SOME OBSERVATIONS ON THE THERMODYNAMICS OF HYDROCARBONS AND RELATED COMPOUNDS[1]

JOHN G. ASTON

School of Chemistry and Physics, The Pennsylvania State College, State College, Pennsylvania

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It is shown that it is necessary to take account of potentials hindering free rotation in calculating thermodynamic functions of hydrocarbons and related compounds from the spectroscopic and molecular data. Values obtained from the third law are correct.

By using the third-law results, down to 10°K., the necessary potentials can be obtained and thermodynamic functions calculated from 300°K. to 1200°K. with the aid of the spectroscopic and molecular data. Thus $\Delta F^0/T$ values are obtained for normal butane, normal pentane, and neopentane from 300°K. to 1200°K. based on thermal data down to 10°K. obtained in this laboratory. The results on the first two make it possible to get free-energy values for the higher normal paraffins. Tables of these are given.

A discrepancy between the entropy change in the reaction $n\text{-}C_4H_{10}(g) \rightarrow \text{iso-}C_4H_{10}(g)$, as calculated from new accurate third-law data and from the measured equilibrium constants and heats of combustion, still exists.

I. GENERAL RELATIONS

A. *The free energy and equilibrium constant*

The best way to obtain free energies is by use of the relationships:

$$F = H - TS \tag{1}$$

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

It is customary to tabulate the free energy of formation (ΔF^0) of a compound from its elements in their most common states at the temperature in question. Gases are always taken at 1 atm. in the ideal state. This quantity is related to the equilibrium constant (K) for pressures expressed in atmospheres by the equation

$$\Delta F^0 = -RT \ln K \tag{3}$$

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To calculate ΔF^0 it is necessary to know ΔH^0 and ΔS^0, the heat content and entropy of formation, respectively.

A value of ΔH^0 of formation can be obtained from accurate values of the heat of combustion of the compound and that of the elements which form it (36). Values at other temperatures can be found using the relation

$$\Delta H^0 = \Delta E_0^0 + \int_0^T \Delta C_p^0 \, \mathrm{d}T$$

B. *Entropy values from the third law*

The value of ΔS^0 can be obtained by use of the third law of thermodynamics, which states that the entropy of all "perfect" crystals at the absolute zero is zero. By "perfect" is meant that they are of a regular pattern that is repeated throughout the crystal.

The thermodynamic relation for the change in entropy of a single phase with temperature is

$$S_2 - S_1 = \int_{T_1}^{T_2} C_p \, \mathrm{d} \ln T \tag{4}$$

where C_p is the heat capacity at constant pressure. The entropy increase accompanying a reversible change in phase is

$$\Delta S = \Delta H/T \tag{5}$$

where ΔH is the heat absorbed in the transition.

If complete thermal data are available on the compound starting with the "perfect" crystal at about 10°K., its entropy can be calculated by the use of the relations 4 and 5. The extrapolation required in equation 4 from 0°K. to 10°K. produces a negligible error.

C. *The entropy from statistical mechanics*

When the energy levels for a molecule are known from its band spectrum, the entropy of the gas can be calculated (11, 7, 13, 19) by the relations

$$S_{r+v} = R \ln \sum_i p_i e^{-\epsilon_i/kT} + \frac{1}{kT} \frac{\sum_i p_i \epsilon_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}} \tag{6a}$$

$$S_t = 3/2\, R \ln M + 5/2\, R \ln T - R \ln P - 2.300 \tag{6b}$$

$$S^0 = S_t + S_{r+v} \tag{6c}$$

where ϵ_i is the energy of the i^{th} group of quantum states of the molecule and p_i is the number of states in the group. S_{r+v} is the entropy due to rotation and vibration and S_t is the translational entropy. M is the molecular weight in grams, and P the pressure in atmospheres.

It will be shown presently that, in the present state of knowledge, both thermal and molecular data are required to obtain the thermodynamic functions of hydrocarbon molecules with reasonable accuracy at high temperatures, and that neither alone is adequate.

