

## The Determination of Energy Levels from Thermodynamic Data. II. The Heights of Potential Energy Barriers Restricting Intramolecular Rotation

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## The Determination of Energy Levels from Thermodynamic Data. II. The Heights of Potential Energy Barriers Restricting Intramolecular Rotation

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The uncertainty in the distribution of the energy levels implies a corresponding uncertainty in the shape of the associated potential energy function. The estimation of barrier heights is known to depend upon the shape of the potential, therefore implicitly upon the energy level distribution. We apply these ideas to the restricted rotation problem by introducing a shape parameter into the assumed potential function, and show that the currently accepted barrier height ranges should be widened. On the basis of our modified function, we found the following barrier heights to be consistent with published thermodynamic data: ethane 1550 to 2700 calories per mole; 1,1,1-trifluoroethane 2300 to 8300; methanol 800 to 3000.

### 1. INTRODUCTION

THE characteristics of internal rotational degrees of freedom of molecules have to be determined indirectly by appeal to thermodynamic data, owing to the inadequacy of the needed spectroscopic information. Because of the difficulties now made plain in Part I of this paper, it has never been found practical to work directly from the thermodynamic data toward the energy levels, but it is customary to start by assuming a plausible shape of potential function opposing the rotation, based on the known internal geometry of the molecule. This assumption is tantamount to selecting, *a priori*, the general pattern of the energy level distribution for this degree of freedom. Inasmuch as the positions of the levels and the calculated thermodynamic properties depend on the height as well as the shape of the potential barrier, it is necessary to repeat the calculation for several heights, until the calculated property reaches agreement with the measured value.<sup>1</sup>

The calculated thermodynamic properties are not very sensitive to changes in the distribution of energy levels, as was discussed in Part I. Therefore it should be possible to meet the given thermodynamic conditions with any one of a variety of energy level distributions, belonging to a corresponding variety of barrier shapes.

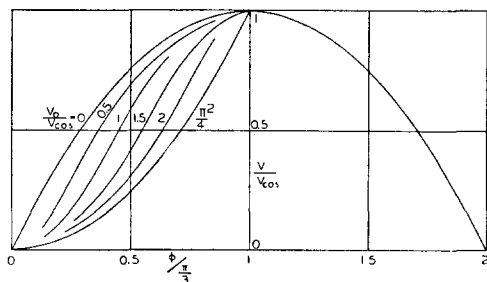


FIG. 1. The two-parabola potential function. This figure shows how the shape of the potential curve can be changed while the barrier height remains fixed.

<sup>1</sup> G. Glockler, *Rev. Mod. Phys.* **15**, 111-173 (1943); E. B. Wilson, Jr., *Chem. Rev.* **27**, 17-38 (1940); K. S. Pitzer, *Chem. Rev.* **27**, 39-57 (1940) and others.

The heights of these barriers will in general depend on their shapes, so the selection of the barrier shape ought to be one of the principal considerations in the study of the restricted rotation problem.

As a matter of fact, on account of the lack of any really complete information about the secondary forces acting within molecules,<sup>2</sup> the selection of barrier shapes has been dictated by mathematical convenience, and the cosine potential

$$V = (V_{\cos}/2)(1 - \cos n\phi) \quad (29)$$

has been almost universally used.<sup>3</sup> On the other hand, there have been numerous warnings that the magnitudes of calculated barriers might come out very differently if other barrier shapes were to be employed.<sup>4</sup> In the succeeding sections of this paper, one such possibility is explored.

### 2. THE TWO-PARABOLA POTENTIAL

It is desirable in this study to have separate parameters for the height and the shape of the potential function. In order to be able to establish a connection with the usually assumed cosine function, we shall start with a parabola whose curvature at its lowest point is the same as that of the cosine. Since this curvature governs the spacing of the lowest levels, the distribution of energy levels will start out in the familiar way, like that belonging to the cosine potential.

For such a potential with three minima, and of double amplitude  $V_{\cos}$ ,

$$V = (V_{\cos}/2)(1 - \cos 3\phi) \quad (30)$$

<sup>2</sup> Compare K. S. Pitzer, *J. Am. Chem. Soc.* **70**, 2140-2145 (1948); Aston, Isserow, Szasz, and Kennedy, *J. Chem. Phys.* **12**, 336-344 (1944); Gorin, Walter, and Eyring, *J. Am. Chem. Soc.* **61**, 1876-1886 (1939), and others.

<sup>3</sup> Tabulations of thermodynamic functions for this form of potential have been provided by the following authors: J. O. Halford, *J. Chem. Phys.* **15**, 364-367 (1947); K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428-440 (1942); K. S. Pitzer, *J. Chem. Phys.* **5**, 469-472 (1937).

