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An Empirical Correlation and Method of Calculation of Barriers Hindering Internal Rotation

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The barriers hindering internal rotation of methyl groups can be calculated by assuming that they are solely due to repulsion between hydrogen atoms according to the law $V_{ij}=4.99 \times 10^5/r_{ij}^5$. For dimethyl ether, dimethyl sulfide, and propylene the empirically calculated values are low. This discrepancy is discussed. This treatment is applied to ethyl and isopropyl alcohol and several normal paraffins. The resulting entropies, heat capacities, and equilibrium constants are compared with the available experimental data.

I. INTRODUCTION

IN 1932 Eyring¹ calculated that a potential function of 360 calories hindered the mutual internal rotation of the methyl groups in ethane. Assuming this barrier Teller and Topley² made a calculation of the equilibrium constant for the hydrogenation of ethylene from the heat of hydrogenation and the spectroscopic and molecular data. They found a discrepancy which they pointed out would disappear if the barrier hindering internal rotation were actually 3000 calories instead of the 360 calculated by Eyring. A similar discrepancy per methyl group in tetramethyl methane³ between the entropy calculated from spectroscopic and molecular data and that obtained using the third law of thermodynamics was wrongly interpreted as due to irregularities in the solid at low temperatures. Kemp, Pitzer, and Witt⁴⁻⁶ measured the third law entropy of ethane, compared it with that calculated from spectroscopic data, and obtained a discrepancy of 1.6 e.u. They pointed out that a potential hindering the internal rotation of the methyl groups of 3150 calories in ethane and 4200 calories in tetramethylmethane⁷ would explain all the existing facts. Since that time, the evidence for these large barriers has accumulated

rapidly,⁸ but an adequate explanation is still wanting. The most thorough investigation of possible causes of these barriers is that of Gorin, Walter, and Eyring.⁹

A summary of the measured values to date for the potential hindering the internal rotation of methyl groups in certain compounds is given in column three of Table I.

That the potential is due to repulsions is now generally agreed, the evidence being the decreasing barriers in going from tetramethyl methane^{3,7} to tetramethyl silicon¹⁰ and from dimethyl ether¹¹ to dimethyl sulfide¹² and the non-planarity of the cyclopentane ring.¹³ In the present paper an empirical method is presented for calculating these potentials on the assumption that the barriers are due to repulsions involving hydrogen atoms only. This method is then applied to ethyl and isopropyl alcohol and normal paraffins.

II. GENERAL METHOD

With a force law for the repulsion between hydrogen atoms, the sum of all the terms due to the simultaneous interactions gives the potential for any arbitrary angular position of the rotating group. The difference between the maximum and

¹ H. Eyring, *J. Am. Chem. Soc.* **54**, 3191 (1932).

² E. Teller and B. Topley, *J. Chem. Soc.*, p. 876 (1935).

³ J. G. Aston and G. H. Messerly, *J. Am. Chem. Soc.* **58**, 2354 (1936).

⁴ J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.* **4**, 749 (1936).

⁵ R. K. Witt and J. D. Kemp, *J. Am. Chem. Soc.* **59**, 273 (1937).

⁶ J. D. Kemp and K. S. Pitzer, *J. Am. Chem. Soc.* **59**, 276 (1937).

⁷ K. S. Pitzer, *J. Chem. Phys.* **5**, 473 (1937).

⁸ Cf. G. Glockler, *Rev. Mod. Phys.* **15**, 111 (1943).

⁹ E. Gorin, J. Walter, and H. Eyring, *J. Am. Chem. Soc.* **61**, 1876 (1939).

¹⁰ J. G. Aston, R. M. Kennedy, and G. H. Messerly, *J. Am. Chem. Soc.* **63**, 2343 (1941).

¹¹ R. M. Kennedy, M. L. Sagenkahn, and J. G. Aston, *J. Am. Chem. Soc.* **63**, 2267 (1941).

¹² D. W. Osborne, R. N. Doescher, and D. M. Yost, *J. Chem. Phys.* **8**, 506 (1940); *J. Am. Chem. Soc.* **64**, 169 (1942).

¹³ J. G. Aston, S. C. Schumann, H. L. Fink, and P. M. Doty, *J. Am. Chem. Soc.* **63**, 2029 (1941); J. G. Aston, H. L. Fink, and S. C. Schumann, *J. Am. Chem. Soc.* **65**, 341 (1943).

TABLE I. Comparison of experimental and calculated potentials hindering rotation of methyl groups.

