

Thermodynamics of Gaseous Hydrocarbons: Ethane, Ethylene, Propane, Propylene, nButane, Isobutane, 1Butene, Cis and Trans 2Butenes, Isobutene, and Neopentane (Tetramethylmethane)

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Thermodynamics of Gaseous Hydrocarbons: Ethane, Ethylene, Propane, Propylene, *n*-Butane, Isobutane, 1-Butene, *Cis* and *Trans* 2-Butenes, Isobutene, and Neopentane (Tetramethylmethane)

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It is pointed out that the assumption of completely free internal rotation in the simpler hydrocarbon molecules is probably responsible for the discrepancies between the results of previous statistical mechanical calculations and the experimental data. Using the formulas and tables of the preceding paper, calculations are presented which show that, for reasonable values of rotation restricting potentials, complete agreement can be obtained with all experimental results. The uncertainty as to the exact height and shape of these potential barriers, together with the possible errors in estimated vibration frequencies make

highly precise calculations of thermodynamic functions out of the question at present. Nevertheless the general agreement with experiment indicates that the potentials and frequencies selected must be approximately correct. These molecular structure data together with the available values of heats of combustion and hydrogenation are then employed in calculations which yield thermodynamic constants and the free energy of formation as a function of the temperature in the range from 300 to 1500°K. The various calculations have been made for all of the hydrocarbons listed in the title.

THE rotational partition functions for several of the simpler hydrocarbons have been calculated with the assumption of completely free rotation about single carbon-carbon bonds.^{2, 3} The results of these calculations are not, however, in accord with experimental data, and in the case of ethane the error has been shown to be the assumption of free internal rotation.^{4, 5} These results strongly suggest that a situation similar to that in ethane exists in many other molecules. In the preceding paper⁶ the procedure is given for treating molecules having restricted internal rotations; however, moments of inertia, potential barriers, and vibration frequencies need to be known. The moments of inertia for the simpler hydrocarbons can be calculated with sufficient accuracy by using the reasonably well established values of the interatomic distances, while the vibration frequencies are known or can be satisfactorily estimated in many cases. The potential barriers are not known independently for any case, but if they are obtained from thermodynamic data for a few molecules, values can sometimes be interpolated for others. It is thus apparent that purely theoretical-spectroscopic calculations of thermodynamic

functions are not possible at present; nevertheless in many cases the procedure and formulas for such calculations are useful as a framework for the correlation of all experimental data available, whether thermodynamic or spectroscopic in nature. If all of the various molecular constants can be determined by this procedure, then accurate calculations of thermodynamic functions can be made just as if the spectroscopic data were complete. In the present paper the various paraffins and olefins having less than four carbon atom and tetramethylmethane are discussed from this point of view. It is found that for reasonable values of potential barriers and vibration frequencies complete agreement with all experimental data can be obtained. While it is not possible at present to make precise calculations of the free energy or other functions, reasonably accurate values of thermodynamic constants are given and approximate values are tabulated for the free energy in the region from 300 to 1500°K.

MOLECULAR STRUCTURE DATA AND CALCULATED ENTROPIES

In the following calculations the C-C distance was taken as 1.53Å, the C=C distance as 1.36Å and the C-H distance as 1.11Å. The angle between single bonds from a given carbon atom was assumed to be the normal tetrahedral angle. These data suffice for the calculation of

¹ Shell Research Fellow, academic year 1936-1937.

² Edinoff and Aston, *J. Chem. Phys.* **3**, 379 (1935).

³ Kassel, *J. Chem. Phys.* **4**, 276 (1936); **4**, 435 (1936).

⁴ Kemp and Pitzer, *J. Chem. Phys.* **4**, 749 (1936); *J. Am. Chem. Soc.* **59**, 276 (1937).

⁵ Howard, *Phys. Rev.* **51**, 53 (1937).

⁶ Pitzer, *J. Chem. Phys.* **5**, 469 (1937).