<sup>4</sup> A. Charlesby, *Proc. Phys. Soc. London* **54**, 471-487 (1942); G. B. Kistiakowsky, J. R. Lacher, F. Stitt, *J. Chem. Phys.* **7**, 289-296 (1939); E. B. Wilson, Jr., *J. Chem. Phys.* **6**, 740-745 (1938); K. S. Pitzer and J. D. Kemp, *J. Am. Chem. Soc.* **60**, 1515-1516 (1938); K. S. Pitzer, *J. Chem. Phys.* **5**, 469-472 (1937).

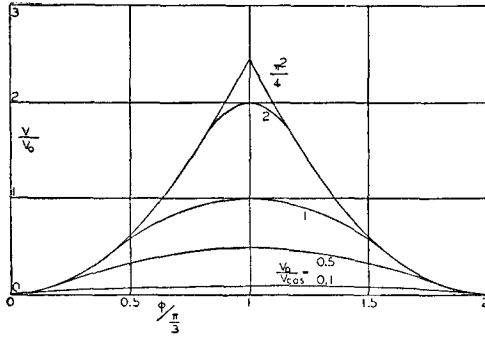


FIG. 2. The two-parabola potential function. This figure shows how the shape of the potential curve can be changed while retaining a fixed curvature at the minima. The nominal barrier height  $V_{\cos}$  is kept constant.

the curvature at each of these minima is

$$\left[ \frac{d^2 V}{d\phi^2} \right]_{\phi=0} = -\frac{9}{2} V_{\cos}. \quad (31)$$

Hence the parabolas for the three lower parts of the potential function must be of the form

$$V_1 = -\frac{9}{4} V_{\cos} \phi^2, \quad (32a)$$

$$\left( -\frac{4}{3\pi} \frac{V_0}{V_{\cos}} \leq \phi \leq \frac{4}{3\pi} \frac{V_0}{V_{\cos}} \right).$$

For the upper three parts we shall take other parabolas, concave downward, of the form

$$V_2 = V_{\cos} \frac{V_0}{V_{\cos}} \left[ 1 - \frac{9}{\pi^2 - 4(V_0/V_{\cos})} \left( \phi - \frac{\pi}{3} \right)^2 \right], \quad (32b)$$

$$\left( \frac{4}{3\pi} \frac{V_0}{V_{\cos}} \leq \phi \leq \frac{2\pi}{3} - \frac{4}{3\pi} \frac{V_0}{V_{\cos}} \right).$$

These parabolas join smoothly at the end points of their respective intervals, and the whole potential is represented by a smooth composite curve of parabolas opening alternately upward and downward.

This potential has the same curvature at its bottoms as the cosine potential of height  $V_{\cos}$ , from which it was derived, and we take this height as the first or height parameter. The second or shape parameter is the ratio  $V_0/V_{\cos}$ , of the actual barrier height  $V_0$ , to the nominal or cosine barrier height  $V_{\cos}$ . The characteristics of these curves are shown in Figs. 1 and 2.

It is not possible, for an arbitrary potential such as (32), to integrate Schroedinger's equation in closed form, therefore we used approximate quantum conditions derived by the phase integral method (WKB

method),<sup>5</sup> namely,

$$\cos \theta_C \cosh(\theta_N + \ln 2) = s^6 \quad (33)$$

$$s = 1 \quad \text{for } S_{6n} \text{ and } A_{6n} \text{ levels.}$$

$$= -\frac{1}{2} \quad \text{for } S_{6n+2} \text{ and } A_{6n+4} \text{ levels.}$$

where

$$\theta_C = \int_C \left[ \frac{8\pi^2 I}{h^2} (E - V) \right]^{1/2} d\phi$$

and

$$\theta_N = \int_N \left[ \frac{8\pi^2 I}{h^2} (V - E) \right]^{1/2} d\phi$$

are the phase integrals, with  $C$  denoting the classical region of motion, and  $N$  the non-classical.  $S$  and  $A$  designate wave functions symmetrical and antisymmetrical respectively, with respect to one of the planes of symmetry. Above the barrier the  $S_{6n}$  and  $A_{6n}$  levels approach each other and finally coalesce to form the  $C_{6n}$  (common) rotational levels. The subscripts on these symbols express the total number of nodes of the wave function per revolution, which is double the rotational quantum number. Figure 3 shows the inter-relations of these quantities. In group-theoretical language, the  $S_{6n}$  levels belong to the representation  $A_1$  of the group  $C_{3v}$ ; the  $A_{6n}$  levels to  $A_2$ ; and the  $S_{6n+2}$  and the  $A_{6n+4}$  to  $E$ .