Compound	Molecular data	V (experi- mental)	V (calcu- lated)
Ethane		3150 ^a 2750 ^b	3150
Propane	<CCC = 114°12' ^c	3300 ^d 3400 ^e	3170
Tetramethylmethane		4500 ^{f,g}	4230
Tetramethylsilicon	C-Si = 1.93Å ^h	1300 ⁱ	1360
Dimethyl ether	<COC = 111° ^j C-O = 1.42Å ^j	3100 ^k 2500 ^l	1600
Dimethyl sulfide	<CSC = 102° ^{b,m} C-S = 1.82Å ^b	2000 ^m	1260
Propylene	C=C = 1.36Å	2120 ⁿ	930
Methyl amine	<HNH ≈ <CNH = 108°06' ^b N-H = 1.016Å C-N = 1.47Å	3000 ^o 1520 ^p	2925
Methyl alcohol	<COH = 105° ^q C-O = 1.42Å ^q O-H = 0.96Å ^q	3400 ^q	2250
Methyl mercaptan	C-S = 1.83Å S-H = 1.35Å <CSH = 100°	1460 ^r	860
Acetone		1000 ^s	1390

^a See references 4 and 6 of text.^b G. B. Kistiakowsky, J. R. Lacher, and F. Stitt, *J. Chem. Phys.*, **7**, 289 (1939).^c S. H. Bauer, *J. Chem. Phys.*, **4**, 406 (1936).^d J. D. Kemp and C. J. Egan, *J. Am. Chem. Soc.*, **60**, 1521 (1938).^e G. B. Kistiakowsky, J. R. Lacher, and W. W. Ransom, *J. Chem. Phys.*, **6**, 900 (1938).^f See references 3 and 7 of text.^g J. G. Aston, *Chem. Rev.*, **27**, 59 (1940).^h L. O. Brockway and H. O. Jenkins, *J. Am. Chem. Soc.*, **58**, 2036 (1936).ⁱ See reference 10 of text.^j L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **57**, 2684 (1935).^k See reference 11 of text.^l G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **8**, 618 (1940).^m See reference 12 of text.ⁿ B. L. Crawford, Jr., G. B. Kistiakowsky, W. W. Rice, A. J. Wells, and E. B. Wilson, Jr., *J. Am. Chem. Soc.*, **61**, 2980 (1939).^o J. G. Aston, C. W. Siller, and G. H. Messerly, *J. Am. Chem. Soc.*, **59**, 1743 (1937). A more accurate treatment by Pitzer's method using the frequencies in reference 19 also gives 3000 cal. for the barrier.^p J. G. Aston and P. M. Doty, *J. Chem. Phys.*, **8**, 743 (1940).^q B. L. Crawford, Jr., *J. Chem. Phys.*, **8**, 744 (1940).^r H. Russell, Jr., D. W. Osborne and D. M. Yost, *J. Am. Chem. Soc.*, **64**, 165 (1942).^s S. C. Schumann and J. G. Aston, *J. Chem. Phys.*, **6**, 485 (1938).

minimum of these sums gives a value for the potential barrier hindering the rotation of the group, if it be assumed that the potential function depends exclusively on hydrogen repulsions. It is simplest to take an expression for the potential of the form

$$V = \frac{k}{r_{ij}^n}, \quad (1)$$

where r_{ij} is the distance between a hydrogen atom i of the rotating group and a hydrogen atom j of the rest of the molecule which is being held stationary. The values of k and n are then

obtained from the known potentials for ethane and tetramethyl methane. Insertion of these values in (1) gives

$$V = \frac{4.99 \times 10^5}{r_{ij}^5}, \quad (1a)$$

where the distance r_{ij} is expressed in angstrom units and the potential V is in calories per mole.

This expression allows the potential barriers to be calculated from the bond lengths and angles. The distance r_{ij} for various hydrogen pairs is expressed as a function of these and ϕ , the angular displacement of the rotating group from some reference position. At various assigned values of ϕ the different distances are evaluated and substituted in Eq. (1a). Thus,

$$V(\phi) = 4.99 \times 10^5 \sum_{i,j} [1/r_{ij}(\phi)]^5. \quad (2)$$

The potential V is finally plotted against the displacement ϕ . The difference between a minimum and an adjacent maximum gives the potential barrier. In some cases mere examination of the tabulated values of V will indicate the location of the maxima and minima but in others a graph is necessary. In certain cases, the angles at which the maxima and minima are located are obvious and the calculation need be performed only at these angles. Different types of molecular models, e.g., Hirschfelder (as manufactured by the Fisher Scientific Company), have been found useful in studying the geometry of the different molecules. It should be noted, however, that at times inspection of these models may lead to conclusions that are erroneous and misleading.

In making the calculations for a single rotating group, a somewhat arbitrary but reasonable assumption has to be made about the position of the other groups in the molecule. It is assumed that all other groups remain in such a position that the potential between the parts of the molecule is at a minimum. The potential hindering rotation of any group in the molecule is thus determined by keeping all the others stationary.

Unfortunately in the case of some compounds there is uncertainty in the electron diffraction data which itself produces an uncertainty in the empirical calculation of the barrier far greater than in its experimental evaluation. The electron

diffraction data are less sensitive to changes in angles than this calculation of potential barriers, as will be seen in the case of dimethylether below.

In all cases the usual C—C and C—H distances, 1.54 and 1.09 angstrom units, respectively,¹⁴ are used except where electron diffraction data definitely indicate other preferred values.