II. THERMODYNAMIC FUNCTIONS FOR COMPLICATED POLYATOMIC MOLECULES FROM STATISTICAL MECHANICS

A. The entropy with internal rotation

Equation 6 cannot be applied to complicated polyatomic molecules, because their spectra are too complicated to allow the energies of all the states to be ascertained. Fortunately in these cases it is possible to separate the energy states of a molecule into those for rotation and those for vibration. In this case:

$$S^0 = S_r + S_v + S_t$$

The expressions for the rotational (S_r) and the vibrational entropy (S_v) are exactly like equation 6a, except that in one case only rotational states are considered and in the other only vibrational.

The vibrational contribution to the entropy is readily ascertained from tables (15) if the fundamental modes of vibration are known from the infrared and Raman spectra.

It was shown by Eidinoff and Aston (10) that there is a very simple method of obtaining the rotational entropy if the molecular dimensions are known. In complicated molecules, of which methyl alcohol is one of the simplest, there are also internal rotations. The method of Eidinoff and Aston and its extension by Kassel (19) allowed the entropy contributions due to internal as well as external rotations to be calculated simply and accurately if zero potential hindered the internal rotations.

Pitzer (30) has extended this method (in an approximate form only) to the case where potentials hinder internal rotation. Pitzer discusses his own and related methods elsewhere in this issue (32).

B. Free energy and heat content

The differences between the free energy of the gaseous compound at the temperature T and the energy at the absolute zero ($F^0 - E_0^0/T$) can be calculated from the spectroscopic and molecular data even more simply than the entropy. This quantity is given by

$$(F^0 - E_0^0)/T = -R \ln \sum_i p_i e^{-\epsilon_i/kT} + F_t^0/T \qquad (7a)$$

$$-(F_t^0/T) = 3/2\, R \ln M + 5/2\, R \ln T - R \ln P - 7.267 \qquad (7b)$$

where F_t^0 is the free energy of translation.

The corresponding difference for the heat content of the gas is given by

$$H^0 - E_0^0 = \frac{N \sum_i p_i \epsilon_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}} + 5/2\,RT \tag{8}$$

(N is Avogadro's number)

For polyatomic molecules both equations 7a and 8 can be treated in the same way as the expression for the entropy.

Equation 8 for the compound, along with values of $H^0 - E_0^0$ for the elements, can be used to get ΔE_0^0, the energy change at the absolute zero for the reaction of formation of the gaseous compound, when the heat of formation is known.

The free energy of formation is given by

$$\Delta F^0/T = \Delta E_0^0/T + \Delta(F^0 - E_0^0)/T \tag{9}$$

The second quantity in the right-hand member of equation 9 is the difference of the quantity, defined in equations 7, between the compound and the elements which form it.

III. CHECKS ON THE VALIDITY OF THE APPROXIMATE STATISTICAL MECHANICAL METHOD

There are three ways to check the statistical method. One of these is to compare the entropy calculated according to equation 6 for the vapors of organic molecules with that obtained using the third law. A second method is to calculate ΔF^0 by the approximate statistical mechanical method (equations 7 and 9) for a gaseous reaction where the number of rotating groups changes. This value is compared with that calculated from the measured equilibrium constant by equation 3. A third method similar to the first compares calculated and measured gaseous heat capacities.

A. Comparison with third-law entropies

The application of the first method soon showed that agreement could only be obtained between the statistical mechanical method and the calorimetric method by one of two assumptions; that either the crystal was not perfect at low temperatures and the third law did not apply, or large potentials restricted internal rotation.

Table 1 lists the comparisons which have been made for reasonably complicated molecules, using thermal data down to 10°K. In column 2 of this table is listed the difference ($S_f - S_c$) between the entropy calculated on the basis of free internal rotation (S_f) and the calorimetric entropy (S_c). Column 3 lists the potential hindering each rotating group which must be assumed to obtain agreement between the statistical mechanical and calorimetric entropies. The number of such groups is given in brackets. Column 4 gives the reference to the original work.