TABLE I. Translation-rotation entropies for rigid molecules.

SUBSTANCE	S_{t+r}	S_{t+r} at 298.1°K
Ethane	$7.21 + 4R \ln T$	52.50
Propane	$13.33 + 4R \ln T$	58.62
Isobutane	$15.22 + 4R \ln T$	60.51
Neopentane	$14.24 + 4R \ln T$	59.53
(St) <i>n</i> -butane	$16.33 + 4R \ln T$	61.62
(Be) <i>n</i> -butane	$17.40 + 4R \ln T$	62.69
Isobutene	$15.76 + 4R \ln T$	61.05

moments of inertia and thereby translation-rotation partition functions for either a rigid molecule or a freely rotating one. The resulting entropies for the latter case have been presented by Kassel³ while those for the former appear in Table I.

The vibration frequencies of the simpler hydrocarbons have been discussed by Kassel^{3, 7} and the treatment used here will be very similar, including, however, more recent experimental results. The vibrations of the hydrogens are grouped into three classes: those involving primarily C-H bond distances, H-C-H bond angles, and H-C-C bond angles. The frequencies of vibrations of the first type are always very near 3000 cm⁻¹ and may be taken as such without appreciable error. Each hydrogen contributes one such frequency. The H-C-H bending frequencies are 1306 (triple) and 1536 (double) in methane;⁸ 1460, 1370, 1480 (double), and 1460 (double) in ethane;⁵ 1342 and 1443 in

ethylene.⁹ For these vibrations an averaged frequency of 1440 cm⁻¹ will be used. Each methyl group contributes three such frequencies, while each methylene group contributes one. The third type of vibrations, which depend essentially on the H-C-C angle, have the lowest frequencies and are therefore the most important. Ethane has two such frequencies, each double. The value 827 cm⁻¹ can be definitely assigned to one of these. The other has been estimated as 1005 cm⁻¹ by Howard⁵ from a force constant calculation, and as 1160 cm⁻¹ by Kemp and Pitzer⁴ from a consideration of gas specific heat data. In ethylene⁹ the frequencies of this group have the values 1100, 950, 950, and 940 cm⁻¹. Although the frequencies for ethylene appear to be slightly higher than those for ethane, the difference is insignificant for the present purpose and the value 950 cm⁻¹ will be used throughout. Each methyl group has two such frequencies, each -CH₂- group three, each =CH₂ group two, and each CH group two. The total number of degrees of freedom in each class is shown in Table II for a number of molecules.

The vibrations of the carbon skeleton are easily classified as bending or stretching modes. From both the available spectral data and the calculations of Kassel,⁷ it is apparent that for each C-C bond there is a frequency near 1000 cm⁻¹. The data on ethylene⁹ suggest that

⁷ Kassel, J. Chem. Phys. **3**, 326 (1935).

⁸ Childs, Proc. Roy. Soc. **A153**, 555 (1936).

⁹ Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

TABLE II. Data concerning internal degrees of freedom.

SUBSTANCE	CARBON SKELETON VIBRATIONS	HYDROGEN VIBRATIONS			TORS. VIB.	S AT 298.1°K	RESTRICTED ROT. V, $I \times 10^{40}$	S _{rr} AT 298°K
		950	1440	3000				
Ethane	1000 (1)	4	6	6		0.62	3000, 2.7 (1)	1.70
Propane	380 (1), 1000 (2)	7	7	8		2.12	3400, 4.7 (2)	4.0
Isobutane	380 (3), 1000 (3)	8	9	10		4.44	3800, 5.2 (3)	5.9
Neopentane	380 (5), 1000 (4)	8	12	12		6.65	4200, 5.3 (4)	7.5
<i>n</i> -Butane	320 (2), 1000 (3)	10	8	10		4.14	{ 3400, 5.0 (2) 3800, 18.6 (1) }	7.3
Propylene	380 (1), 1000 (1), 1600 (1)	6	4	6	570 (1)	2.38	<800, — (1)	—
1-Butene	320 (2), 1000 (2), 1600 (1)	9	5	8	570 (1)	4.4	{ 3400, 5.0 (1) <800, — (1) }	—
<i>Cis</i> 2-butene	320 (2), 1000 (2), 1600 (1)	8	6	8	270 (1)	5.4	<800, — (2)	—
<i>Trans</i> 2-butene	320 (2), 1000 (2), 1600 (1)	8	6	8	270 (1)	5.4	<800, — (2)	—
Isobutene	380 (3), 1000 (2), 1600 (1)	6	7	8	570 (1)	4.6	1800, 5.2 (2)	5.7