The expressions for the nine distances between hydrogen atom number 1 on the rotating methyl group and the nine others on the stationary groups in tetramethylmethane are as follows, where ϕ is zero for the position in which the C—H bonds lie in the planes bisecting the angles between the bonds joining the other methyl groups to the central atom.

$$r_{1,4}^2 = 15.4571 + 2.9853 \cos \phi, \quad (3a)$$

$$r_{1,5}^2 = 9.9289 + 4.0421 \cos \phi - 1.8298 \sin \phi, \quad (3b)$$

$$r_{1,6}^2 = 9.9289 + 4.0421 \cos \phi + 1.8298 \sin \phi, \quad (3c)$$

$$r_{1,7}^2 = 15.4559 - 1.4927 \cos \phi - 2.5844 \sin \phi, \quad (3d)$$

$$r_{1,8}^2 = 9.9306 - 3.6062 \cos \phi - 2.5864 \sin \phi, \quad (3e)$$

$$r_{1,9}^2 = 9.9304 - 0.4359 \cos \phi - 4.4163 \sin \phi, \quad (3f)$$

$$r_{1,10}^2 = 15.4559 - 1.4927 \cos \phi + 2.5844 \sin \phi, \quad (3g)$$

$$r_{1,11}^2 = 9.9304 - 0.4359 \cos \phi + 4.4163 \sin \phi, \quad (3h)$$

$$r_{1,12}^2 = 9.9306 - 3.6062 \cos \phi + 2.5864 \sin \phi. \quad (3i)$$

For each of atoms 2 and 3 on the rotating group there are nine distances respectively equal to a corresponding one of those given above. Thus the potential due to all three hydrogens is three times that due to hydrogen atom number one. Use of Eq. (2) thus gives an expression which approximates very closely to

$$V = V_{\min} + V_0/2(1 - \cos 3\phi). \quad (4)$$

By similar calculations, Eyring¹ deduced the expression

$$d^2 = 7.53 - 2.27 \cos \phi \quad (5a)$$

for the distance d of a hydrogen on one methyl group in ethane from a hydrogen on the other. The corresponding expression used in the calcu-

lations of this paper is

$$d^2 = 7.2484 - 2.1136 \cos \phi. \quad (5b)$$

The smaller constants are due to our use of 1.09A for the C—H distance instead of 1.13A used by Eyring.

III. SIMPLE PARAFFINS

In this section the potential barriers hindering the internal rotation of methyl groups in certain simple hydrocarbons are calculated by the empirical method. The results are compared with the most recent experimental results in Table I.

The distances and angles used are given in the second column of the table. In all cases the C—H distance used was 1.09A and angles not given in column two were taken as tetrahedral.

The agreement for the paraffins, which make up the first four entries in Table I, is exceptionally good. The essential validity of this empirical

TABLE II. Calculation of hindering potentials considering the seat of repulsive force at covalent radius.

Compound	V (experimental)	V (calculated)	
		$n=5$	$n=6$
Ethane	3150	3150	3150
Tetramethyl methane	4500	5920	4760
Tetramethyl silicon	1280	1410	920
k		7.84×10^5	1.16×10^6

method for compounds in which all the valence electrons are shared in single bonds seems established.

Since there is no *a priori* reason for considering the centers of the repulsions to be on the hydrogen nuclei, it is desirable to study the effect of treating the centers elsewhere. For this reason, the calculations for the first three compounds were repeated with the centers of repulsion located at a point on the bond removed from the hydrogen nucleus by a distance equal to the covalent radius of the hydrogen atom, namely, 0.32A (the most probable position of the bonding electrons). The results obtained by these calculations are summarized in Table II. The calculations were performed with the power $n=5$ and $n=6$. In each case the constant k was adjusted to obtain the experimental value for ethane. This constant is listed in the last row of the table. With either integral power, the agreement is not quite as satisfactory as it was in the

¹⁴ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition.

previous calculation (see Table I). It does seem reasonable, however, to conclude that at least semi-quantitatively, conclusions obtained by considering the seat of the repulsions either at the hydrogen atoms or at the most probable position of the bonding electrons are substantially the same.

It has been assumed that there is no interaction due to the carbon atom in tetramethyl methane. A hydrogen atom on the rotating methyl group comes much closer to hydrogen atoms on the other methyl groups than it does to the carbon atoms of the other methyl groups. Thus it does not follow that there is any real difference between hydrogen hydrogen and hydrogen carbon interactions insofar as the force law is concerned.

It seems reasonable to believe that, whatever its meaning, calculation on the basis of Eq. (2), in most cases, should give a minimum value of the potential barrier hindering internal rotation of a group. As just mentioned no allowance is made for a repulsive effect of other atoms similar to that of hydrogen or due to permanent dipoles; nor is any allowance made for "steric" effects in the usual sense of the term. Occasionally these effects may reduce the barriers by tending to equalize the potential field but more usually they will increase them.

IV. DIMETHYL ETHER AND DIMETHYL SULFIDE

A calculation was also made of the barriers hindering the internal rotation of the methyl groups in dimethyl ether and dimethyl sulfide. The results are also compared with the most recent experimental values in Table I. The agreement is not as satisfactory as desired. Examination of the electron diffraction data for dimethyl ether¹⁵ reveals that the assigned C—O—C angle 111° has an uncertainty of $\pm 4^\circ$. The calculation was therefore repeated taking the C—O—C angle as 107°. With this smaller valence angle a barrier of 2370 calories was calculated. While these calculations can hardly be taken as a basis for suggesting that the valence angle in methyl ether is near the lower limit of the electron diffraction results, i.e., 107°, in view of the sensitivity of the calculated barrier to the valence angle and the

¹⁵ See reference j, Table I.

presence of electrons not shared in single bond, it is believed that the agreement between the experimental and calculated values is satisfactory.