This diagram, for a hypothetical case, shows how the energy levels are distributed for various potentials. The harmonic oscillator levels are found along the straight line, at places where the phase integral  $\theta_C$  reaches the

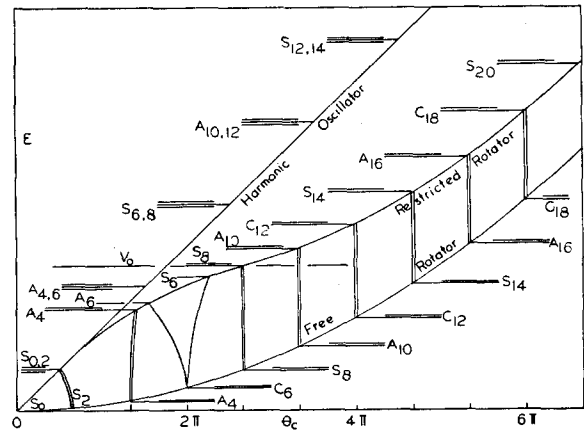


FIG. 3. Relation of the levels of the restricted rotator to those of the limiting oscillator and the limiting free rotator.

<sup>5</sup> W. H. Furry, Phys. Rev. **71**, 361-371 (1947); A. K. Saha, Proc. Nat. Inst. Sci. India **10**, 373-385 (1944); E. Persico, I. Nuovo Cimento **15**, 133-138 (1938); R. E. Langer, Phys. Rev. **51**, 669-676 (1937); E. C. Kemble, Phys. Rev. **48**, 549-561 (1935), and others.

<sup>6</sup> We derived this condition from the two given by H. D. Koenig, Phys. Rev. **44**, 657-665 (1933) in the forms

$$\theta_C = (n + \frac{1}{2})\pi - (-1)^n \cdot 2 \arctan \frac{1}{2} e^{-\theta_N},$$

$$\theta_C = (n + \frac{1}{2})\pi + (-1)^n \cdot 2 \arctan \frac{2e^{\theta_N}}{1 + 4e^{2\theta_N} + (1 + 4e^{2\theta_N} + 16e^{4\theta_N})^{1/2}}.$$

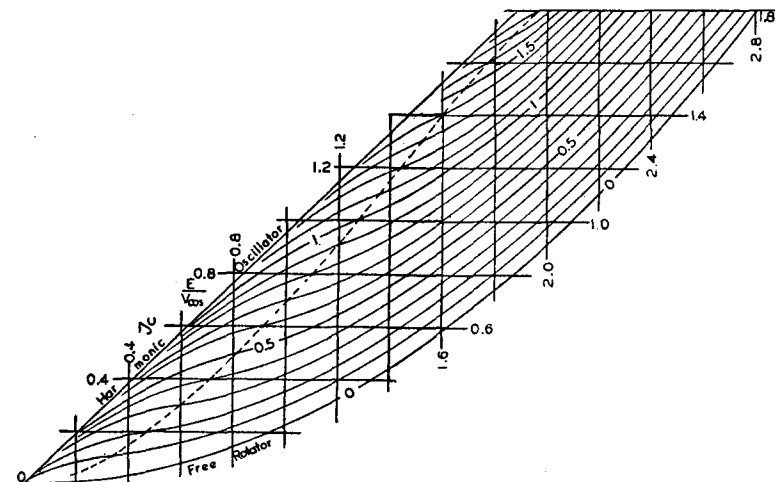


FIG. 4. Energy level diagram.

values  $(2n+1)\pi/2$ . These levels, alternately symmetric (*S*) and antisymmetric (*A*), would ordinarily be single, but the presence of three equal potential minima results in a treble degeneracy. The numerical subscripts express the number of nodes per revolution, in the wave function to which the respective levels belong.

At the other extreme, the levels of the plane rotator, without any restricting potential, are distributed along the parabola wherever the phase integral  $\theta_C$  reaches the values  $2n\pi/3$ . The initial rotational level  $S_0$  (not marked) is single; the rest are doubly degenerate. The members of each pair belong to a symmetric and an antisymmetric wave function, respectively. The symbols *S*, *A*, and *C* (common) designate the fate of these levels in the presence of a parabolic potential, corresponding to a harmonic oscillator. The rotational quantum numbers are half the number of nodes of the wave functions, expressed by the subscripts.

The vertical joining-lines and curves between the free-rotator-line and the restricted-rotator-line connect the positions of the levels under these two potential conditions. The *S* and *A* rotational levels remain doubly degenerate as the potential increases from zero, but the *C*-levels below the barrier  $V_0$  split into two parts. In the transition zone, just below the barrier top, these levels

remain separate single levels in the restricted rotator. In the lowest or vibrational region of the restricted rotator, the splitting *C*-levels join with their doubly degenerate neighbors on both sides, and go over into the treble degenerate levels of the harmonic oscillator.