The numbers in parentheses or in the columns under "Hydrogen Vibrations" indicate the number of degrees of freedom. The contributions to thermodynamic quantities may be calculated using tables of Einstein functions for the vibrational degrees of freedom, and using the equations and tables of the preceding paper⁴ for the restricted rotational degrees of freedom. The symmetry number for the restricted rotations is three, except for the central bond of *n*-butane and 1-butene. These two rotations are discussed in the text.

for the C=C bond the value should be about 1600 cm^{-1} . The bending frequencies are much lower and consequently much more important. The values from Raman spectra¹⁰ are for propane 374; for *n*-butane 222, 320 and 428; for isobutane 370, 438; and for tetramethylmethane 330, 416 cm^{-1} . The data for the series propane, isobutane, neopentane are thus reasonably well known and the experimental frequencies may be used; or an averaged value, 380 cm^{-1} , may be taken for each of the one, three, and five degrees of freedom, respectively, which are present in these molecules. The case of *n*-butane is less certain, since two isomers are probably present in equilibrium. This situation will be discussed below. In any event no gross error would be made if the two expected frequencies are assigned the value 320 cm^{-1} . Unfortunately data are not available for propylene or the various butenes; consequently it was necessary to make some assumption. Comparison of the bending frequencies of ethane and ethylene, as mentioned above, indicates that the carbon skeleton bending frequencies of the olefins are probably but slightly higher than those of the corresponding paraffins, and consequently the same values will be used. The selected vibration frequencies are summarized in Table II.

The only remaining data needed are those concerning the internal rotational oscillational degrees of freedom. Unfortunately these frequencies are active as fundamentals in neither the Raman nor the infrared spectra. Thus their determination by these methods is difficult at best. In the case of the double carbon-carbon bond the rotation restricting barriers are so high that the harmonic oscillator treatment is satisfactory. Bonner, in discussing ethylene, gives 825 cm^{-1} as the most probable, though not completely certain value of this frequency. Since better data are not available this value will be used to determine the force constant for all the olefins. The frequency then becomes about 570 cm^{-1} when heavy groups are substituted at one end as in propylene, 1-butene and isobutene, and about 270 cm^{-1} for both of the 2-butenes. Fortunately this frequency appears but once, so that any moderate error would not be serious. The frequency cannot be much smaller than the

value given in the case of ethylene, for the total vibrational heat capacity of the gas is only 0.08 cal./deg. at 143°K .¹¹

The heights of potential barriers restricting rotation about single bonds have, as yet, been determined only from thermodynamic data, although Howard⁵ has employed spectral data to set a lower limit of 2000 cal./mole for the barrier in ethane. Previous calculations⁴ have shown that the various thermodynamic data yield a value of 3000 cal./mole for ethane, while an application of the formulas and tables of the preceding paper⁶ to the accurate third law entropy of tetramethylmethane, which was obtained by Aston and Messerly,¹² gives 4200 cal./mole for that case. Both of these values are probably correct within about 300 cal. The interpolation of 3400 cal. for propane and 3800 cal. for isobutane should be a safe procedure. The situation of the end methyl groups in *n*-butane and 1-butene is so similar to that in propane as to allow considerable confidence in the use of the same height of barrier. The central bond in *n*-butane does not have exact threefold symmetry, although there are presumably three maxima and minima. About all that can be said is that the potential maxima are probably about 3800 cal. high and that the minimum corresponding to the straightened position is most likely lowest.