Of course, adoption of a smaller valence angle for the molecules would reduce the product of the principal moments and thus necessitate a lower barrier for each methyl group to obtain agreement with the experimental data. Thus, reduction of the valence angle tends to improve the agreement by moving both the value calculated by this method and that calculated from the third law, spectroscopic and molecular data towards an intermediate value.

A similar situation arises in the case of dimethyl sulfide. The electron diffraction measurements of Brockway and Jenkins¹⁶ indicate that "the sulfur bond angle in this compound is very probably between 100° and 110°." The angle used in our calculations was 102°, the same as that used by Osborne, Doescher, and Yost¹² in their calculations of the experimental barrier. Here again the discrepancy may perhaps be overcome by assuming a smaller valence angle. We have, however, not attempted a calculation on the basis of a smaller angle.

V. PROPYLENE

Propylene is the only olefin for which a calculation has been performed by this method. Whereas the experimental barrier is 2120,¹⁷ the calculated value is 930 calories. Here again the extra pair of electrons may have an effect.

VI. METHYL AMINE, METHYL ALCOHOL, METHYL MERCAPTAN, AND ACETONE

The last four rows of Table I compare experimental barriers for methyl amine, methyl alcohol, methyl mercaptan, and acetone with those calculated by the empirical method.

The first experimental estimate of the methyl amine barrier¹⁸ was made using spectroscopic data which were incomplete and have since been superseded by the complete assignment of Owens and Barker based on their infra-red data.¹⁹ A recalculation of the free rotational plus the

¹⁶ See reference h, Table I.

¹⁷ See reference n, Table I.

¹⁸ See reference o, Table I.

¹⁹ R. G. Owens and E. F. Barker, *J. Chem. Phys.* **8**, 229 (1940).

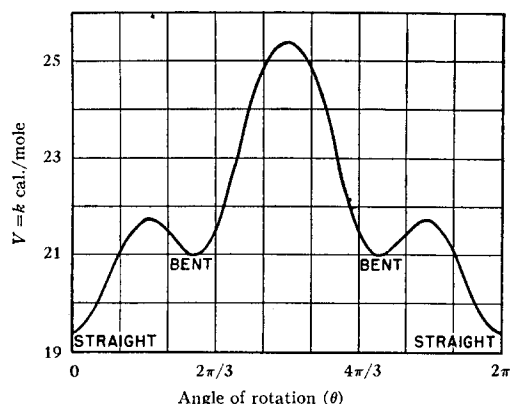


FIG. 1. The potential energy of the hydroxyl group in ethyl alcohol.

vibrational entropy using this assignment yields a value for the ideal gas at the normal boiling point 266.84°K and 1 atmos. 57.73 e.u. compared to the experimental value of 56.42 e.u. Using Pitzer's method²⁰ a difference of 1.31 e.u. corresponds to a hindering potential of 3000 cal. taking the reduced moment of the internal rotation as 1.92×10^{-40} g cm². This is the first value given in Table I. The second value of 1520 cal. is calculated from a band at 270 cm^{-1} in the infra-red spectrum which was only provisionally assigned to the mode of vibration. The empirical calculation of 2925 cal. confirms the calorimetric value and is evidence against the assignment of 270 cm^{-1} to the torsion. If the interaction with non-bonded pairs is a reason for the higher experimental value for dimethyl ether, dimethyl sulfide, and propylene then one would expect a higher experimental value for methyl amine than 2925 cal. However, for methyl amine the H—N—H and H—N—C angles were taken equal to H—N—H in ammonia, namely, as $108^\circ 6'$. If the actual angles are bigger the empirically calculated value would be lower and a contribution assignable to non-bonded electrons might be necessary.

In the case of methyl alcohol the discrepancy may be reduced when the experimental barrier becomes better established,²¹ but the non-bonded electrons may be partly responsible as was suggested in the case of dimethyl ether and sulfide. For methyl mercaptan an analogous discrepancy

²⁰ K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. **10**, 428 (1942).

²¹ See reference q, Table I.

is found. The discrepancy in the case of acetone is not serious in view of the uncertainty in the experimental barrier and also in the C—C—C angle which was taken as tetrahedral in the absence of other information.

VII. ETHYL AND ISOPROPYL ALCOHOLS

The method applied thus far to methyl groups may be extended to other internally rotating groups. The application of this method to the hydroxyl group in ethyl alcohol has been given in a preliminary communication.²² Figure 1 is a graph of the potential energy of the hydroxyl group in ethyl alcohol as a function of the angular displacement calculated by the above method. This graph has three minima and three maxima. The middle maximum ($\theta = \pi$) is higher than the other two equal maxima, and the two equal minima, $\theta = 104^\circ$, 256° adjacent to this highest maximum, are higher than the third minimum at $\theta = 0$.