The energy levels can be found by the following method: If we introduce the parameter  $\alpha$  defined by

$$\alpha = [(8\pi^2 I/h^2) V_{\cos}]^{1/2} \quad (34)$$

then  $\theta_C = \alpha J_C$  and  $\theta_N = \alpha J_N$ , where

$$J_C = \int_C \left( \frac{E-V}{V_{\cos}} \right)^{1/2} d\phi, \quad (35)$$

$$J_N = \int_N \left( \frac{V-E}{V_{\cos}} \right)^{1/2} d\phi.$$

For a given ratio  $V_0/V_{\cos}$ , we can plot  $E/V_{\cos}$  as a function of  $J_C$ , the energy level diagram, and  $J_N$  as a function of  $J_C$ , the phase integral diagram. These plots, for a number of values of  $V_0/V_{\cos}$ , are shown in Figs. 4 and 5 respectively.

Now if  $\theta_N$  is large, Eq. (33) takes the approximate form

$$\cos \theta_C = 0 \quad (36)$$

or

$$J_C = \frac{(n + \frac{1}{2})\pi}{\alpha} \quad (37)$$

where  $n$  is an integer. For any given  $n$  we can find an approximate value of  $J_C$  from (37). Then, from the phase integral diagram, Fig. 5, we can find an approximate value of  $J_N$ . This value of  $J_N$  gives a value of  $\theta_N$  which can be used in Eq. (33) to obtain an improved value of  $\theta_C$  and hence  $J_C$ . This process can be iterated, to find values of  $J_C$  and  $J_N$  which simultaneously satisfy Eq. (33) and the relationship portrayed in Fig. 5. The iteration converges rapidly, especially for the levels which are not very close to the top of the barrier. For

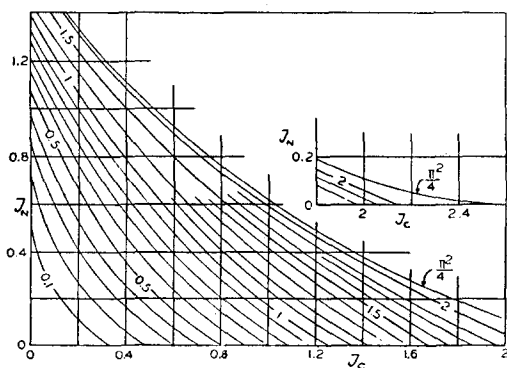


FIG. 5. Phase integral diagram.

TABLE I. Restricted rotational heat capacity in ethane.

$T^{\circ}\text{K}$	92.4	93.1	93.5	94.3	97.4	98.4	99.6	100.5	134.1
$C_v$	6.57	6.51	6.55	6.55	6.59	6.60	6.64	6.64	7.22
$C_v/R$	3.307	3.277	3.297	3.297	3.317	3.322	3.342	3.342	3.634
Less 3	0.307	0.277	0.297	0.297	0.317	0.322	0.342	0.342	0.634
$C_{vib}/R$	0.001	0.001	0.001	0.001	0.002	0.002	0.002	0.002	0.027
$C_{rr}/R$	0.306	0.276	0.296	0.296	0.315	0.320	0.340	0.340	0.607

these levels, the first approximation, given by (37), is sufficiently close for many purposes.

In practice it is convenient to modify Eq. (33) to the form

$$\sin\Delta\theta_C = (-1)^{n+1} s \operatorname{sech}(\theta_N + \ln 2) \quad (38)$$

in which  $\Delta\theta_C = \theta_C - (n + \frac{1}{2})\pi$  is the correction to the original  $\theta_C = (n + \frac{1}{2})\pi$ . This procedure gives the values of  $\theta_C$  for levels below the top of the barrier. Above the barrier the levels occur in pairs, the approximate quantization being like that of the free rotator,

$$J_C = \frac{2\pi n}{\nu\alpha} \quad (39)$$

where  $\nu$ , the symmetry number for restricted rotation, is 3 for the ethane-like systems under discussion here.

Figure 3 shows the results for a typical case. This plot is similar to Fig. 4, and shows a comparison of restricted rotator levels for  $V_0/V_{\cos}$  equal to 0.5, with the corresponding levels of the related harmonic oscillator and of the completely free rotator. The abscissae and ordinates are  $\theta_C$  and  $E$ , respectively.

The statistical calculations of entropy for the various modes of motion, referred to in the following section, are based on the formulas:

$$\frac{S_{\text{trans}}}{R} = \ln \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{kT}{p} e^{5/2}, \quad (40)$$

$$\frac{S_{\text{rot}}}{R} = \ln \frac{[2^9 \pi^7 (kT)^3 ABC e^3]^{\frac{1}{2}}}{\sigma h^3}, \quad (41)$$

$$\frac{S_{\text{vib}}}{R} = \frac{x}{e^x - 1} - \ln(1 - e^{-x}), \quad (42)$$

where  $x = h\nu_0/kT$ .

