	1	6	8	2	0	0	10	92.41	92.3
Heptane	6	5	4	5	1	8	18	12	2	0	40	101.54	101.3
Octane	7	6	5	6	1	10	32	38	16	2	144	110.67	110.0
Δ per CH_2	1	1	1	1	0	2						9.13	

* Experimental error about 1 calorie per degree.

Table 2 contains the assembled data for calculations for normal paraffins. The steric parameter a was given the value 800 cal. per mole to obtain agreement with the accurate experimental entropies of n-butane and n-heptane obtained by Aston (1) and the writer (33), respectively[3].

At their boiling points the following values were obtained: n-butane,—experimental, 72.0, calculated, 72.1 cal. per degree; n-heptane,—experimental, 111.78 ± 0.3, calculated, 111.6 cal. per degree. Since only one arbitrary constant was fixed, the agreement for both substances may be

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[3] After completion of these calculations, the writer received an unpublished value of the entropy of n-pentane of 83.46 ± 0.3 cal. per degree at 298.1°K., from the work of Messerly (28). The agreement with the calculated value is perfect.

said to verify the potential barrier of 3600 cal. selected above. The observed values[3] in table 2 are from Parks and coworkers (30), with vaporization data from various sources.

TABLE 3

Molal entropies of the branched-chain paraffins, together with data used in their calculation

SUBSTANCE	N_1	N_2	N_3	N_4	N_5	N_6	N_7	NUMBER OF POSITIONS WITH ENERGY						σ	$S^0_{298.1}$	
								0	*a*	*2a*	*3a*	*4a*	∞		Calculated (gas)	Experimental (liquid)
															cal. per degree	*cal. per degree*
2-Methylbutane........	4	4	1	3	1	1	0	2	0	1	0	0	0	1	82.0	60.8
2,2-Dimethylbutane....	5	6	1	4	1	0	1	1	0	0	0	0	0	1	85.7	64.4
2,3-Dimethylbutane....	5	6	1	4	0	2	0	1	0	2	0	0	0	2	86.5	
2-Methylpentane........	5	5	2	3	2	1	0	2	0	3	0	0	4	1	90.1	69.9
3-Methylpentane........	5	5	2	3	2	1	0	2	0	2	0	2	3	1	90.0	
2,2,3-Trimethylbutane.	6	8	1	5	0	1	1	1	0	0	0	0	0	1	92.3	64.8
2,2-Dimethylpentane...	6	7	2	4	2	0	1	1	0	0	0	0	2	1	93.4	68.1
2,3-Dimethylpentane...	6	7	2	4	1	2	0	4	0	0	0	0	5	1	98.8	72.4*
2,4-Dimethylpentane...	6	7	2	4	1	2	0	2	0	0	0	2	5	2	94.7	69.7
3,3-Dimethylpentane...	6	7	2	4	2	0	1	5	0	2	0	0	2	2	95.4	70.1
3-Ethylpentane.........	6	6	3	3	3	1	0	11	0	0	0	0	16	3	98.3	74.6
2-Methylhexane.........	6	6	3	3	3	1	0	2	4	3	4	0	14	1	99.5	75.3
3-Methylhexane.........	6	6	3	3	3	1	0	4	4	4	0	0	15	1	101.3	74.0*
2,2,3,3-Tetramethylbutane...............	7	10	1	6	0	0	2	1	0	0	0	0	0	6	94.1	61.4 (solid)
2,2,4-Trimethylpentane	7	9	2	5	1	1	1	2	0	0	0	0	1	1	101.4	75.2

* The experimental entropies in this table are for the liquid, except as noted. All are from the work of Parks and Huffman (30) except the data for 2,2-dimethylbutane and 2-methylpentane, which are from the work of Stull (38). Those values designated by an asterisk are especially uncertain; the others are probably self-consistent to within 1 or 2 cal. per degree and somewhat low. The substances marked by an asterisk are, interestingly, also the two cases where optical isomers occur. The calculated values include an $R \ln 2$ term to account for this fact.