To obtain an approximate partition function corresponding to Fig. 1, the molecule is treated as three forms corresponding to the three minima, one straight (the lowest, $\theta = 0$ in Fig. 1) and two bent ($\theta = 104^\circ$, 256°), which are optical isomers of each other. The difference in E_0° (heat of formation at the absolute zero) is calculated to be $\Delta E_0^\circ = 1560$ cal./mole, by subtracting the

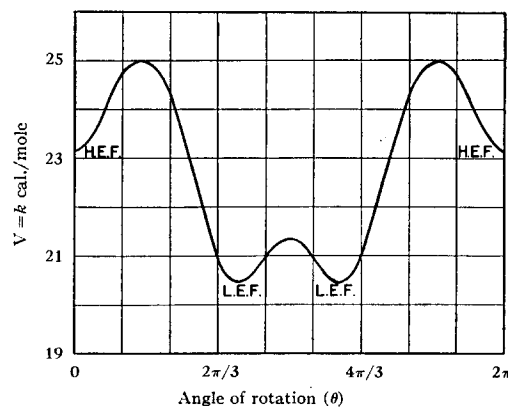


FIG. 2. The potential energy of the hydroxyl group in isopropyl alcohol.

potential energy of the lower minima (bent forms), from that of the higher minima (straight form). The "composition" has to be estimated

²² J. G. Aston, G. J. Szasz, and S. Isserow, J. Chem. Phys. **11**, 532 (1943).

at each temperature from

$$\Delta F^\circ = \Delta E_0^\circ + \Delta(F^\circ - E_0^\circ), \quad (6)$$

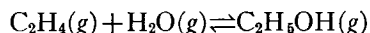
where the value of $F^\circ - E_0^\circ$ for each form is calculated as usual. The rest of the calculation is then like that used by Pitzer⁷ for *n*-butane, which includes the entropy of mixing of the forms. It should be noted Pitzer originally took ΔE_0° as zero which is not the case here. The data used were essentially those employed in the earlier calculations on ethyl alcohol.²³ The same "average" moment was used for both forms together with the previous vibrational assignment; the only change made in the frequency assignment was the use of 985 cm⁻¹²⁴ for the average of the six δ frequencies, instead of 905 cm⁻¹.

The following values have been used in the calculations for restricted rotation:

	V_{CH_3}	V_{OH}
"Straight" form	1800 cal.	2375 cal.
"Bent" form	3000 cal.	4410 cal.
	$I_{CH_3} = 4.83 \times 10^{-40}$ g cm ² ,	
	$I_{OH} = 1.40 \times 10^{-40}$ g cm ² .	

The barriers for the hydroxyl group were estimated from Fig. 1. The difference between the potential energy of a minimum and an adjacent maximum is the barrier hindering the rotation of the hydroxyl group past the angular position corresponding to the maximum. The barriers for the methyl groups were thus calculated by the method given in Section II to be 1070 cal. for the straight and 2500 cal. for the bent form. These values were arbitrarily enlarged by the average difference between the calculated and experimental values for other oxygen containing compounds. The calculation and comparison of the entropies are summarized in Table III.

The equilibrium in the reaction



has been discussed previously.²⁵

The new value used for ΔE_0° of formation of ethyl alcohol from its elements is -52,060 cal./mole. The free energy changes recalculated at

²³ S. C. Schumann and J. G. Aston, J. Chem. Phys. **6**, 480 (1938).

²⁴ B. P. Dailey and W. A. Felsing, J. Am. Chem. Soc. **65**, 44 (1943).

²⁵ J. G. Aston, Ind. Eng. Chem. **34**, 514 (1942).

TABLE III. The entropy of ethyl alcohol from molecular data.

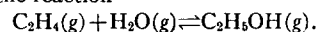
	351.5°K		403.2°K	
	Straight	Bent	Straight	Bent
S_{T+R}	61.03	62.41*	62.20	63.58*
S_{vib}		2.77		3.85
$S_f(CH_3)$		3.67		3.80
$S_f(OH)$		2.44		2.58
$(S - S_f)CH_3$	-0.58	-1.15	-0.48	-0.96
$(S - S_f)OH^{**}$	-0.71	-1.37	-0.59	-1.24
S	68.62	68.77	71.36	71.61
% present	88	12	84	16
Mixing		0.73		0.87
S_T°		69.4		72.3
3rd law entropy†		69.8		72.1

* S_{T+R} includes the entropy of mixing of the optical isomers, but does not include the rotational entropy of the methyl and hydroxyl groups.

** $S_f = R(-0.775 + \frac{1}{2} \ln T + \frac{1}{2} \ln I_{red} \times 10^{40} - \ln n)$. Placing $n = 3$ limits the rotation to one-third of a revolution.

† See reference 23 of text.