The entropy for the remaining degree of freedom, that of restricted rotation, has to be obtained directly from the individual energy levels. It lies somewhere between that for pure oscillation, Eq. (42), and that for pure rotation, given by

$$\frac{S_{\text{free rot}}}{R} = \ln \frac{2\pi}{\sigma} \left( \frac{2\pi I_{\text{red}} kT e}{h^2} \right)^{\frac{1}{2}}. \quad (43)$$

### 3. APPLICATIONS

#### Ethane

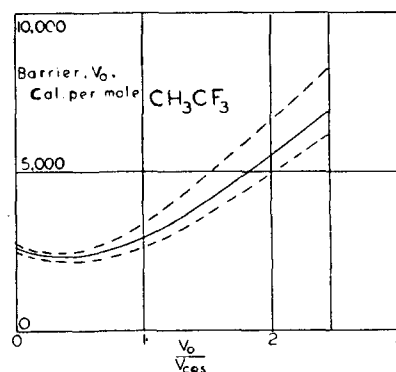
The low temperature heat capacity data on gaseous ethane, published by Kistiakowsky, Lacher, and Stitt,<sup>4</sup>

TABLE II. Ethane barrier heights based on two-parabola potential.

Curve	$V_{\cos}$ nominal barrier $\text{cm}^{-1}$	$V_0/V_{\cos}$	$V_0$ $\text{cm}^{-1}$	$V_0$ cal./mole $\pm 150$
1.	791	0.88	700	2000
2.	936	0.80	745	2150
3.	1250	0.48	595	1700
4.	692	1.24	858	2450
5.	813	1.10	892	2550

and the vibrational frequency assignment of Karweil and Schaefer or of Stitt,<sup>7</sup> was used to obtain the residual heat capacity data in Table I, corresponding to the internal oscillation-rotation. We fitted the experimental heat capacity from the last line of this table, with four curves as follows, assuming a 1 percent spread in the original data, as given by the authors: 1. through the upper limits of the data, 2. through the lower limits of the data, 3. through the lower limit at the lowest temperature and the upper limit at the highest temperature, and 4. through the upper limit at the lowest temperature and the lower limit at the highest temperature.

The ground state was taken as the zero of energy. It was found necessary to use three excited levels to make these curves pass through the given data, but no more than three were determinable because of the absence of heat capacity data for the immediately higher temperatures. The fitting was done by assuming a set of energy levels, computing the corresponding heat capacity over the given temperature range, and plotting these results on the same diagram with the experimental data. The

FIG. 6. Barrier-height ranges for  $\text{MeCF}_3$ .

<sup>7</sup> J. Karweil and K. Schaefer, *Zeits. f. physik. Chemie* **40B**, 357-375 (1938); F. Stitt, *J. Chem. Phys.* **7**, 297-307 (1939).

TABLE III. Entropy and barrier heights for methanol.

	Crawford 1940*	French, Rasmussen 1946**			Rowlinson 1948†	Eucken, Franck 1948††	This paper
$S(\text{MeOH, liquid, 298.16K})$	30.26‡	30.26‡	30.26	30.26			30.26‡
$S(\text{vaporization, 298.16K})$		30.015 <sup>a</sup>	30.447 <sup>b</sup>	30.688 <sup>c</sup>			30.006
$S(\text{MeOH, vapor, 298.16K})$		60.28	60.71	60.95			60.27
$S(\text{sat. vapor to ideal gas, 1 atmos.})$		-3.566	-3.566	-3.566			-3.458
$S(\text{calorimetric, 298.16K, 1 atmos.})$	56.63 <sub>s</sub> <sup>d</sup> ‡‡	56.71	57.14	57.38	56.63‡‡	— <sup>e</sup>	56.81
$S(\text{translational})$							36.324
$S(\text{rotational})$							19.020
$S(\text{translational plus rotational})$	55.331	55.291	55.291	55.291			55.344
$S(\text{vibrational})$	0.257	0.220	0.220	0.220			0.220
$S(\text{restricted rotation})$ —by difference	1.05	1.20	1.63	1.87			1.25
$S(\text{statistical})$	56.64	56.71	57.14	57.38	57.62 <sup>f</sup>	— <sup>e</sup>	56.81
Estimated barrier, calories per mole	3400 <sup>g</sup>	2360	1340¶, ¶¶	—	1300¶, ¶¶	1800	800 to 3000

\* See reference 11d.

\*\* See reference 11c.

† See reference 11b.

†† See reference 11a.

‡ See reference 12.

‡‡ See reference 11h.

§ See reference 11e.

¶ See reference 11f.