When the calculations were carried out in the same fashion for the branched-chain isomers, the entropies obtained were too large. This is not surprising when one considers the high potential barriers found for tetramethylmethane, and the higher bending vibration frequencies observed in isobutane and tetramethylmethane. No account has yet been taken of these factors. Since an accurate entropy is available for only one branched-chain paraffin above neopentane, any complex way of accounting for these factors would be absurd. The following simple procedure was adopted:

Thermodynamic functions were calculated for isobutane and tetramethylmethane, using the approximate methods of this latter section, and from these were subtracted the accurate values given above. The differences obtained were then applied as a correction to the higher branched-chain isomers,—one isobutane correction being used wherever a carbon atom is bonded to three other carbon atoms, and a tetramethylmethane correction wherever a carbon atom is bonded to four others. The 2,2,4-trimethylpentane entropy now comes within 1 cal. per degree of the experimental value (33) (which has a ±0.3 cal. per degree error) and this is as high accuracy as can be expected with such compounds at this time.

Table 3 contains the assembled data for the branched-chain paraffins. The number of CH groups, N_6, is, of course, also the number of carbon atoms bonded to three other carbons; N_7 is the number of carbons bonded to four others.

The only severe test to be applied is the case of 2,2,4-trimethylpentane already mentioned. However, in the last column the available entropies of the liquids are listed. Data for conversion to the gaseous state are not available. All these entropies involve long extrapolations from 90 to 0°K., which, however, were made consistently throughout. On the other hand, the writer (33) found the 2,2,4-trimethylpentane extrapolation was 3 cal. per degree too low, while the *n*-heptane extrapolation was almost exactly right, which indicates that confidence can be placed in these values only to an accuracy of 2 or 3 cal. per degree. Actually the calculated and experimental values show remarkably similar variations, and their differences are very reasonable as entropies of vaporization.

Except for the simplest hydrocarbons (23, 24), the data on specific heats of gases are so sparse and inaccurate as to be of little value at present in checking values calculable by the methods discussed above. No serious discrepancies arise except in cases where the experimental data are very doubtful. On the other hand, no great confidence can be placed in values calculated by these methods until they have been checked experimentally. Fortunately, the likely chemical equilibrium calculations are not sensitive to the heat capacity values.

V. UNSATURATED HYDROCARBONS

Thermodynamic functions for acetylene and ethylene have been calculated by Kassel (18) and the writer (32) and are included without change.

There is some doubt as to the correct potential barrier for the methyl group rotation in propylene. On the basis of the data of Frey and Huppke (11), and of Kistiakowsky and coworkers on the hydrogenation reaction, the writer (32) obtained a result of less than 800 cal. for this quantity. Kistiakowsky, Lacher, and Ransom (23) measured the heat capacity of gaseous propylene and placed the value at about 600 to 800 cal. per mole^{-1}, in good agreement. Powell and Giauque[4] (34), taking the average as 700, obtained a third-law entropy of propylene which was 1.1 cal. per degree too low on the basis of this barrier. They attributed this discrepancy to a lack of discrimination between the CH_2 and CH_3 ends in the orientation of the molecule in the crystal. Then Crawford, Kistiakowsky, Rice, Wells, and Wilson (7) reported that the value of 700 cal. was wrong and that the correct value was about 2100 cal., a value which gives agreement with the third-law entropy. These last authors failed to discuss the results of Frey and Huppke, which can hardly agree with this last conclusion. In fact the barrier of 2100 cal. for propylene will give hydrogenation equilibrium constants differing by about a factor of 2. There seems no reason to believe Frey and Huppke's work to be in error by such a factor. On the other hand, the latest results of Kistiakowsky and his coworkers are not to be disregarded.

It is unfortunate that the third-law entropy can be said to agree with either result. In passing it might be noted that since both ends of the molecule of 2-butene are the same, there would be no uncertainty in the third-law entropy there. Either the *cis-* or the *trans-*isomer could be used to get a definite value for the potential barriers in this case.

In view of the present uncertainty there seems no justification for changing the thermodynamic functions calculated by the writer (32) in 1937 for propylene and the various butenes. On the other hand, the results must be regarded as much less certain than those for the corresponding paraffins. The errors may even exceed the 1 cal. per degree limits suggested in 1937.