The single bonds adjacent to a double bond will have a plane group on one end and a group with threefold symmetry (at least approximately) on the other end. As the two sides of the plane group become more equal, the three potential barriers will tend to be canceled out, eventually leaving six much lower ones. Consequently one would expect in propylene, 1-butene, and the 2-butenes a much lower barrier than in ethane. Actually heat and free energy of hydrogenation data indicate quite free rotation, the potential maxima being not more than 800 cal. high. Isobutane, however, has two methyl groups at the same end of the double bond, and their mutual restriction should predominate over any from the other end of the molecule, giving a higher barrier in this case. The experimental

¹⁰ Landolt-Bornstein, *Tabellen*.

¹¹ Eucken and Parts, *Zeits. f. physik. Chemie* **B20**, 184 (1933).

¹² Aston and Messerly, *J. Am. Chem. Soc.* **58**, 2354 (1936).

TABLE III. Comparison of calculated and observed free energies for hydrogenation reactions.

OLEFIN	$\Delta F/T_{\text{exp}}$	$\Delta F/T_{\text{calc}}$ ($V=0$)	$\Delta F/T_{\text{calc}}$ ($V=800$ cal.)
Propylene	12.16	12.26	12.37
1-Butene	12.16	12.53	12.64
<i>Cis</i> 2-butene	11.90	12.06	12.28
<i>Trans</i> 2-butene	11.02	11.24	11.46
Isobutene	9.15	(8.54)	9.38 ($V=1800$ cal.)

value is 1800 cal./mole, obtained chiefly from the heat and free energy of hydrogenation, but giving some weight to the less accurate third law entropy. The resulting data regarding potential barriers are listed in Table II, while the calculations involving heat and free energy of hydrogenation data are summarized in Table III and the comparison with third law entropies in Table IV.

Before considering in detail these comparisons with experiment, the calculations for *n*-butane and 1-butene should be further discussed. All the other molecules have internal rotations involving only symmetrical methyl groups; consequently the simple treatment given in the preceding paper⁶ is at once applicable for any height of potential barrier. The torsional oscillations about the double bonds are not included as rotations in the preceding statement; however, their treatment as harmonic oscillators is satisfactory.

Rotation about the middle bond in 1-butene seems to be so slightly restricted that the free rotation calculation of Kassel³ should be quite satisfactory. A small correction can be made for a low barrier if desired.

In *n*-butane, on the other hand, the potential is large compared to RT at ordinary temperatures. Consequently, the rotational partition function should be set up for the rigid molecule in the equilibrium positions. Of these one may be described as a configuration in which the molecule is straightened out and the other two as "bent" configurations which are mirror images of each other. The translation-rotation entropies for these molecules are listed in Table I, wherein an amount $R \ln 2$ has been added to the entropy of (Be) *n*-butane because of the two optically isomeric forms present. Strictly, the internal entropy contributions would be different for the

TABLE IV. Comparison of calculated and third law entropies for olefin hydrocarbons at their respective boiling points.

SUBSTANCE	b.p.	S_{exp}	S_{calc} ($V=0$)	S_{calc} ($V=800$ cal.)
Propylene	225.3	60.4	61.8	61.5
<i>Cis</i> 2-butene	276.8	72.7	72.4	71.9
<i>Trans</i> 2-butene	274.1	70.5	71.7	71.2
Isobutene	266.0	67.8	(70.5)	68.8 ($V=1800$ cal.)

In Tables III and IV, V is the potential barrier restricting rotation about bonds adjacent to the double bond.