<sup>a</sup> Latent heat 8949.4, reference 13.<sup>b</sup> Latent heat 9078, from S. Young (1911).<sup>c</sup> Latent heat 9150, from E. Bartoszewicz, Roczniki Chem. 11, 90-94 (1931).<sup>d</sup> Based on reference 12, 13 and ICT vapor-pressure data, as reported by L. S. Kassel (reference 11h).<sup>e</sup> Eucken and Franck did not base their estimate on entropy values.<sup>f</sup> Rowlinson reported that a barrier of 1300 is consistent with his own supersonic heat capacity measurements, 64 to 176°C, but there still remain 0.99 entropy units unaccounted for, which he ascribes to possible partial disorder in the MeOH crystal at low temperatures, due to H-bonding (max. =  $R \ln 2$ ), as previously suggested by Kassel (reference 11h).<sup>g</sup> The alternative to the high barrier was thought to be the existence of partial disorder in the crystal (max. =  $R \ln 3$ ).

first four of the partition functions below represent the fitted curves. Number five corresponds to the energies proposed by Kistiakowsky, Lacher, and Stitt, namely 275, 520, and 725  $\text{cm}^{-1}$ .

1.  $Q_1 = 1 + e^{-390/T} + e^{-640/T} + e^{-900/T},$
2.  $Q_2 = 1 + e^{-425/T} + e^{-685/T} + e^{-900/T},$
3.  $Q_3 = 1 + e^{-490/T} + e^{-565/T} + e^{-775/T},$
4.  $Q_4 = 1 + e^{-365/T} + e^{-720/T} + e^{-960/T},$
5.  $Q_5 = 1 + e^{-395/T} + e^{-748/T} + e^{-1041/T}.$

In fitting the two-parabola potential function to the energies of these five systems, we made the assumption (validated later) that the first levels were sufficiently far below the barrier top to justify the harmonic oscillator approximation. The nominal barrier height  $V_{\text{cos}}$  and the quantized abscissae  $J_{HO}$  were therefore determined by the relations

$$\frac{E_0}{V_{\text{cos}}} = \frac{3}{\pi} - \frac{(J_{HO})_0}{\pi \alpha} = \frac{3 \pi/2}{(8\pi^2 I/h^2)^{1/2} (V_{\text{cos}})^{1/2}} = \frac{1.5}{(8\pi^2 I/h^2)^{1/2} (V_{\text{cos}})^{1/2}}.$$

With the abscissae  $J_{HO}$ , established from the first energy level, taken with the ordinates  $E/V_{\text{cos}}$  corresponding to the higher levels, we plotted points on the energy level diagram to determine preliminary values of the ratio  $V_0/V_{\text{cos}}$ . In general, each such point fell on a different curve of the family, so a compromise value of

the ratio had to be used. Then, with the established value of  $V_{\text{cos}}$ , and several trial values of  $V_0/V_{\text{cos}}$ , we recomputed the energy levels, including the splitting, for comparison with the initially given set of levels. The results of this study are presented in Table II. Because of the difficulty of making the given empirically found energies exactly fit an energy level curve of the family, particularly in the presence of the splitting, the precision of the barrier heights in the last column may be taken to be about 150 calories per mole.

The wide variety of energy level distributions which can be used to fit the observed heat capacity data illustrates the indeterminacy of this type of calculation, discussed in Part I. This indeterminacy results in a spread of possible barrier heights, ranging from 1700 to 2550 calories per mole, all capable of agreement with the thermodynamic data, under the assumption of the two-parabola potential. In view of the uncertainty of 150 calories per mole, in selecting the ratio  $V_0/V_{\text{cos}}$ , the range may be taken as 1550 to 2700. It is interesting to note that most of the possible fits give barriers lower than those commonly assumed.

### 1,1,1-trifluoroethane

Russell, Golding, and Yost<sup>8</sup> measured the heat capacity of  $\text{MeCF}_3$  from 15 to 225K, and on the basis of

<sup>8</sup> Russell, Golding, and Yost, J. Am. Chem. Soc. 66, 16-20 (1944).

the vibrational frequency assignment of Hatcher and Yost<sup>9</sup> they estimated the cosine barrier hindering internal rotation of this molecule to lie between 3040 and 3950 calories per mole. Their results are based on a calculated entropy for internal rotation, of  $1.47 \pm 0.14$  cal./deg./mole. With their mean entropy value we were able to choose parameters for the two-parabola potential in such a way as to find barrier heights ranging from 2400 to 6800 calories per mole (Fig. 6), the lower value being for the broad-topped barrier, and the higher one for the barrier with the cusp-top (see Figs. 1 and 2). When we used the extreme entropy values, which included the uncertainties of measurement, we found values ranging from 2300 to 8300 calories per mole.