Detailed calculations for the higher olefins obviously would be prema-

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[4] Professor Giauque and Dr. Powell have requested that attention be called to a numerical error in the calculation of the restricted rotation contribution to the entropy at 298.1°K. The entropy correction for hindered rotation given as −1.00 cal. deg.$^{-1}$ mole^{-1} at 298.1°K. in Table XI of their paper should have been −0.15 when a potential barrier of 700 cal. mole^{-1} is used. This leads to a value of 64.9 cal. deg.$^{-1}$ mole^{-1} for the entropy of propylene from molecular data at 298.1°K., instead of the value 64.0 which was given. However, if one agrees with Kistiakowsky that his value of 700 cal. mole^{-1} is wrong and accepts the later value of 2119 cal. mole^{-1} proposed by Kistiakowsky and coworkers, the value 64.0 cal. deg.$^{-1}$ mole^{-1} is by fortuitous circumstance about the correct answer. The value at the boiling point 225.35°K. is correct, assuming a 700 cal. mole^{-1} barrier.

ture. Estimates can be made in particular cases by considering the corresponding paraffin and the difference between the most analogous butene and butane. Also, possible differences in the heats of hydrogenation and symmetry numbers should be taken into account.

VI. TABULATION OF THERMODYNAMIC FUNCTIONS

While in many cases the thermodynamic functions calculated by the methods outlined above are not as accurate as one might desire, they are, for the most part, at least as good as the available heat of combustion data. The precision needed in the latter is, of course, much greater. All the heats of formation used in the tables to follow are from Rossini's complete review of the available data (35), except for a few branched-chain paraffins not included by Rossini. For the latter, the writer has given provisional values based on the available experimental data (30) and on empirical

TABLE 4

Thermodynamic constants for the formation of gaseous hydrocarbons at 298.1°*K.*

$n\text{C (graphite)} - m\text{H}_2\text{(g)} = \text{C}_n\text{H}_{2m}\text{(g)}$

SUBSTANCE	ΔS	ΔH	ΔF
	cal. per degree	*kcal.*	*kcal.*
Methane	−19.39	−17.865 ± 0.074	−12.085
Ethane	−41.61	−20.191 ± 0.108	−7.787
Propane	−64.4	−24.750 ± 0.124	−5.55
n-Butane	−87.5	−29.715 ± 0.153	−3.63
Isobutane	−91.2	−31.350 ± 0.132	−4.16
n-Pentane	−111.1	−34.739 ± 0.213	−1.62
2-Methylbutane	−112.3	−36.671 ± 0.153	−3.19
Tetramethylmethane	−121.1	−39.410 ± 0.227	−3.31
n-Hexane	−134.5	−40.01 ± 0.50	+0.08
2-Methylpentane	−136.8	−41.8 ± 0.7	−1.0
2,2-Dimethylbutane	−141.2	−44.4 ± 0.7	−2.3
n-Heptane	−158.0	−45.35 ± 0.80	+1.75
2-Methylhexane	−160.1	−47.1 ± 1.0	+0.6
2,2-Dimethylpentane	−166.2	−49.8 ± 1.0	−0.3
n-Octane	−181.5	−50.70 ± 1.0	+3.4
2,2,4-Trimethylpentane	−190.8	−56.2 ± 2.0	+0.7
n-[$\text{C}_n\text{H}_{2n+2}$] ($n > 6$)	[$-23.49n$ $+6.4$]	$-[5.35n - 7.90]$ $\pm 0.12n$	[$+1.65n$ -9.80]
Ethylene	−12.49	+12.556 ± 0.067	+16.279
Propylene	−32.8	4.956 ± 0.110	14.73
1-Butene	−55.1	0.383 ± 0.181	16.81
cis-2-Butene	−56.9	−1.388 ± 0.181	15.57
trans-2-Butene	−57.5	−2.338 ± 0.181	14.80
"Isobutene" (2-methylpropene)	−59.2	−3.205 ± 0.162	14.44
Acetylene	+14.07	+54.228 ± 0.233	50.034

