

tion of acetone is quite complex and need not be discussed in detail here.⁹ Some evidence exists for the assumption that an excited acetone molecule may dissociate directly into ethane and carbon monoxide.¹⁰ Since ΔH for the reaction $\text{CH}_3\text{COCH}_3 = \text{C}_2\text{H}_6 + \text{CO}$ is nearly zero, an excited or metastable molecule might dissociate by falling to a repulsive state giving these products. The transfer could be accompanied by the

⁹ For a review see W. Davis, Jr., *Chem. Rev.* **40**, 201 (1947).

¹⁰ R. Spence and W. Wild, *J. Chem. Soc.* 352 (1937); 590 (1941); M. H. Feldman, M. Burton, J. E. Ricci, and T. W. Davis, *J. Chem. Phys.* **13**, 440 (1945).

emission of continuous radiation. This possibility has been suggested.³ The existence of bands in the fluorescence spectrum makes the postulation of immediate dissociation following emission of fluorescent radiation unnecessary and indeed improbable. On the other hand, this evidence cannot be taken to prove that a single step dissociation into ethane and carbon monoxide by some other mechanism does not occur. The best evidence on the latter point can be obtained from a detailed study of the photo-chemical reaction kinetics. Such a study will be published in the near future.

Thermodynamic Properties of the Internal Rotator. Double Minimum with Repulsive Forces

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The basis for calculating the thermodynamic properties of the unsymmetrical internal rotator from energy levels derived from the old quantum theory is described, and a method is outlined for calculations with a potential energy function consisting of linked sections of cosine curve with the width of each section proportional to the barrier height. A table of values of a general quantum number index for the cosine function is presented and its application to the unsymmetrical internal rotator is illustrated. Thermodynamic properties are calculated for a double minimum system of optical isomers for which the forces restricting rotation must be repulsive. It is found that the entropy of such a system may be greater by nearly 0.5 unit than that of the limiting system with equal potential maxima, that is, with the symmetrical cosine potential function.

THE contributions of internal rotation to the thermodynamic properties of a molecule consisting of a rigid framework with one symmetrical top attached have been calculated in detail by Pitzer and Gwinn.¹ Their results are published in the form of extensive tables of free energy, heat content, entropy, and heat capacity for various combinations of the variables $1/Q_f$ and V/RT , with Q_f denoting the partition function for free rotation and V representing the height of the potential energy barrier. The energy states used by these workers to obtain the thermodynamic properties were calculated by means of the wave mechanics and are based

upon a potential energy function of the form $V = V_0(1 - \cos n\theta)/2$ in which n is the symmetry number of the rotation, or the number of potential energy maxima in the cycle.

Pitzer and Gwinn have demonstrated that their tables may be used for a molecule having several internal rotations if the potential energy can be expressed as a simple sum of terms $V = V_0(1 - \cos n\theta)/2$, that is, if there are no significant cross products in the potential energy expression. Further, they have developed an approximation valid for lower temperatures and higher moments of inertia which can be applied when such cross products are significant. They go on to consider changes in the shape of the potential energy curve to forms with broader

¹ K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428 (1942).

valleys and narrower peaks and *vice versa*, and to show graphically what effect such changes will have upon the thermodynamic properties.

The accuracy of the tables is limited by a coupling between the internal rotation and the rotation of the entire molecule by which the energy level is dependent upon the quantum state of an external rotation. Fortunately, the uncertainty from this effect is small relative to that of experimental data throughout the useful range of the variables. As a result, however, the tabulated properties are mean values within ranges determined by the coupling effect, or they may be said to be based upon average positions of the energy levels.

In a recent paper² the writer showed that energy levels derived from the quantization rule of Wilson and Sommerfeld could be used to reproduce the tabulated free energies to a high degree of accuracy. This approach provides an alternative and more readily accessible set of mean positions of the energy states, which do not, in general, coincide with the mean positions used by Pitzer and Gwinn, but nevertheless yield the same free energies within narrow limits. In the region of close approach to free rotation, however, it was found to be necessary to apply an empirical correction to the position of the ground state if the partition function and the quantity $-F/T$ were to be kept from exceeding the values for free rotation. When the results of this approximation were published it was stated that the other thermodynamic properties must be in close agreement with those of Pitzer and Gwinn. This statement has since been checked by the calculation of a number of heat contents and entropies. In the useful range of the variables it is correct to a high degree of accuracy, but where the above described downward revision of the ground state has been found necessary it develops that the heat content and entropy are subject to a somewhat larger uncertainty than the free energy, such that values lower than those of Pitzer and Gwinn by amounts of the order of 0.05 cal./mole/degree may be obtained. This uncertainty occurs, however, in a limited and relatively unimportant region of the variables.