(St) and (Be) forms, however, this difference will be neglected since it is probably small but not readily ascertained. We may then write for the reaction:

$$(\text{St}) \text{ } n\text{-butane} = (\text{Be}) \text{ } n\text{-butane}$$

$$R \ln K = -\Delta F^\circ/T = 1.07 - \Delta H_0^\circ/T,$$

where ΔH_0° is probably positive and not more than a few hundred calories. Assuming for the moment that ΔH_0° is known, then the mole fractions N_{St} and N_{Be} can be obtained and the entropy of the mixed gas written:

$$S = N_{\text{St}} S_{\text{St}} + N_{\text{Be}} S_{\text{Be}} - R(N_{\text{St}} \ln N_{\text{St}} + N_{\text{Be}} \ln N_{\text{Be}}).$$

Although the magnitude of ΔH_0° is not known, for temperatures near 300°K, values of ΔH_0° up to 300 cal. have a negligible effect on the entropy while a value of 600 cal. reduces the entropy by less than 0.3 cal./deg. mole from the result for ΔH_0° equal to zero. Since the temperatures of interest are near or above 300°K and it seems unlikely that ΔH_0° is more than 600 cal. one may use the result for a zero value with considerable confidence. Note should be made of one additional element concerning the calculation of the entropy contribution from the torsional oscillation about the central C—C bond. While the symmetry number for a rotator would be one, nevertheless a term ($-R \ln 3$) is introduced because only the energy levels corresponding to oscillation about one of the three minima are desired. For calculation of the quantity ($10^{-36} n^2 / IV$) or the equivalent harmonic oscillator frequency, n should be given the value three. If the existence of the different forms of *n*-butane had been neglected, and averaged values of the moments of inertia used, then the ($-R \ln 3$) term would be omitted as

would the entropy of mixing terms which have as a maximum value, $(+R \ln 3)$. This treatment, however, would be less accurate.

COMPARISON WITH EXPERIMENT

The experimental data with which comparison can be made are entropies obtained from low temperature heat capacities and combinations of heat and free energy data for hydrogenation reactions. The entropies of all of the paraffins here considered except propane are known experimentally, however the more accurate values which are for ethane and tetramethylmethane have been used to fix the heights of potential barriers. The assumptions made in the calculations for propane and isobutane were reasonably safe and very similar; consequently a satisfactory agreement in the case of isobutane will serve as confirmation of the values for both molecules. Parks, Shomate, Kennedy, and Craw-

ford¹³ obtained 67.2 ± 1.1 cal./deg. mole for the entropy of isobutane gas at its boiling point (260.9°K) while the calculated value is 67.7 cal./deg. mole.

Huffman, Parks, and Barmore¹⁴ obtained 72.5 cal./deg. mole for the entropy of *n*-butane at its boiling point. Recently the extrapolation below liquid-air temperatures has been reconsidered by Parks and co-workers,¹³ who give a revised value of 73.7 cal./deg. mole. The calculated result 72.8 cal./deg. mole lies between those obtained from the experimental data. This is a very satisfactory confirmation of the calculated value and indicates that the rather uncertain assumptions were at least approximately correct.

The heats of hydrogenation at 355°K of ethylene, propylene, and the various butenes

¹³ Parks, Shomate, Kennedy and Crawford, J. Chem. Phys. 5, 359 (1937).

¹⁴ Huffman, Parks and Barmore, J. Am. Chem. Soc. 53, 3876 (1931).

TABLE V. Thermodynamic constants for twelve hydrocarbons in the gaseous state.