TABLE 5

Thermodynamic functions for some gaseous paraffins

FUNCTION	T	METHANE	ETHANE	PROPANE	*n*-BUTANE	ISO-BUTANE	*n*-PENTANE	2-METHYL-BUTANE	TETRA-METHYL METHANE	*n*-HEXANE	*n*-HEPTANE	*n*-OCTANE	Δ PER CH$_2$
$\frac{H_0^0 - F_T^0}{T}$ in calories per degree	298.1	36.42	45.25	52.83	58.54	56.14	64.19	64.70	56.28	69.86	75.52	81.18	5.66
	400	38.82	48.20	56.62	63.56	60.85	70.32	70.40	61.87	77.12	83.91	90.70	6.79
	500	40.72	50.72	59.98	68.02	65.13	75.80	75.64	67.13	83.63	91.46	99.29	7.83
	600	42.36	53.06	63.13	72.16	69.21	80.89	80.63	72.18	89.69	98.47	107.25	8.78
	800	45.18	57.28	69.00	79.93	76.90	90.51	90.12	81.71	101.15	111.78	122.39	10.61
	1000	47.62	61.12	74.44	87.12	83.99	99.37	98.87	90.55	111.68	123.98	136.27	12.29
	1500	52.81	69.49	86.30	102.65	99.54	118.49	118.01	109.96	134.40	150.29	166.17	15.88
$H_T^0 - H_0^0$ in kilocalories	298.1	2.397	2.865	3.535	4.66	4.29	5.68	5.17	5.05	6.71	7.74	8.77	1.03
	400	3.31	4.27	5.59	7.43	7.08	9.12	8.63	8.56	10.83	12.54	14.24	1.71
	500	4.35	6.02	8.08	10.77	10.46	13.26	12.84	12.84	15.77	18.27	20.77	2.50
	600	5.55	8.03	11.06	14.63	14.39	18.04	17.70	17.81	21.46	24.89	28.30	3.42
	800	8.3	12.78	17.91	23.68	23.50	29.21	28.98	29.37	34.76	40.31	45.86	5.55
	1000	11.4	18.37	25.92	34.13	34.00	42.08	41.91	42.54	50.04	58.00	65.95	7.95
	1500	21.4	34.56	48.77	63.74	64.00	78.42	78.69	79.50	93.10	107.79	122.46	14.67
ΔH_0^0 of formation, in kilocalories		−15.96 ±0.07	−16.48 ±0.1	−19.44 ±0.15	−23.25 ±0.2	−24.52 ±0.2	−27.03 ±0.3	−28.45 ±0.3	−31.07 ±0.3	−31.05 ±0.5	−35.15 ±0.8	−39.25 ±1.0	−4.11 ±0.2

relationships found for the simpler molecules. These are assigned a 2 kcal. error in table 6.

Thermodynamic constants for the formation of the gaseous hydrocarbons from hydrogen and graphite at 298.1°K. are given in table 4. The entropies of hydrogen and graphite are taken respectively as 31.23 and 1.39 cal. per degree.

For use in calculations at arbitrary temperatures, the free-energy function $(H_0^0 - F_T^0)/T$ and the heat content function $(H_T^0 - H_0^0)$ are given for the range 298.1 to 1500°K., together with values of ΔH_0^0 of formation. These appear in tables 5, 6, and 7. Although interpolations can be made by other methods, the graphical one will probably be most satisfactory. In this regard it is suggested that the values for the higher branched-chain isomers (where values for only 298.1, 600, and 1000°K. are given) be plotted alongside those of the normal compound as an aid in drawing the curve.

Probably the most important use to be made of these results is the calculation of equilibrium constants. For the reaction:

$$a\text{A} + b\text{B} + \cdots = m\text{M} + n\text{N} + \cdots$$

the equilibrium constant

$$K = P_{\text{M}}^m P_{\text{N}}^n \cdots / P_{\text{A}}^a P_{\text{B}}^b \cdots$$

is given by the expression

$$R \ln K_T = -\Delta F/T = \sum (H_0^0 - F_T^0)/T - (1/T) \sum \Delta H_0^0 \qquad (1)$$

where the sums are over the reaction products with a plus sign and the reagents with a minus sign thus:

$$\sum (\ \ ) = m(\ \ )_{\text{M}} + n(\ \ )_{\text{N}} + \cdots - a(\ \ )_{\text{A}} - b(\ \ )_{\text{B}} - \cdots \qquad (2)$$

The values of ΔH_0^0 for elements in their standard states are zero and may be omitted, but the function $(H_0^0 - F_T^0)/T$ has a non-zero value for all substances above 0°K.

The values of the free-energy function for methane in table 5 and for acetylene in table 7 were taken from the work of Kassel (18), but have had the contributions of nuclear spin removed to correspond to the now generally accepted convention.