TABLE IV. The free energy change and the equilibrium constant in the reaction



$T^\circ K$	Experimental		Calc. (previous)*		Calc. (this research)	
	ΔF°	$\log_{10} K$	ΔF°	$\log_{10} K$	ΔF°	$\log_{10} K$
298.2	-1200	+0.88	-1630	+1.20	-1705	+1.25
351	+315	-0.20	-350	+0.22	-362	+0.22
403	+1800	-0.98	+1570	-0.85	+1457	-0.79
600	+7480	-2.72	+7700	-2.80	+7460	-2.72

* See reference 25 of text.

several temperatures, using this value in conjunction with the data for ethylene and water, are summarized in Table IV. The agreement between the experimental and calculated values is excellent. Although the previous agreement confirmed the presence of hindering potentials, the curves for experimental and calculated $\log K$ crossed. The new values show no such trend.

It is probably significant that the removal of the necessity for ridiculously high barriers for the hydroxyl group has resulted in a better agreement with experiment. Obviously every case with an unsymmetrical barrier should at least be treated in this approximate fashion, e.g., acetic acid,²⁶ compounds with one unsymmetrical rotating group substituted in ethane, etc.

A compound of this type is isopropyl alcohol. Treatment of the rotation of the hydroxyl group in isopropyl alcohol according to the approximate method yields potential energies during rotation as shown in Fig. 2. To obtain a partition function three forms are taken to correspond to the three

²⁶ J. O. Halford, J. Chem. Phys. **10**, 582 (1942).

potential energy minima; a high energy form (H.E.F. $\theta=0$) and two low energy forms (L.E.F. $\theta=140^\circ, 220^\circ$). The latter two are optical isomers. The difference in E_0° between the high and low energy forms is estimated to be 2700 calories per mole. The "composition" has to be calculated at each temperature from (6). The rest of the calculation follows that used for ethyl alcohol. The same "average" moment was used for both forms as in the earlier treatment of Schumann and Aston.²⁷ The only change made in the earlier frequency assignment was the use of 1100 cm^{-1} for the average of the seven δ frequencies.²⁴ The following values of the potentials and reduced moments have been used in the calculation of terms due to restricted rotation:

	V_{CH_3}	V_{OH}
High energy form	3500 cal.	1850 cal.
Low energy form	3500 cal.	900 cal.
	$I_{\text{CH}_3} = 5.07 \times 10^{-40}\text{ g cm}^2$,	
	$I_{\text{OH}} = 1.40 \times 10^{-40}\text{ g cm}^2$.	

The barriers for the methyl group were taken as 3500 calories by analogy with isobutane. The barrier for the hydroxyl group was taken from the curve in Fig. 2 using the same procedure as

TABLE V. The entropy of isopropyl alcohol from spectroscopic and molecular data at 355.5°K .

S_{T+R}^*	65.48
S_{vib}	5.42
$S_f \text{ CH}_3$	7.66
$S_f \text{ OH}$	2.45
$(S - S_f)_{\text{CH}_3}$	-2.66
$(S - S_f)_{\text{OH}}^{**}$	-0.17
S_{mixing}	+0.10
S_{calc}°	78.29 e.u.
$S_{\text{calorimetric}}^\circ$	78.28 e.u.

Composition: L.E.F. = 99.1%, H.E.F. = 0.9%.

Assumed no H.E.F. in calculation.

* S_{T+R} includes the entropy of mixing of the optical isomers.

** $S_f = R(-0.775 + \frac{1}{2} \ln T + \frac{1}{2} \ln I_{\text{red}} \times 10^{40} - \ln n)$. Placing $n=3$ limits the rotation to one third of a revolution.

† See reference s, Table I.

TABLE VI. The heat capacity of isopropyl alcohol vapor.

$T^\circ\text{K}$	$C_p \text{ exp.}^*$	$C_p \text{ calc.}$
427.9	28.4	29.35
457.7	30.5	30.80
480.3	32.4	31.86

* See reference 28 of text.

²⁷ See reference s, Table I.

TABLE VII. The free energy change and the equilibrium constant in the reaction
 $(\text{CH}_3)_2\text{CO}(g) + \text{H}_2(g) \rightleftharpoons (\text{CH}_3)_2\text{CHOH}(g)$.

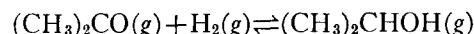
$T^\circ\text{K}$	Calculated composition of isopropyl alcohol		Experimental*		Calculated	
	H.E.F.	L.E.F.	ΔF°	$\log_{10} K$	ΔF°	$\log_{10} K$
355.5	0.9%	99.1%	—	—	-3391	+2.09
450	2.0%	98.0%	-1145	+0.56	-779	+0.38
500	2.8%	97.2%	+411	-0.18	+630	-0.28

* See reference 29 of text.

for ethyl alcohol. The calculation of the entropy and the comparison of it with the experimental value are given in Table V.

The heat capacity of isopropyl alcohol vapor has been measured by Parks and Shomate.²⁸ Their experimental values and the values calculated from the molecular data given above are compared in Table VI. As can be seen, the agreement is not as satisfactory as desired. The fact that the experimental curve has a different slope in this region indicates that the experimental data may be in error.