In the series of energy levels on which these results are based, the elevation of the first excited state above the ground state ranged from 200 to 300  $\text{cm}^{-1}$ . The lowest of these values is not much higher than the infrared determination of 180  $\text{cm}^{-1}$  recently reported by J. R. Nielsen,<sup>10</sup> but is in somewhat greater disagreement with the 165  $\text{cm}^{-1}$  estimated by B. P. Dailey,<sup>10</sup> on the basis of microwave spectra.

In spite of the fact that the discrepancy between 200  $\text{cm}^{-1}$  and 180  $\text{cm}^{-1}$  seems small, the shift occurs in a region where its effect on the entropy is large. If Nielsen's figure of 180  $\text{cm}^{-1}$  is accepted, the entropy of internal rotation based on a two-parabola potential calculates to be a minimum of 1.82 cal./deg. mole, and with most such barriers considerably higher. The discrepancy is so large that either the shape of the barrier is very different from the two-parabola type, or there is some difficulty in the calculation of the entropy of internal rotation.

### Methanol

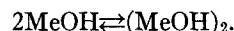
The rotational energy barrier in methanol has been estimated at various values from about 1300 to 3400 calories per mole.<sup>11</sup> At least a part of this spread may be ascribed to the sensitivity of the barrier calculation toward the variations in reported entropy values (Table III) (see Part I of this paper).

In our calculation we used Kelley's calorimetric entropy of the liquid,  $30.26 \pm 0.2$ ,<sup>12</sup> and Fiock, Ginnings, and Holton's latent heat, 1168.4 international joules per gram,<sup>13</sup> or 8946.6 calories per mole. The ideal-gas

entropy change for compression to 1 atmos. from the vapor pressure, 0.1632 atmos.,<sup>13</sup> is  $R \ln P = -3.602$ , but the saturated vapor is not quite ideal. If we attribute the departure from ideality to the presence of a small amount of dimeric methanol, following the suggestion of DeVries and Collins,<sup>14</sup> the entropy correction is found to be

$$\begin{aligned} R \ln P - \theta \Delta S^0 + R \ln [\theta^{\theta} (1 - \theta)^{(1-\theta)} (1 - \theta)^{(-1+\theta)} P^{-\theta}] \\ = -3.602 + 0.299 - 0.155 \\ = -3.458 \end{aligned}$$

where  $\theta$  is the mole-fraction of methanol in the dimeric form, and  $\Delta S^0 = -10.302^*$  is the standard entropy change for the reaction



In our statistical calculations we used the molecular constants of Koehler and Dennison, based on the work of Borden and Barker,<sup>11</sup> and we used the vibrational assignment of Noether.<sup>15</sup>

Our entropy value, 1.25, admits barrier heights of the two-parabola potential function, between about 1400 and 2000 calories per mole, not taking into consideration the uncertainties in the calorimetric data. If the aggregate of these uncertainties is taken to be  $\pm 0.3$ , the range of admissible barrier heights increases to 800 and 3000 calories per mole (Fig. 7).

The shape of the barrier-height curve for methanol differs fundamentally from that for trifluoroethane, pointing to a probable difference in the nature of the forces responsible for the barrier.

### 4. CONCLUSIONS

An important application of the calculation of energy levels from thermodynamic data is the prediction of barrier heights, for example, those restricting internal rotation of molecules. Thermal data, by themselves, are insufficient for this purpose, because of the inherent indeterminacy of the energy level distribution. By choosing various shapes of potential curves, which is the same thing as rearranging the relative positions of the energy levels, one arrives at an excessively wide range of barrier heights, all consistent with published thermodynamic data. That is, the best modern thermodynamic

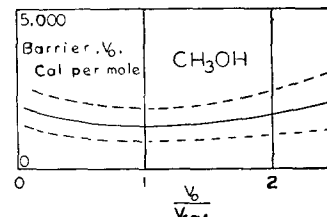


FIG. 7. Barrier-height ranges for methanol.

<sup>9</sup> J. B. Hatcher and D. M. Yost, *J. Chem. Phys.* **5**, 992-993 (1937).

<sup>10</sup> Indirect private communication.

<sup>11</sup> a. A. Eucken and E. U. Franck, *Zeits. f. Elektrochemie* **52**, 195-204 (1948); b. J. S. Rowlinson, *Nature* **162**, 820-821 (1948); c. F. A. French and R. S. Rasmussen, *J. Chem. Phys.* **14**, 389-394 (1946); d. B. L. Crawford, Jr., *J. Chem. Phys.* **8**, 744 only (1940); e. J. S. Koehler and D. M. Dennison, *Phys. Rev.* **57**, 1006-1021 (1940); f. A. Borden and E. F. Barker, *J. Chem. Phys.* **6**, 553-563 (1938); g. J. O. Halford and B. Pecherer, *J. Chem. Phys.* **6**, 571-575 (1938); h. L. S. Kassel, *J. Chem. Phys.* **4**, 493-496 (1936); i. J. O. Halford, *J. Chem. Phys.* **2**, 694-696 (1934).