It was stated by the writer that the old

² J. O. Halford, J. Chem. Phys. 15, 645 (1947).

quantum theory offered a less complicated method of calculation for the symmetrical rotator with a potential function different from the simple cosine curve, and that there were some indications that a function with broader valleys and narrower peaks would be more representative. Although various assumptions about the nature of the forces restricting the rotation suggest such a revision, especially for the symmetry number 2, it has not proved possible to demonstrate the point in a convincing manner, and efforts in this direction have been discontinued.

The problem of the thermodynamics of the internal rotator as it now stands may be described as follows. Accurate tables are available for the molecule with one symmetrical internal rotation and these tables may be reproduced through the probable useful range of the variables by an approximate method based upon the quantization rule of Wilson and Sommerfeld. The tables are accurate for molecules with several internal rotations if there are no cross terms in the potential energy, and thermodynamic data for such molecules are usually interpreted upon the basis that such cross terms may be neglected. An approximate method of limited application has been proposed which takes these cross terms into account. It has been shown that the assumption of a simple cosine potential function may introduce errors of the order of 0.1 cal./mole/degree, but no sufficient reason has been advanced for departing from the simple potential function thus far used.

Thermodynamic data for molecules with unsymmetrical internal rotations have been interpreted approximately with the aid of the tables calculated for the symmetrical internal rotator. The unsymmetrical rotator is regarded as an equilibrium mixture of isomers, for each of which the thermodynamic properties can be taken from the tables. The concentrations of the several forms are estimated and the appropriate mixing terms are added to give the properties of the system. For each of the so-called isomers a potential barrier must be assumed, and the width of the potential valley is taken as one n th of the rotational cycle if n isomers have been assumed to be present.

Obviously this treatment of the unsymmetrical

rotator is based upon only a roughly approximate description of the system. The valleys will deviate in width from the assumed form and each one will have two potential barriers, raising the question as to which of the two should be used in connection with the Pitzer-Gwinn tables. In the present study the old quantum theory will be applied to the general unsymmetrical internal rotator for which the potential energy has n valleys of varying depth and breadth with the maxima and minima occurring at any positions on the scale of energies and on the rotational coordinate. The method is then illustrated with a double minimum problem with the minima at the arbitrary zero of energies and two maxima at different heights. In the limit for high potential barriers this becomes a simple system of optical isomers at equilibrium. Since for this kind of problem no demonstrably more valid method has been proposed, there is no way of estimating the accuracy of the calculated results. It seems safe to assume, however, that the method is just as applicable here as with the symmetrical rotator and will get into difficulties of the same type or of analogous types under comparable circumstances. Thus, just as an uncertainty appeared with the symmetrical rotator for systems having widely separated states relative to the barrier height, a similar uncertainty may be expected with the unsymmetrical system if any of the several barriers is too low.

THE GENERAL CASE

The general potential energy curve will have n maxima and n intervening valleys of varying depth. There will be $2n$ potential barriers V_i , each representing the height of a maximum above an adjacent minimum. Any selected energy, on an arbitrary scale, will lie at a distance E_i above the minimum of the i th half-valley. For a given energy there will then be n quantities E_i .

The energy states within a valley can be found by applying the Wilson-Sommerfeld condition,

$$\oint p d\theta = rh, \quad (1)$$

where r is a quantum number, p is the momentum and θ is the rotational coordinate. That the quantization is independent of the selected zero

of energies is evident from the expression

$$p = [2I(E_i - V_i f(\theta))]^{\frac{1}{2}}. \quad (2)$$

If the integration is carried out separately for each half-valley according to Eq. (1), the sum of the two integrals, for a common value of E_i , will give the value of the quantum number at this level. This procedure will establish a relation between the energy and the quantum number, and the states can then be placed at the assumed or permitted values of this number.

In the vibrational region above two valleys, four similar integrals, one for each half-valley, may be evaluated, each one giving a contribution to the quantum number, and, in general,

$$\Sigma \int p d\theta = rh, \quad (3)$$

with the appropriate number of integrals included. In the rotational region $2n$ integrals will be summed, each one taken from a minimum to an adjacent maximum.

If the molecules are regarded as a set of rotational isomers, they may be classified as n vibrational types corresponding to the individual potential valleys, $n-1$ types executing wide vibrations in the region above two or more potential valleys, and finally a rotational type whose behavior at high energies will approach that of the free rotator. The total number of such classification is $2n$, which reduces to 2 for the symmetrical rotator. Naturally, for such a system the coupling with external rotation will be greater than in the case of the symmetrical rotator, and there will be some interaction with other internal degrees of freedom such as low frequency vibrations. These factors will limit the accuracy of calculations in which the unsymmetrical internal rotation is treated as an independent motion.