The equilibrium in the reaction



has been discussed previously.²⁹ The heat of this reaction, namely, $-13,426\text{ cal./mole}$ at 355°K , has been accurately determined by Dolliver, Gresham, Kistiakowsky, Smith, and Vaughan.³⁰ From these data and the relation

$$\frac{\Delta E_0^\circ}{T} = \frac{\Delta H^\circ}{T} - \frac{\Delta(H^\circ - E_0^\circ)}{T}$$

ΔE_0° has been found to be $-11,586\text{ calories per mole}$. The free energy changes calculated at several temperatures from this value in conjunction with the data for acetone and hydrogen³¹ are summarized and compared with those of Parks and Kelley in Table VII. The agreement between the experimental and calculated values is satisfactory.

²⁸ G. S. Parks and C. H. Shomate, J. Chem. Phys. **8**, 429 (1940).

²⁹ G. S. Parks and K. K. Kelley, J. Phys. Chem. **32**, 734 (1928). See also reference s, Table I.

³⁰ M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughan, J. Am. Chem. Soc. **60**, 440 (1938).

³¹ See reference s, Table I.

VIII. NORMAL PARAFFINS

An obvious extension of these calculations leads to the calculation of the change in potential energy as one ethyl group rotates with respect to the other in *n*-butane assuming no other interaction than that of hydrogen atoms. Figure 3 is a graph of the potential energy plotted against the angle of rotation taking the reference point ($\theta=0$) as the so-called "straight" modification. This curve leads to the conclusion that most of the hydrocarbon would be in the straight form. Whitcomb, Nielsen, and Thomas³² have calculated the active normal modes of gaseous *n*-undecane assuming only the straight form and obtained excellent agreement with the spectrum. Cleveland and Murray³³ have measured the Raman spectrum of liquid 1-bromododecane and have concluded that the number of lines indicates the presence of only one form, thus confirming the results obtained by Whitcomb, Nielsen, and Thomas. Moreover, Kohlrausch and Köppl³⁴ have pointed out that the infra-red spectrum of gaseous *n*-butane has much fewer lines than would be expected if forms of symmetry lower than C_{2h} were present in appreciable quantities. On the other hand, Kohlrausch and Köppl have used the Raman spectrum of the liquid to show that the straight and bent forms are present. Mizushima, Morino, and Nakamura³⁵ have confirmed these conclusions by showing that certain lines disappear altogether in the spectrum of the solid while others remain, indicating that the bent form passes over into the straight form in the solid. It may well be that the forces in the liquid allow a stability of the bent form due to molecular interaction. The situation, however, is not clear.

By fitting a curve of the type

$$V = \frac{1}{2} V_0 (1 - \cos 3\theta)$$

to the calculated potential curve near the position of minimum energy, the barrier associated with the lower energy levels of the oscillation in

the straight form of *n*-butane would be about 3000 calories.

Pitzer³⁶ has obtained excellent agreement with experiment using a very logical but semi-empirical treatment for long chain hydrocarbons. This treatment assumes very much less preference for the straight form of the hydrocarbon than indicated by Fig. 3, an assumption justified by the spectrum of the liquid. It is therefore of interest to see if the thermodynamic data can be fitted by the assumption of the straight form alone. To do this the average value of the carbon-carbon bending frequencies must be adjusted to give the correct value of the entropy at one temperature and the rocking frequencies of the methyl groups must be chosen to fit the heat capacity curves in the gas. The barrier hindering internal rotation of the end methyl groups was taken as 3000 calories in keeping with the previous calculations while that of the mutual oscillation of higher alkyl groups was taken as 3000 calories for the reason given above in the case of the ethyl groups in *n*-butane.

Only in the case of *n*-butane were detailed spectroscopic data available.^{34, 37-41} These data were assigned as follows to get the best fit with experiment:

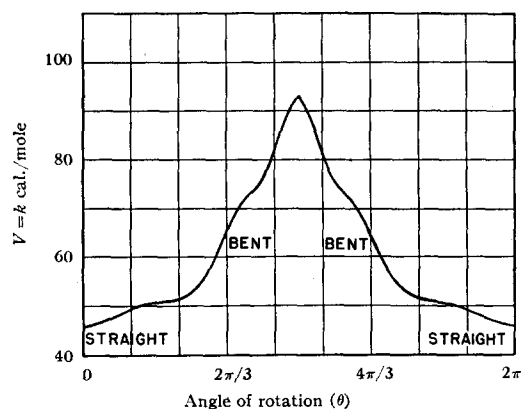


FIG. 3. The potential energy of the ethyl groups in *n*-butane.

³² S. E. Whitcomb, H. H. Nielsen, and L. H. Thomas, *J. Chem. Phys.* **8**, 143 (1940).

³³ F. F. Cleveland and M. J. Murray, *J. Chem. Phys.* **8**, 867 (1940).

³⁴ K. W. F. Kohlrausch and F. Köppl, *Zeits. f. physik. Chemie* **B26**, 209 (1934).

³⁵ S. Mizushima, Y. Morino, and S. Nakamura, *Tokyo Inst. Phys. Chem. Res.* **37**, 208 (1940).

³⁶ K. S. Pitzer, *J. Chem. Phys.* **8**, 711 (1940).

³⁷ Ananthakrishnan, *Proc. Ind. Acad.* **A5**, 285 (1937).

³⁸ S. Bhagavantam, *Ind. J. Phys.* **6**, 595 (1932).