TABLE 1

Potentials hindering internal rotation in certain compounds as ascertained from low-temperature thermal data

COMPOUND	$S_f - S_c$	POTENTIALS	REFERENCE
	calories per degree per mole	*calories*	
Methyl alcohol	1.75	6,400	Kassel (19)
Tetramethylmethane	8.6	4,500(4)	Aston and Messerly (3); Pitzer (31)
Ethane	1.55	3,150(1)	Kemp and Pitzer (21)
Methylamine	1.64	3,000(1)	Aston, Siller, and Messerly (5)
Propane	3.4	3,300(2)	Kemp and Egan (20)
Ethyl alcohol	3.2	3,000(1) 10,000(1)	Schumann and Aston (37)
Isopropyl alcohol	4.2	3,400(2) 5,000(1)	Schumann and Aston (38)
Acetone	0.6	1,000(2)	Schumann and Aston (38)
Dimethylamine	3.73	3,460(2)	Aston, Eidinoff, and Forster (1)
Dimethylacetylene	−0.3	0	Osborne, Garner, and Yost (27)

TABLE 2

Equilibria in certain reactions which have confirmed potentials hindering internal rotation

EQUILIBRIUM	PER CENT AGREEMENT IN "K" WITH POTENTIALS IN TABLE 1	AUTHORS
$C_2H_6 = C_2H_4 + H_2$	Exact	Smith and Vaughan (39) Teller and Topley (40) Kemp and Pitzer (21) Pease and Byers (29)
$CO + 2H_2 = CH_3OH$	Exact	Kassel (18)
$C_2H_4 + H_2O = C_2H_5OH$	Exact	Schumann and Aston (37)
$(CH_3)_2CHOH = (CH_3)_2CO + H_2$	16 per cent	Schumann and Aston (38)

B. Comparison with equilibrium data

The second method has been applied to a number of gaseous reactions in which the number of rotating groups changes. In order to yield equilibrium constants in agreement with those experimentally determined, the statistical mechanical calculation had to be made on the assumption that potentials hindered the internal rotation of certain groups. The adoption of potentials of the values necessary to get agreement with the third-law entropies yielded satisfactory checks of the "statistical" with the measured equilibrium constants.

This means that the equilibrium constants calculated from equations 2 and 3, using third-law entropies, checked the experimental ones and that the third law was correctly applied to these compounds.

Table 2 lists the several equilibria which have been used for such comparisons. Without exception the third law has been substantiated, and previously estimated potentials hindering internal rotation have been confirmed. The second column of table 2 gives the average percentage difference between the observed equilibrium constants and those calculated from statistical mechanics with potentials hindering internal rotation as given in table 1 (i.e., to fit the third-law data).

TABLE 3

Potentials hindering internal rotations from gaseous heat capacities

SUBSTANCE	V	REFERENCE
	calories	
Ethane	2750	Kistiakowsky, Lacher, and Stitt (23)
Propane	3400	Kistiakowsky, Lacher, and Ransom (22)
Propylene	2120	Crawford, Kistiakowsky, Rice, Wells, and Wilson (8)
Dimethylacetylene	<500	Crawford and Rice (9)

C. Comparison with measured heat capacities

The third way to check the statistical method is to calculate the heat capacity of the gas from spectroscopic and molecular data and compare with the values found experimentally. Kistiakowsky and his collaborators have done remarkably accurate work in this field (23, 24, 8, 9). It is necessary to assume potentials hindering internal rotation, of the same magnitude as found using the third law, to obtain agreement with the experimental heat capacities. The potentials found by this method are shown in table 3.

Finally, the fine structure of perpendicular infrared absorption bands of ethane (16), methyl alcohol (6), and methylamine (42, 41) turns out to be that due to a rigid top in each case, placing the potentials hindering internal rotation greater than 2000 cal.

The accumulated evidence in favor of relatively high potentials restricting internal rotation is so great that the existence of such high potentials must be accepted as a fact. The absence of an adequate theoretical explanation (14) is a challenge, but in no way reduces the importance of the experimental evidence. One by one apparent experimental contradictions in the evidence regarding high restricting potentials have been removed. One which still remains is discussed at the end of this paper.

IV. CALCULATING THERMODYNAMIC QUANTITIES BY COÖRDINATING MOLECULAR AND THERMAL DATA

In order to calculate thermodynamic properties from the molecular data the values of these potentials must be known. At present the only way to obtain them is by comparison with the experimental thermodynamic data. This means that it is not possible to calculate thermodynamic data from the molecular and spectroscopic data alone. On the other hand, while the entropy data and heats of combustion are available to calculate free energies and equilibrium constants at room temperature for a number of simple organic compounds, including several lower hydrocarbons, the necessary heat capacity data on the gases are not available to carry out the calculation for higher temperatures. Yet it is just in the region of higher temperatures where free-energy and equilibrium data are desirable. The same may be said of heat content data. Reliable gaseous heat capacity data are not easy to obtain at high temperatures.