It is difficult to state briefly what the errors are in these functions. Errors have been assigned to the ΔH_0^0's on the basis of Rossini's work. The errors in the free-energy function may be divided roughly into two classes:—those entering at low temperatures and present at 298.1°, and those entering at higher temperatures. Where accurate experimental entropies are available, the former are largely eliminated. Thus in table 5 the error in the free-energy function is probably less than 0.1 cal. per degree in methane, and is only a few tenths in the worst cases. On the other hand, in tables 6 and 7, excepting ethylene and acetylene, the errors may exceed 1 cal. per degree. The errors entering at higher tem-

TABLE 6

Thermodynamic functions for the higher branched-chain paraffins

SUBSTANCE	$(H_0^0 - F_T^0)/T$			$(H_T^0 - H_0^0)$			ΔH_0^0 OF FORMATION
	298.1	600	1000	298.1	600	1000	
	cal. per degree	*cal. per degree*	*cal. per degree*	*kcal.*	*kcal.*	*kcal.*	*kcal.*
2-Methylpentane	69.7	88.7	110.4	6.07	21.1	49.9	−32.2 ± 0.7
3-Methylpentane	69.7	88.6	110.4	6.04	21.1	50.1	−32 ± 2
2,2-Dimethylbutane	66.0	84.6	106.4	5.87	20.9	50.2	−34.6 ± 0.7
2,3-Dimethylbutane	66.3	85.4	107.3	6.02	21.3	50.3	−34 ± 2
2-Methylhexane	75.5	97.6	122.9	7.15	24.5	57.8	−36.3 ± 0.8
3-Methylhexane	77.8	99.5	124.6	6.98	24.2	57.5	−36 ± 2
3-Ethylpentane	75.7	96.8	121.5	6.74	23.8	56.9	−35 ± 2
2,2-Dimethylpentane	71.0	92.2	117.3	6.69	24.1	57.8	−38.5 ± 1.0
2,3-Dimethylpentane	76.5	97.7	122.4	6.65	23.9	57.2	−36 ± 2
2,4-Dimethylpentane	72.3	93.6	118.6	6.66	24.1	57.7	−37 ± 2
3,3-Dimethylpentane	72.8	94.3	119.4	6.73	24.2	58.0	−37 ± 2
2,2,3-Trimethylbutane	70.2	91.5	116.6	6.59	24.2	58.1	−38 ± 2
2,2,4-Trimethylpentane	76.5	100.5	128.9	7.41	27.3	65.7	−43.4 ± 2
2,2,3,3-Tetramethylbutane	69.4	93.6	122.3	7.35	27.6	66.6	−43 ± 2

TABLE 7

Thermodynamic functions for some unsaturated hydrocarbons

FUNCTION	T	ETHYLENE	PROPYLENE	1-BUTENE	*cis*-2-BUTENE	*trans*-2-BUTENE	"ISO-BUTENE"	ACETYLENE
$\frac{H_0^0 - F_T^0}{T}$ in calories per degree	298.1	44.05	54.3	62.0	60.0	59.4	57.0	40.01
	400	46.7	57.6	66.3	64.3	63.7	61.6	42.49
	500	48.8	60.6	70.2	68.2	67.6	65.6	44.56
	600	50.8	63.3	73.9	71.7	71.1	69.4	46.38
	800	54.4	68.3	80.6	78.4	77.8	76.3	49.50
	1000	57.5	72.9	86.8	84.4	83.8	82.5	52.14
	1500	64.2	82.8	100.3	97.5	96.9	95.9	57.43
$H_{298.1}^0 - H_0^0$ in kilocalories		2.59	3.20	3.99	4.06	4.06	4.25	2.41
ΔH_0^0 of formation, in kilocalories		14.51 ±0.07	8.58 ±0.2	5.49 ±0.2	3.65 ±0.3	2.70 ±0.3	1.64 ±0.3	54.34 ±0.24

peratures are difficult to estimate but may amount to several per cent in either function. This percentage should be applied only to the increases over the 298.1° values. In this connection it should be noted that ΔH_0^0 is not a purely experimental quantity but is calculated using the $H_{298} - H_0$ values. Thus it is important to use ΔH_0^0's calculated with the same functions as are to be applied later.