<sup>12</sup> K. K. Kelley, *J. Am. Chem. Soc.* **51**, 180-187 (1929).

<sup>13</sup> Fiock, Ginnings, and Holton, *Nat. Bur. Stand. Research Paper* 312 (1931).

<sup>14</sup> T. DeVries and B. T. Collins, *J. Am. Chem. Soc.* **63**, 1343-1346 (1941).

\* Calculated from the orthobaric data of Fiock, Ginnings, and Holton.

<sup>15</sup> H. D. Noether, *J. Chem. Phys.* **10**, 693-699 (1942).

technique is inadequate for the determination of barrier heights.

The barrier height range can be narrowed down when thermodynamic properties of the gas can be obtained for low temperature ranges, as with ethane. The uncertainty is greatest when the barrier height has to be estimated from data at a single temperature only, especially if this temperature is relatively high, as with the methanol calculation.

We cannot look for a complete answer to the restricted rotation problem until we have a better understanding

of intramolecular forces, upon which to rest better assumptions about the shape of the potential function. Nevertheless, the gathering of improved barrier information, on a considerable variety of molecule types, will certainly lead to new ideas about the forces, so the barrier problem and the force problem are two aspects of the same unknown. More complete thermal data at very low temperatures would be a great help, because through their use we could decrease the range of uncertainty. The expected improvement would be much greater for some compounds than for others.

## On the Fluctuation of Energy of Gases in the Bose-Fermi Quantum Statistics

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The energy fluctuation of monatomic gases is calculated in the Bose-Fermi quantum statistics computing the mean values by the Bose and Fermi distribution functions and on the base of the entropy equation. The obtained results are compared with Fürth's calculations.

IN the Bose-Fermi quantum statistics fluctuations deviating from classical statistics occur. Fürth<sup>1</sup> dealt with phenomena of fluctuation of monatomic gases obeying the Bose-Fermi quantum statistics. Fürth calculated the energy fluctuation on the base of the fundamental assumptions of the Bose-Fermi statistics without the distribution function. These fundamental assumptions are as follows: According to Bose in the phase space of an atom of the gas system any number of atoms can be present in one cell of the size of  $h^3$  ( $h$  is Planck's constant). In the Fermi quantum statistics, which are based on Pauli's principle, one cell can at the most contain one atom. In the classical statistics where there are no interactions among the particles there should be the probability of the  $i$ th cell containing only one particle:  $p_i$  and the counter probability:  $q_i = 1 - p_i$ . The probability that  $n_i$  atoms are in the  $i$ th cell is

$$w(n_i) = (n_i^N) p_i^{n_i} q_i^{N-n_i},$$

where  $N$  is the number of the atoms of the gas system.

In the Bose quantum statistics

$$w(n_i) = \text{constant } p_i^{n_i} q_i^{N-n_i},$$

where  $A$  can be determined from the equation

$$\sum_{n_i=0}^{\infty} w(n_i) = 1.$$

In the Fermi quantum statistics

$$w(0) \neq 0, \quad w(1) \neq 0, \quad w(2) = w(3) = \dots = w(N) = 0.$$

<sup>1</sup> R. Fürth, *Zeits. f. Physik* 48, 323 (1928).

Fürth investigated on the base of these equations the energy fluctuations of the monatomic gases. It follows from the Bose-Fermi's quantum assumptions that there are interactions among the particles of the system which are not classical interactions.

In the following, the energy fluctuation of the Bose, respectively Fermi gases is calculated in a small partial volume at weak degeneration. The author computes in two ways: by calculation of the mean values employing the Bose, respectively Fermi distribution function and on the base of the entropy equation. In contrast with Fürth's calculations, in the first approximation the energy fluctuation of the molecules are considered as independent of one another in the small partial volume at slight degeneration.

The energy fluctuation of gas in a partial volume consists of two parts. The first part is the consequence of the change of velocity of molecules in the partial volume, the average velocity will be greater or smaller. The second part ensues through the variation of the number of molecules of the partial volume. Sometimes it is greater, sometimes it is smaller than an average value. The two parts of the energy fluctuation are: the *heat fluctuation* and *density fluctuation*, respectively.

### 1. HEAT FLUCTUATION

Let us consider a system of monatomic gases having uniform temperature  $T$ . The walls of the vessel containing the gas should be heat isolators. Let us investigate a small partial volume  $V_1$  of the volume of the vessel  $V = V_1 + V_2$ .