Yet if the third-law data are used in conjunction with the spectroscopic and molecular data, quite reliable free-energy values can be obtained for the gas over the range from 300°K. to 1500°K.

A. Evaluation of potentials empirically from third-law data

If a third-law value is available for the entropy of the gaseous compound at room temperature (or at the normal boiling point) and if the spectroscopic and molecular data are relatively complete, the potentials hindering internal rotation can be obtained so as to make the entropy calculated statistically, agree with the third-law value. These potentials are then used with the molecular and spectroscopic data to obtain the heat capacity, heat content, and free energy of the gaseous compound over the desired temperature range.

Frequently there will be more than one group whose internal rotation is hindered by potential barriers, so that only the total entropy contribution due to the groups whose rotation is hindered can be found. One therefore assumes that the potential hindering the rotation of a group depends on its environment, and assumes all the potentials but one to have values already found in other compounds. Then the remaining one can be solved for. The hindered rotation whose potential is solved for is that which has more novel features of structural environment than any of the other hindered rotations.

For example, in normal pentane there are potentials hindering the rotations of the two end methyl groups. These are taken to be equal to those in propane. Also two ethyl groups rotate about bonds joining them to the central carbon atom. The potentials hindering these rotations are solved for. It is assumed that there are three equal barriers hindering the rotation in each case. This cannot be correct, because two of the barriers are due to hydrogen and one of them is due to an ethyl group. The empirical method partly compensates for this error in subsequent calculations using the potentials and frequencies. Any error in the vibration frequencies is also partly compensated for by the empirical method.

B. Potentials from measured heat capacities

Instead of an entropy value at room temperature, measured heat capacities of the gas may be compared with those calculated from statistical mechanics and the potentials solved for.

C. Convenient thermodynamic functions for tabulation

It is the quantities $F^0 - E_0^0$ and $H^0 - E_0^0$ that are obtained from the thermodynamic and molecular data. It is convenient to regard the energy of the elements in their standard states as zero at the absolute zero, that is, for them E_0^0 is taken as zero. Then for compounds E_0^0 is equal to ΔE_0^0.

This definition makes the quantities

$$F^0 = (F^0 - E_0^0) + \Delta E_0^0 \tag{10}$$

$$H^0 = (H^0 - E_0^0) + \Delta E_0^0 \tag{11}$$

refer to the process:

elements in standard states at 0°K. = compound in standard state at T°K.

The F^0 and H^0 values for the elements at T°K. are then the $F^0 - E_0^0$ and $H^0 - E_0^0$ values, respectively.

The F^0 and H^0 values may be used exactly like ΔF^0 and ΔH^0 of formation values to compute free-energy and heat content changes in a reaction. The only difference is that in this latter system the free energy and heat content of the elements are not zero but the $F^0 - E_0^0$ and $H^0 - E_0^0$ values, respectively.

This is the system used by Rodebush in the *International Critical Tables.* It has the obvious advantage that a table of H^0 *values can be used to get sensible heats directly.* A table of heats of formation cannot be used for this purpose. *"Single thermodynamic"* functions suggests itself as a name for these quantities.

It is hoped that the practice of including these functions in tables of thermo-

dynamic quantities will become frequent. When the method outlined above is followed it is no extra labor to obtain these quantities.

V. APPLICATION OF THE METHOD TO SPECIFIC HYDROCARBONS: TETRAMETHYLMETHANE (NEOPENTANE)

Table 4 is a table of thermodynamic quantities for gaseous tetramethylmethane. As this table will not be published elsewhere it is included as an illustration of the method.