For convenience in practical calculations the functions for graphite (3), hydrogen (12, 8), steam (13, 40), carbon monoxide (3, 15), carbon dioxide (19), and oxygen (16) have been included in table 8. All values

TABLE 8

Thermodynamic functions for graphite, hydrogen, steam, carbon monoxide, and carbon dioxide

FUNCTION	T	GRAPHITE	H_2	H_2O (g)	CO	CO_2	O_2
$\frac{H_0^0 - F_T^0}{T}$ in calories per degree	298.1	0.545	24.436	37.191	40.364	43.578	42.081
	400	0.854	26.438	39.529	42.408	45.848	44.127
	500	1.180	27.965	41.316	43.963	47.681	45.691
	600	1.510	29.218	42.789	45.238	49.261	46.984
	800	2.164	31.204	45.153	47.271	51.921	49.062
	1000	2.798	32.752	47.039	48.876	54.137	50.715
	1500	4.206	35.605	50.647	51.880	58.513	53.826
$H_T^0 - H_0^0$ in kilocalories	298.1	0.251	2.023	2.365	2.073	2.240	2.069
	400	0.51	2.731	3.190	2.784	3.197	2.798
	500	0.83	3.430	4.019	3.490	4.227	3.524
	600	1.20	4.128	4.874	4.209	5.328	4.280
	800	2.07	5.537	6.669	5.701	7.697	5.855
	1000	3.07	6.966	8.583	7.258	10.233	7.499
	1500	6.0	10.696	13.89	11.363	17.02	11.77
ΔH_0^0 of formation, in kilocalories		0.00	0.00	−57.108 ±0.010	−27.18 ±0.03	−93.949 ±0.011	0.00

are from the cited literature except the heat content function of graphite, which was obtained by the writer by differentiating the free-energy function.

Equilibrium constants for a few reactions have been calculated and are given in table 9. It is beyond the scope of this paper to calculate, or to discuss the significance of the equilibria for the many reactions for which the necessary data have been given above. There are very few direct equilibrium measurements for hydrocarbon systems. The only data considered in this work so far are those on the hydrogenation of propylene and the various butenes (11). In addition, the work of Montgomery, McAteer, and Franke (29) on the butane isomerization may be mentioned. Their results indicate a constant of about 5.5 favoring isobutane, which may be compared with the value 2.5 from table 9. This difference, which corresponds to a little over 1 cal. per degree, is about the limit of error to be associated with the calculated value.

Heats of chemical reactions may be calculated in a manner analogous to that for equilibria:

$$\Delta H_T = \sum (H_T^0 - H_0^0) + \sum \Delta H_0^0 \tag{3}$$

TABLE 9

Examples of equilibrium constants calculated from the above data

REACTION	K_{298}	K_{600}	K_{1000}
n-C_4H_{10} = iso-C_4H_{10}	2.5	0.7	0.4
$C_3H_8 = C_3H_6 + H_2$	1.3×10^{-15}	1.7×10^{-4}	5
$C_3H_8 = CH_4 + C_2H_4$	7×10^{-8}	1.0	6×10^{2}
n-$C_nH_{2n+2} = C_2H_4 + n$-$C_{n-2}H_{2n-2}$ $(n > 7)$	3×10^{-10}	0.09	170
$(CH_3)_3CCH_2CH(CH_3)_2$ = iso-C_4H_{10} + iso-C_4H_8	9×10^{-8}	7	5×10^{3}
n-$C_7H_{16} = (CH_3)_2CHCH_2CH_2CH_2CH_3$	7	1.6	1.0
n-$C_7H_{16} = (CH_3)_3CCH_2CH_2CH_3$	29	0.7	0.2
n-$C_7H_{16} = (C_2H_5)_3CH$	1.1	0.4	0.3
n-$C_7H_{16} = (CH_3)_3CCH(CH_3)_2$	10	0.4	0.1

TABLE 10

Examples of heats of reaction calculated from the above data

REACTION	HEATS OF REACTION	
	ΔH_{600}	ΔH_{1000}
	kcal.	*kcal.*
$C_3H_8 = CH_4 + C_2H_4$	20.0	21.6
$C_3H_8 = C_3H_6 + H_2$	31.1	34.6
$C_7H_{16} + 11O_2 = 7CO_2 + 8H_2O$	−1074.65	−1079.56
n-$C_5H_{12} = (CH_3)_4C$	−4.46	−3.58

where the sums are as defined in equation 2. A few typical calculations are given in table 10.