SUBSTANCES	CONSTANTS OF FORMATION FROM H _{2(g)} AND C(β -graphite)				
	$S^{\circ}_{298.1}$ cal./deg. mole	$\Delta S^{\circ}_{298.1}$ cal./deg. mole	$\Delta H^{\circ}_{298.1}$ kcal./mole	$\Delta F^{\circ}_{298.1}$ kcal./mole	ΔH°_0 kcal./mole
Methane	44.60 \pm 0.0	-19.22	-18.07 \pm 0.12	-12.34	-16.15
Ethane	54.82 \pm 0.2	-41.59	-20.60 \pm 0.23	- 8.20	-16.86
Propane	64.8 \pm 0.5	-64.2	-25.39 \pm 0.32	- 6.25	-20.14
<i>n</i> -Butane	75.1 \pm 1	-86.5	-30.57 \pm 0.43	- 4.78	-23.90
Isobutane	70.8 \pm 0.8	-90.8	-32.20 \pm 0.43	- 5.13	-25.45
Neopentane	73.7 \pm 0.5	-120.5	-40.7 \pm 1.2	-4.8	-32.4
Ethylene	52.75 \pm 0.1	-12.43	+12.09 \pm 0.25	+15.80	+14.06
Propylene	65.1 \pm 0.7	-32.7	+4.48 \pm 0.38	+14.23	+8.12
1-butene	75.4 \pm 1	-55.0	-0.41 \pm 0.5	+15.99	+4.72
<i>Cis</i> 2-butene	73.6 \pm 1	-56.8	-2.14 \pm 0.5	+14.79	+2.92
<i>Trans</i> 2-butene	73.0 \pm 1	-57.4	-3.09 \pm 0.5	+14.02	+1.97
Isobutene	71.3 \pm 1	-59.5	-4.02 \pm 0.5	+13.72	+0.85

The uncertainty in $S^{\circ}_{298.1}$ applies also to $\Delta S^{\circ}_{298.1}$ and the uncertainty in $\Delta H^{\circ}_{298.1}$ to $\Delta F^{\circ}_{298.1}$ and ΔH°_0 .

TABLE VI. Values of $\Delta F^{\circ}/T$ of formation for twelve hydrocarbons in the gaseous state. (Units: cal./deg. mole).

T, °K	METHANE*	ETHANE	PROPANE	<i>n</i> -BUTANE	ISOBUTANE	NEO-PENTANE	ETHYL-ENE	PROPYL-ENE	1-BU-TENE	<i>Cis</i> 2-BUTENE	<i>Trans</i> 2-BUTENE	ISO-BUTENE
300	-40.9	-27.0	-20.3	-15.2	-16.4	-15.1	52.8	47.7	53.7	49.7	47.2	46.1
350	-32.2	-17.0	- 8.1	- 0.5	- 0.9	+ 4.5	47.2	45.8	54.1	51.0	48.8	48.0
400	-25.5	- 9.4	+ 1.4	+10.9	+11.2	19.8	43.0	44.5	54.6	52.1	50.4	49.8
450	-20.2	- 3.2	8.9	20.0	20.7	31.7	39.9	43.6	55.2	53.2	51.7	51.3
500	-16.0	+ 1.8	15.1	27.4	28.4	41.5	37.6	43.1	55.8	54.2	53.0	52.6
600	- 9.4	9.7	24.5	38.7	40.2	56.4	34.0	42.4	56.9	56.0	55.1	54.9
700	- 4.5	15.4	31.5	47.1	49.0	67.5	31.7	42.0	57.9	57.6	56.8	56.7
800	- 0.8	19.7	37.0	53.6	55.9	76.0	30.0	41.9	58.9	59.0	58.3	58.3
900	+ 2.1	23.1	41.2	58.8	61.2	82.6	28.7	41.9	59.7	60.1	59.6	59.6
1000	4.5	25.7	44.6	62.6	65.1	87.5	27.6	41.8	60.1	60.7	60.4	60.5
1200	8.1	29.1	48.7	67.2	69.8	93.4	25.9	41.3	60.0	61.1	61.0	61.3
1500	11.8	31.5	50.9	68.8	71.8	96.2	22.8	39.0	58.1	59.7	59.6	59.9

* The values for methane are taken from Kassel, J. Am. Chem. Soc. 55, 135 (1933).