The following frequencies were chosen (3, 20, 5), the number in brackets representing the number of modes for each frequency: 335(2), 414(3), 733(1), 925(3), 3000(12), 1252(4), 1455(8), 950(8). With these frequencies the vibrational entropy of the gas was calculated at the boiling point. The entropy due to rotation of the molecule was then calculated, assuming a rigid symmetrical top with moments 186.2 × 10^{-40} g. cm.^{2} The sum of these two and that due to translation was subtracted from the measured entropy, determined in this laboratory (3), for the gas at the normal boiling point. The difference was taken as due to the four hindered rotations of the methyl groups. The reduced moments of these rotations are 5.3 × 10^{-40} g. cm.^{2} from which, using Pitzer's table (30), it was deduced that three potential minima of 5000 cal. hindered the rotation of each methyl group.

TABLE 4

Thermodynamic functions of tetramethylmethane (ideal gas at 1 atm.)*

$\Delta E_0^0 = E_0^0 = -31{,}070 \pm 330$ cal. per mole

T	$\frac{-(F^0 - E_0^0)}{T}$	$\frac{-F^0}{T}$	$\frac{+\Delta F^0}{T}$	$+H^0$
°*K.*	*cal. per degree per mole*	*cal. per degree per mole*	*cal. per degree per mole*	*cal. per degree per mole*
300	56.38	159.94	−10.31	−25,900
400	62.00	139.67	+23.23	−22,400
500	67.83	129.96	+43.74	−17,800
600	72.17	123.95	+58.91	−12,700
700	77.26	121.64	+69.23	−7,400
800	82.10	120.93	+77.11	−1,400
900	86.65	121.17	+83.38	+5,100
1000	90.99	122.06	+88.44	+11,900
1200	99.19	125.08	+95.87	+26,300
1500	110.49	131.20	+103.46	+48,800

* While the individual values may be in error in the first decimal place, the second decimal place is of significance if derivatives are desired.

The value of the heat of formation of the gas is found to be $\Delta H_{298.16}$ =

−39,448 at 298.16°K. from the heat of combustion data of Knowlton and Rossini (24) and the newest combustion data on hydrogen (35) and graphite (35). From the spectroscopic and molecular data with the empirically determined potentials, $H^0 - E_0^0$ was calculated for tetramethylmethane at 298.16°K. and combined with the corresponding values for hydrogen and graphite. The value of ΔE_0^0 was then computed.

The spectroscopic and molecular data were then used to compute $F^0 - E_0^0/T$ and $H^0 - E_0^0$ at rounded temperatures. These combined with ΔE_0^0 gave F^0/T and H^0.

The sum of the F^0/T values for graphite (7) (five atoms) and hydrogen (six molecules) at 1 atm. (12) was subtracted from the F^0/T value in table 4 (column 3) at each temperature. This gave the $\Delta F^0/T$ values in column 4 for the reaction of formation at 1 atm. The values of $(F^0 - E_0^0)/T$ in this table are probably correct to a few tenths of a calorie per degree per mole, owing to the use of a potential hindering internal rotation chosen to fit the entropy at the normal boiling point. This can be shown to be true for any compound where the vibrational frequency assignment is even roughly correct and is one of the advantages of the method (4).

A. The free energy of the normal paraffins

For several years the efforts of this laboratory have been directed towards the evaluation of similar tables for all lower hydrocarbons. The necessary data are now available for the computation of such tables for the normal hydrocarbons. Thermal measurements down to 10°K. have recently been completed in this laboratory which yield the entropies at the normal boiling points of *n*-butane (4) and *n*-pentane (25) in the gaseous state. From these results and the data on the heats of combustion (33), tables such as table 4 have been computed.

The complete tables will be published elsewhere, but table 6 contains the values of $\Delta F^0/T$ of formation at 1 atm. over the temperature range 300°K. to 1200°K. Similar tables have already been compiled by others for methane (17), ethane (31), and propane (31). These tables were corrected to the basis of the new results for graphite (35) at each temperature. The difference

$$\Delta_n^{n+1} = \Delta F^0/T(\mathrm{C}_{n+1}\mathrm{H}_{2n+4}) - \Delta F^0/T(\mathrm{C}_n\mathrm{H}_{2n+2})$$

was computed between the free energies of the successive normal paraffins. Four values with $n = 1, 2, 3,$ and 4 were thus obtained from the data on the first five members at each of the temperatures. These results are tabulated in table 5 and plotted in figure 1. The alternating effect is noteworthy. The differences evidently approach constant values at about $n = 5$. The extrapolated constant difference for $n = 5$, shown in

TABLE 5

Differences in $\Delta F^0/T$ between successive members of the homologous series of normal paraffin hydrocarbons (ideal gases at 1 atm.)