The heat content function has been calculated for the unsaturated hydrocarbons only at 298.1°K. As a rough approximation the changes in heat content above this temperature may be assumed to be the same as for the corresponding paraffin. These values will be too large, particularly at the higher temperatures, but will not err grossly.

Heat content changes for a single substance are given by the function $(H_T^0 - H_0^0)$, whose temperature derivative is the molal heat capacity. On the whole there is little difference between the heat capacities of isomers above room temperature.

The entropy is given by the equation:

$$S^0_T = (H^0_0 - F^0_T)/T + (H^0_T - H^0_0)/T$$

The first function is tabulated in this form; the second must be divided by the temperature and converted to small calories.

VII. COMBINED FUNCTIONS

As can be seen easily from equations 1 and 3 above, the summation of two functions in calculating an equilibrium constant or heat of reaction could be reduced to a single sum by tabulating the combined functions:

TABLE 11

Combined free-energy and heat functions

$$F^*_T/T = (H^0_0 - F^0_T)/T - \Delta H^0_0/T$$

$$H^*_T = (H^0_T - H^0_0) + \Delta H^0_0$$

FUNCTION	T	METHANE	ETHANE	PROPANE	n-BUTANE	ISOBUTANE
$\frac{F^*}{T}$	298.1	89.96	100.53	118.04	136.54	138.40
	400	78.72	89.40	105.22	121.69	122.15
	500	72.64	83.68	98.86	114.52	114.17
	600	68.97	80.53	95.54	110.92	110.09
	800	65.13	77.88	93.30	108.99	107.55
	1000	63.58	77.60	93.88	110.37	108.51
	1500	63.45	80.48	99.26	118.15	115.89
H^*	0	−15.96	−16.48	−19.44	−23.25	−24.52
	298.1	−13.56	−13.62	−15.91	−18.59	−20.23
	400	−12.65	−12.21	−13.85	−15.82	−17.44
	500	−11.61	−10.46	−11.36	−12.48	−14.06
	600	−10.41	−8.45	−8.38	−8.62	−10.13
	800	−7.66	−3.70	−1.53	+0.43	−1.02
	1000	−4.56	+1.89	+6.48	10.88	+9.48
	1500	+5.44	18.08	29.33	40.49	39.48

$$-F^*_T/T = (H^0_0 - F^0_T)/T - \Delta H^0_0/T$$

$$H^*_T = (H^0_T - H^0_0) + \Delta H^0_0$$

These can be considered to give the free energy and heat changes for the hybrid reaction:

elements (standard state, 0°K.) = compound (T°K.)

This scheme was used by Rodebush in the *International Critical Tables* and has been advocated recently by Aston (1). It has the advantage of some simplicity, although the numbers are now ordinarily larger and may change more rapidly with temperature, making interpolation and graphing more difficult. The separate functions have the important advantage of keeping errors from different sources separated. Thus when accurate heats of combustion for the higher branched-chain paraffins become available, only the ΔH_0^0 values need be changed, but this would change the whole tables of combined functions.

As an example, table 11 contains these combined functions for the paraffins through the butanes. For the elements, with ΔH_0^0 by definition zero, the separate and combined functions become identical. Anyone finding the combined functions desirable can easily construct his own table or graph in a very short time from the tables of separate functions.

VIII. CONCLUSION

In concluding, the writer wishes to recall rather carefully the purposes and point of view of this work. The principal aim was to develop a method of correlating the available thermodynamic data for hydrocarbons, which would allow interpolation and extrapolation to different temperatures, different thermodynamic functions, and different but related molecules. The accuracy of the results depends in some cases solley on the experimental thermodynamic data employed. In other cases it depends also on the accuracy of the picture drawn from molecular structure data, and on the accuracy of the statistical methods employed. In addition, by these methods certain of the missing elements in our picture of the hydrocarbon structures can be filled in.

These data should be very useful to chemists working with reactions involving these substances. The fact that hydrocarbon equilibria are so hard to measure directly makes indirect data of this type even more valuable. The information obtained with respect to internal rotation potentials, steric hindrances, etc. should be useful also in non-thermodynamic fields.

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