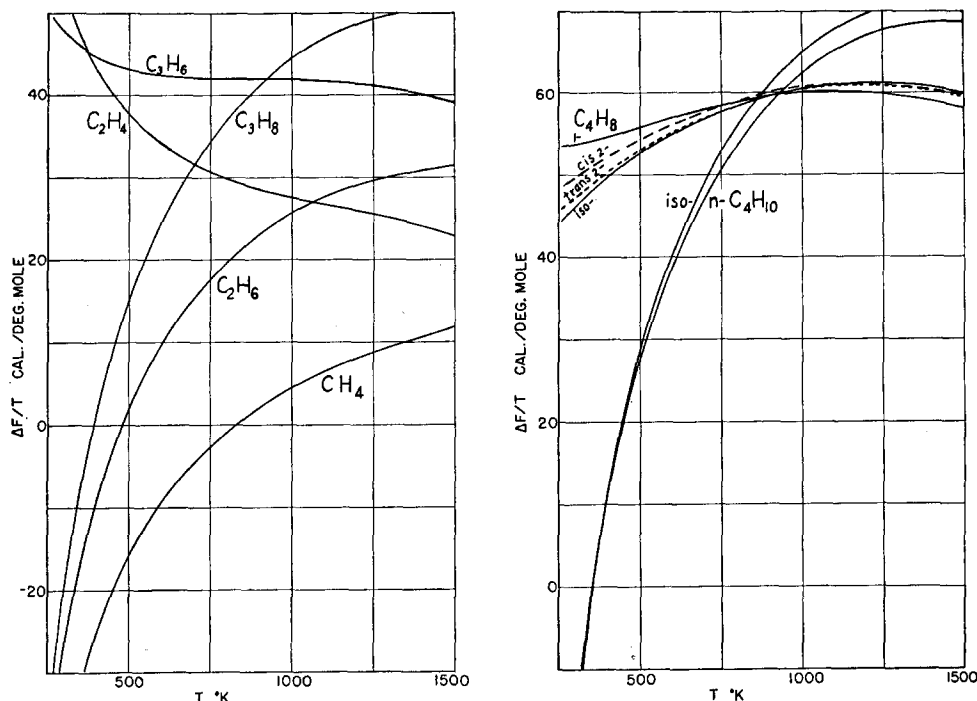


FIG. 1. The free energy of formation of gaseous hydrocarbons.

have been accurately measured by Kistiakowsky and co-workers.¹⁵ The equilibrium constants of the same reactions have been obtained by Frey and Huppke¹⁶ for several temperatures, including 673°K. Table III gives a comparison of the experimental values of $(-R \ln K = \Delta F/T)$ for 673°K with those calculated with the aid of the heat data. In all the olefins except isobutene, the potentials restricting rotation should be about the same, and rather small. Table III shows that the agreement is satisfactory for values up to about 800 cal., since the experimental errors may be taken as at least 0.4 cal./deg. mole. With isobutane a higher potential is expected, and a value of 1800 cal. gives a good agreement.

The experimental entropies of the olefins are all from the work of Parks and co-workers^{14, 17} and have been increased over the originally published values by 10 percent of the extrapolated portion as has been recently recommended.¹³ The comparison with calculated

values in Table IV shows complete agreement within the experimental errors.

THERMODYNAMIC FUNCTIONS FOR TWELVE HYDROCARBONS

While the partition functions set up in the preceding paragraphs are not very precise, the general agreement of thermodynamic quantities calculated from them with experimental values indicates that they must be approximately correct. These partition functions appear to be, in fact, accurate enough for use with the best heat of formation data now available without significantly increasing the uncertainties except at high temperatures. Table V contains the values of several thermodynamic functions at 298.1°K and the values of the heat of formation at the absolute zero for twelve hydrocarbons. In Table VI the free energies of formation are listed for various temperatures in the range from 300 to 1500°K. The data of Table VI are presented graphically in Fig. 1.

In the various calculations the heats of formation of the paraffins are taken from the work of

¹⁵ Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.* **57**, 65 (1935); Kistiakowsky, Ruhoff, Smith, and Vaughan, *ibid.* **57**, 876 (1936).

¹⁶ Frey and Huppke, *Ind. Eng. Chem.* **25**, 54 (1933).