$\Delta F^0/T$ for $C_{n+1}H_{2n+4}$ minus $\Delta F^0/T$ for C_nH_{2n+2}

T	$\Delta_n^{n+1} = \Delta F^0/T(C_{n+1}H_{2n+4}) - \Delta F^0/T(C_nH_{2n+2})$ IN CALORIES PER DEGREE PER MOLE				
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$ and $n > 5$
°*K*.					
300	14.57	7.28	7.08	6.49	6.45
400	16.65	11.17	11.44	10.93	11.15
500	18.17	13.70	14.02	13.61	13.80
600	19.28	15.54	15.59	15.46	15.45
700	20.09	16.59	17.13	16.60	16.90
800	20.75	17.20	18.37	17.65	18.00
900	21.27	17.96	19.16	18.35	18.70
1000	21.66	18.76	19.58	18.92	19.05
1200	22.27	20.06	20.04	19.89	19.90

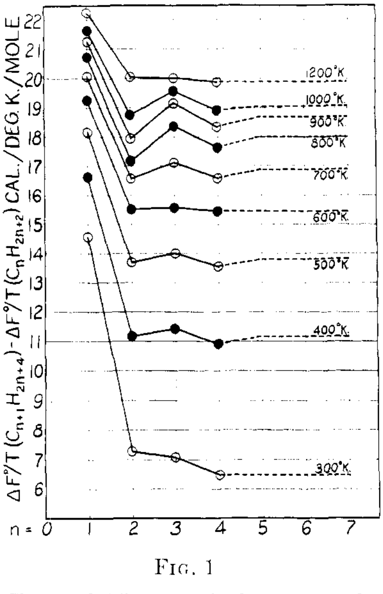

FIG. 1

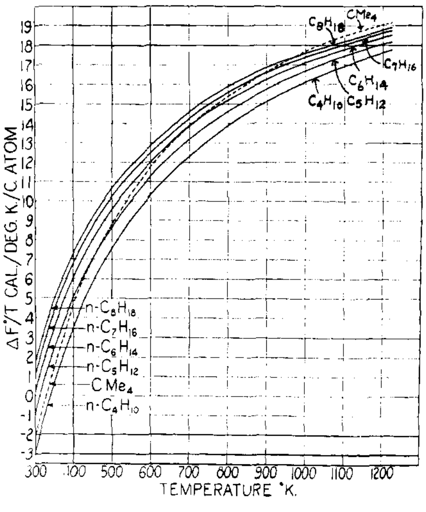

FIG. 2

FIG. 1. Differences in free energy between successive paraffin hydrocarbons (ordinate) *versus* number of carbon atoms (in lower of pair). Shaded circles, odd hundreds of degrees; open circles, even hundreds of degrees.

FIG. 2. Function $\Delta F^0/T$ (per carbon atom) for normal paraffins and tetramethylmethane

figure 1 and in table 5 (column 6), was used to calculate the $\Delta F^0/T$ values at each temperature for gaseous *n*-hexane, *n*-heptane, and *n*-octane from those for *n*-pentane. These values are also given in table 6.

TABLE 6

$\Delta F^0/T$ for normal paraffins (ideal gases at 1 atm.)

T	$\Delta F^0/T$ IN CALORIES PER DEGREE PER MOLE				
	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
°K.					
300	−11.43	−4.94	1.51	7.96	14.41
400	+14.07	+25.00	36.15	47.30	58.45
500	+30.17	+43.78	57.58	71.38	85.18
600	+41.20	+56.66	72.11	87.56	103.01
700	+49.38	+65.98	82.88	99.78	116.68
800	+55.57	+73.22	91.22	109.22	127.22
900	+60.54	+78.89	97.59	116.29	134.99
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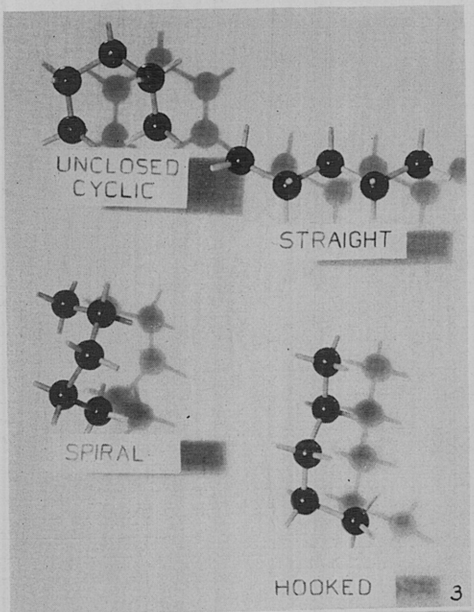
1200	+70.48	+90.37	110.27	130.17	150.07