The above outlined integration may be carried out over half of each vibrational cycle and over the entire rotational cycle to give for each region a relation between the energy and a quantum number index which can be represented by \mathcal{R} . For a given moment of inertia and temperature, fixing Q_f and a set of ratios V_i/RT , there will be within each region a fixed proportionality between \mathcal{R} and a set of integral or quantum numbers r , by which the mean positions of pairs of

energy levels can be found. Within each region individual states can then be located which should be satisfactory averages for the calculation of thermodynamic properties. The mean positions of the pairs are definitely determined by the method, but the location of individual states making up the pairs is necessarily somewhat arbitrary.

With the symmetrical rotator the individual states were located by placing the two components corresponding to a given integral number r in the vibrational region at the points $r \pm \frac{1}{4}$, and in the rotational region at $r \pm V/4E$, the latter separation being an obvious first-order assumption which would connect smoothly with the separation $r \pm \frac{1}{4}$ at the top of the barrier and approach the degenerate pairs characteristic of the free rotator in the high energy limit. For the problem at hand a more general expression is needed which reduces to the above form in the symmetrical case. The levels in the first valley may be set at $r_{12} \pm \frac{1}{4}$, those in the second valley at $r_{34} \pm \frac{1}{4}$ and those in the vibrational region above these two valleys at $r_{1234} \pm [\frac{1}{4} + (V_2/8E_2) + (V_3/8E_3)]$ which at high energies approaches $r_{1-4} \pm \frac{1}{4}$ as it should for a vibrational system. At the lower end of the double minimum region the upper component of the pair at r is close to the lower component of the pair at $r+1$ and the separation approximates that of the valleys which lie below. The separation is thus changed slowly, as the energy increases, from that of the individual valleys toward that characteristic of a single minimum vibration, with uniform spacing on the scale of quantum numbers. In other words, upon coming down from higher energies, the states take on the character of regions lying below, just as occurs with the symmetrical system in the rotational region.

In the region above a triple minimum the corresponding locations are at

$$r_{1-6} \pm \left(\frac{1}{4} + \sum_2^5 V_i/8E_i \right),$$

and, finally, in the rotational regional region at

$$r_{1-2n} \pm \sum_1^{2n} V_i/8E_i.$$

This will be exactly consistent with the device

used for the symmetrical rotator, for which $r_{1-2n} = nr_s$ and the states are at $r_s \pm (2n/n)(V/8E)$ or $r_s \pm V/4E$, but will cause overlapping of the component parts of successive pairs when $n > 2$.

Such overlapping does not seem reasonable but, fortunately, this is a question of secondary importance. As long as the rule is retained that the mean position of successive pairs is at integral values of r , the separation of the components in the higher energy regions has relatively little effect upon the calculated thermodynamic properties. The states may be separated according to the above scheme, with overlapping, or the separations may be decreased to eliminate the overlapping and the thermodynamic properties will not be materially affected. In fact, for most calculations it is satisfactory to leave the states as degenerate pairs at integral values of r in all regions except the individual valleys. Free energy variations due to this latitude of choice are in general less than 0.005 cal./mole/degree.

When fewer than three states lie within any potential valley, it will presumably be necessary, as it was with the symmetrical rotator, to make an empirical downward adjustment of the lowest state. A method of adjustment based upon the one that proved to be satisfactory for the symmetrical rotator will be proposed and illustrated in the later section concerned with the double minimum system of optical isomers.

UNSYMMETRICAL ROTATOR WITH POTENTIAL ENERGY IN THE FORM OF LINKED SECTIONS OF COSINE CURVE

To proceed beyond the above general description requires the adoption of a potential energy function. For the i th half-valley, with the minimum at (E_I, θ_i) , the potential energy is taken to be

$$V = E_I + V_i[1 - \cos a_i(\theta - \theta_i)]/2. \quad (4)$$

Here E_I and V are referred to an arbitrary zero of energies, but V_i is the height of the potential barrier. A series of such equations adapted to the entire cycle will express the potential energy as a succession of linked sections of cosine curve which will be discontinuous in the second derivative at the maxima and minima. The factor a_i measures the width of a half-valley and is not limited to integers as it was in the case of the symmetrical rotator.

TABLE I. Energy of the internal rotator in terms of the quantum number index. (Extension of Table II in reference 2.)