³⁹ W. W. Coblentz, *Investigations of Infra-Red Spectra*, Carnegie Inst. Pub. **35**, 142 (1905).

⁴⁰ P. Lambert and J. Lecomte, *Ann. de physique* **10**, 566 (1938).

⁴¹ J. W. Murray and D. H. Andrews, *J. Chem. Phys.* **1**, 406 (1933).

TABLE VIII. Comparison of experimental and calculated entropies for gaseous normal paraffins.

$T^{\circ}\text{K}$	$S(\text{exp})$	$S(\text{calc})$
<i>n</i> -butane		
210.00	67.05 ^a	66.88
230.00	68.60	68.62
272.66	72.05	72.16
<i>n</i> -pentane		
298.16	83.13 ^b	83.24
<i>n</i> -heptane		
298.16	101.54 ^c	102.00
371.5	111.78 ^d	111.59

^a J. G. Aston and G. H. Messerly, *J. Am. Chem. Soc.* **62**, 1917 (1940). The entropy values at 210.00 and 230.00°K were calculated in the usual manner from the data given in this paper.

^b See reference 42 of text.

^c See reference 36 of text.

^d K. S. Pitzer, *J. Am. Chem. Soc.* **62**, 1224 (1940).

Carbon chain bending: 240 (2).

Carbon chain stretching: 837, 893, 1059.

Hydrogen rocking: 954, 980, 1003, 1041, 1050, 1123 (3), 1146 (2).

Hydrogen bending and stretching: 1282, 1300, 1450 (6), 2861, 2939 (4), 2965, 2978 (2), 3000 (2).

For *n*-pentane the frequency assignment was that of Messerly and Kennedy⁴² except that the bending frequencies at 250 (1) and 326 (2) cm^{-1} were replaced by three at 192 cm^{-1} and the thirteen hydrogen rocking frequencies at 950 cm^{-1} were changed to thirteen at 1070 cm^{-1} . For *n*-heptane the frequency assignment was the following schematic one:

Carbon chain bending: 165 (5).

Carbon chain stretching: 1000 (6).

Hydrogen rocking, bending and stretching: 1070 (19), 1400 (11), 3000 (16).

The assignments chosen are self-consistent except for the carbon-carbon bending frequencies chosen to fit the thermodynamic data. The calculated values of the entropy are compared with experiment in Table VIII while the heat capacity values are compared in Table IX.

The significant fact about the average carbon-carbon bending frequencies is their decrease with the increase in the length of the chain. This decrease is roughly according to the square root of the mass. The values are: *n*-butane, 240 (214); *n*-pentane 192; *n*-heptane 165 (163). The values

⁴² G. H. Messerly and R. M. Kennedy, *J. Am. Chem. Soc.* **62**, 2988 (1940).

TABLE IX. Comparison of experimental and calculated heat capacities for gaseous normal paraffins.

$T^{\circ}\text{K}$	$C_p(\text{exp})$	$C_p(\text{calc})$
<i>n</i> -butane		
400	29.94 ^a	29.95
500	35.67	35.80
600	40.68	40.65
700	44.73	44.87
<i>n</i> -pentane		
331	31.26 ^b	31.58
371	34.4	34.90
427	38.0	38.71
<i>n</i> -heptane		
423	53.9 ^c	53.14
450	57.5 ^d	56.57

^a See reference 24 of text.

^b K. S. Pitzer, *J. Am. Chem. Soc.* **63**, 2413 (1941).

^c See reference d, Table VIII.

^d A. Eucken and B. Sarstedt, *Zeits. f. physik. Chemie* **B50**, 143 (1941). *Chem. Abs.* **37**, 2648 (1943).

given in parentheses are calculated from the *n*-pentane value assuming inverse proportionality to the square root of the mass. Kassel⁴³ finds bending frequencies whose algebraic average values are: *n*-butane 323 (338); *n*-pentane 302; *n*-heptane 285 (256). The values in parentheses have the same relative significance as above.

IX. EFFECT OF OTHER ATOMS BESIDES HYDROGEN

It has been found^{44,45} that 1,1,1-trifluoroethane and 1,1,1-trichloroethane have barriers of 3450 and 2700 cal., respectively, hindering the internal rotation of methyl groups. These barriers must be due to interaction of hydrogen with the fluorine and chlorine atoms, respectively, or with the electrons in the bonds joining these atoms to carbon. There is no *a priori* reason to assume that the interaction is one of repulsion but this can be ascertained experimentally by studies of the mono and 1,1-dihalogen derivatives which will have barriers of about 3000 cal. if the interaction due to the halogen atoms corresponds to repulsion but only of about 1000 cal. if this interaction be one of attraction. Experiments on ethyl chloride and ethylidene dichloride will be carried out in this laboratory as soon as the opportunity arises.

⁴³ L. S. Kassel, *J. Chem. Phys.* **3**, 326 (1935).

⁴⁴ H. Russell, Jr., D. R. V. Golding, and D. M. Yost, *J. Am. Chem. Soc.* **66**, 16 (1944).

⁴⁵ T. R. Rubin, B. H. Levedahl, and D. M. Yost, *J. Am. Chem. Soc.* **66**, 279 (1944).