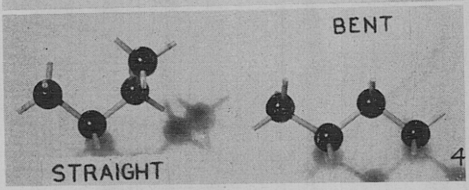


FIG. 3. The four forms of normal pentane (carbon atoms only)
FIG. 4. The two forms of normal butane (carbon atoms only)

In figure 2 the $\Delta F^0/T$ values *per carbon atom* for the gaseous normal paraffins from butane to octane are plotted against T.

It is necessary to resort to this procedure in order to obtain the $\Delta F^0/T$ values for the higher normal paraffins, not only because the vibration spectra are incomplete but because the computation becomes extremely complicated. For example, in calculating the thermodynamic functions of *n*-pentane the four forms shown in figure 3 had to be considered, whereas in the case of *n*-butane there were only the two forms shown in figure 4. The approximate ratio of each had to be computed and thermodynamic values for each had to be calculated separately. The number of such forms increases enormously as the homologous series is ascended. The $\Delta F^0/T$ values should not be in error by more than 1.5 cal. per degree per mole for octane and correspondingly less for the other hydrocarbons.

B. The effect of branching on free energy

A similar procedure to the above can be carried out for the branched-chain paraffins, when the data become available. To illustrate the effect of branching, a graph of the free energy per carbon atom for gaseous tetramethylmethane is included in figure 2. Tetramethylmethane has an increasingly higher free energy than normal pentane at higher temperatures. In other words, except below 450°K. the normal hydrocarbons are somewhat more stable than the corresponding branched-chain ones, and this extra stability increases with rise of temperature. Below 450°K. the branched-chain hydrocarbon is the more stable.

VI. THE BUTANE–ISOBUTANE EQUILIBRIUM

In this laboratory complete thermal data on *n*-butane (4) and isobutane (2) have been obtained which allow us to eliminate the extrapolation of Parks, Shomate, Kennedy, and Crawford (28). In addition, we have obtained accurate values for the heat of vaporization of both at the normal boiling point (2, 4). Thus it is possible to obtain accurate values for the entropies of the gases at 298.16°K. From these values was calculated the entropy difference

$$\Delta S = -3.66 \pm 0.2 \text{ cal. per degree per mole at } 298.16°\text{K.}$$

for the reaction

$$n\text{-}C_4H_{10}\ (\text{gas}) \longrightarrow i\text{-}C_4H_{10}\ (\text{gas})$$

This is to be compared with the value obtained from the equilibrium measurements of Montgomery, McAteer, and Franke (26) and the heat of isomerization found by Rossini (34). This value is -2.08 ± 0.55 cal. per degree per mole. The discrepancy of 1.58 cal. per degree per mole is outside the probable errors. It is perhaps not outside the accidental errors. If this difference were real it would necessarily indicate a failure of the third law for one or both of these compounds. Further work on the equilibrium or heat of isomerization may reduce this decrepancy, which is more than five times the maximum error in the thermal data, assuming the third law to be valid.

A similar comparison can be made for the isomeric pentanes as soon as the equilibrium data are available. Thermal data on 2-methylbutane down to 10°K. are in progress and are complete on the other two isomers (3, 25).

If the third law were not valid the method of calculating the potentials from the third-law data would fail, of course.

VII. CONCLUSION

The purpose of the foregoing review is to show that, by combining the molecular data with experimental thermal data and heats of combustion, satisfactory thermodynamic data on gaseous organic compounds may be obtained over a wide temperature range.

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