¹⁷ Todd and Parks, *J. Am. Chem. Soc.* **58**, 134 (1936).

Rossini,¹⁸ while the values for the olefins are obtained by combining the heat of hydrogenation¹⁴ with the heat of formation of the resulting paraffin. In the case of ethylene, precise heat of combustion data¹⁹ are available and the value used is a compromise one. The remaining calculations were made using the data and methods described in this and the preceding paper.⁶ All values of the constants of formation are based on H₂ gas and β -graphite. The contribution due to nuclear spin is omitted from all entropies. In obtaining the values listed in Tables V and VI the following constants were used either in the present work or that of Rossini.

For $\text{H}_{2(g)} + 1/2\text{O}_{2(g)} = \text{H}_2\text{O}_{(l)}$,
 $\Delta H^\circ_{298.1} = -63.313 \pm 0.01$ kcal./mole,

$\text{C}_{(\beta\text{-graphite})} + \text{O}_{2(g)} = \text{CO}_{2(g)}$,
 $\Delta H^\circ_{298.1} = -94.24 \pm 0.10$ kcal./mole,

$\text{C}_{(\text{diamond})} = \text{C}_{(\beta\text{-graphite})}$,
 $\Delta H^\circ_{298.1} = -0.22 \pm 0.07$ kcal./mole,

¹⁸ Rossini, Nat. Bur. Stand. J. Research **13**, 21 (1934); **15**, 357 (1935); J. Chem. Phys., **3** 438 (1935).

¹⁹ Rossini, Nat. Bur. Stand. J. Research **17**, 629 (1936).

1 kcal. = 1000 cal. = 4183.3 int. joules;

for H_2 , $S^\circ_{298.1} = 31.23$ cal./deg. mole

and $(H^\circ_{298.1} - H^\circ_0) = 2.028$ kcal./mole;

for $\text{C}_{(\beta\text{-graphite})}$, $S^\circ_{298.1} = 1.36$ cal./deg. mole

and $(H^\circ_{298.1} - H^\circ_0) = 0.25$ kcal./mole.

In Table VI some of the values have been obtained by graphical interpolation. The values for 450, 1000 and 1500°K were directly calculated while those calculated for 298.1 and 763°K (in Tables III and V) were also used in making the interpolations. The slope of the curve at 298.1°K was made to correspond to the known ΔH° at that temperature. It should be noted that the values in Table VI are not sufficiently precise to allow accurate differences to be taken. Thus heat contents and heat capacities must be calculated separately if other than very rough estimates are desired.

The data in Table VI should be useful in obtaining equilibrium constants for a large number of hydrocarbon reactions.

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On the Theory of Optical Rotatory Power

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The Born theory of optical activity in quantum-mechanical form is simplified with the aid of certain approximations. It leads to a simple expression for the rotatory parameter of an active molecule in terms of the geometrical configuration and the polarizability tensors of its constituent groups. Optical anisotropy of the component groups and inhibited internal rotation are found to play an

important role in determining rotatory power. The proposed theory has points of similarity both with the polarizability theories of Gray, de Mallemann, and Boys and also with Kuhn's specialization of Born's classical theory of optical activity. To illustrate its use, the absolute configuration and the specific rotation of *d*-secondary butyl alcohol are calculated.

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A PHYSICAL theory of optical activity was first formulated by Fresnel,¹ who attributed the phenomenon to circular double refraction. In seeking a structural explanation in crystals he postulated a helicoidal arrangement of the atoms, anticipating the screw axis revealed by modern x-ray investigations of crystal structure.

This type of structural explanation was inadequate to account for the optical activity of liquids and solutions, discovered by Biot.² It was necessary to attribute the optical rotatory power of a liquid to a characteristic structure of its component molecules, themselves, rather than to their arrangement. The principles of stereochemistry, enunciated by Le Bel and van't

¹ Fresnel, Bull. Soc. Philomat., p. 147 (1824).

² Biot, Bull. Soc. Philomat., p. 190 (1815).