E/V	A (radians)	ρ
0.8214	2.1255	0.2699
0.9330	2.5201	0.3200
0.9891	2.7642	0.3510
1.015	2.9129	0.3699
1.03	2.9826	0.3788
1.06	3.1066	0.3945
1.15	3.4238	0.4348
1.70	4.8118	0.6110
2.4	6.0972	0.7743
4.	8.3012	1.0541

The quantization according to Eq. (3) leads to the equation

$$r = [Q_f / (2\pi)^{\frac{1}{2}} (kT)^{\frac{1}{2}}] \sum (V_i^{\frac{1}{2}} / a_i) \times \int_0^{\pi \text{ or } \phi_0} (2[E_i / V_i - 1] + 1 + \cos \phi_i)^{\frac{1}{2}} d\phi_i, \quad (5)$$

in which Q_f is the partition function for free rotation, E_i is the excess of energy over E_f at the quantum level r , and ϕ_i is defined as $a_i(\theta - \theta_i)$. The integral is the same one that entered into the quantization for the symmetrical rotator, for which E/V was expressed as a function of a quantum number index ρ defined as

$$\rho = r / Q_f' (V/RT)^{\frac{1}{2}} = \text{Integral} / 2^{\frac{1}{2}} \pi^{\frac{1}{2}}. \quad (6)$$

By eliminating the integral between Eqs. 5 and 6 it follows that

$$r / Q_f = \frac{1}{2} \sum (\rho_i / a_i) (V_i / RT)^{\frac{1}{2}}. \quad (7)$$

The index ρ is a quantity determined by quantizing the rotator with a cosine potential function and is expressed as a function of E/V by a single set of graphical integrations. Each term in Eq. (7) is the contribution of a half-valley to the value of r/Q_f at a selected level of energy. For a given energy on the arbitrary scale, the energies E_i and V_i and consequently E_i/V_i are known for each half-valley. From a table or curve of E/V against ρ , the value of ρ_i is taken corresponding to the known ratio E_i/V_i , and is multiplied by $(V_i/RT)^{\frac{1}{2}}/a_i$ to obtain the quantity required according to Eq. (7). The index ρ is based upon an integration over an entire symmetrical potential valley, and the sum over a given number of valleys is divided by 2 to obtain the quantity required for the summation over an equal number of half-valleys.

Any one of the potential barriers can be

introduced into the equation to yield the form

$$r / Q_f = \sum (\rho_i / a_i) (V_i / V_0)^{\frac{1}{2}} (V_0 / RT)^{\frac{1}{2}} / 2$$

or

$$r / Q_f (V_0 / RT)^{\frac{1}{2}} = \sum (\rho_i / a_i) (V_i / V_0)^{\frac{1}{2}} / 2 = \mathcal{R}, \quad (8)$$

by which \mathcal{R} becomes a quantum number index comparable to ρ and expressible as a function of E/V_0 within the region over which the summation has been taken. If the conditions for a symmetrical rotation are introduced into Eq. (8), namely $V_i = V_0$, $Q_f' = Q_f/n$, $n = a_i$, and two terms are included for a single valley, the equation reduces to the first equality of Eq. (6) as it should.

In order to use Eq. (8) conveniently it is necessary to assign the values a_i and to have equations or tables expressing ρ as a function of E/V . The assignment of a_i involves some knowledge of assumption concerning the relation between the height and width of the half-valley. It is reasonable to suppose that the higher sections of the potential energy curve will spread over broader regions of the rotational coordinate than the lower sections. A simple assumption consistent with this supposition is that $a_i V_i = \text{constant}$ or $a_i/a_0 = V_0/V_i$. Whatever assumption is made in this connection, it will always be required that $\sum 1/a_i = 2$, thus completing a set of $2n$ independent equations by which the $2n$ factors a_i are determined.

For the index ρ as a function of E/V , a number of additional integrations, as shown in Table I, have been added to those given in the earlier paper. The entire set of integrations has been used to obtain several overlapping empirical equations, from which the values given in Table II have been calculated.

Table II is designed for use with Eq. (8), but will apply equally well to the special case of Eq. (6), the symmetrical rotator, and may therefore be used to reproduce the properties tabulated by Pitzer and Gwinn. A choice of Q_f and V/RT fixes the proportionality between r and ρ , and permits the selection, from the table, of the values of E/V corresponding to $r \pm \frac{1}{2}$ within the valley, and to $r \pm V/4E$ in the rotational region. The partition function is calculated from $[(E - E_0)/V][V/RT]$ where E_0 is the energy of the lowest state. The table is accurate enough, with linear interpolation, to reproduce the Pitzer-Gwinn free energies within 0.005 cal./mole/degree in the useful range of the variables.

In the general case, to which Eq. (8) applies, an energy ratio E/V_0 is selected and the several contributions summed in the equation are found by multiplying ρ values taken from Table II by the appropriate constants. For example, within the first valley, with the minimum at $\theta=0$, take $V_{2n}=V_0/2$ and assume that a_0 is 2 and therefore $a_{2n}=4$. At $E/V_0=0.5$, $E/V_{2n}=1.0$, for which, respectively, ρ is 0.1521 and 0.3592. Then $2\mathcal{R}=0.1521/2+0.3592/4 \times 2^{\frac{1}{2}}=0.1396$. The similarly obtained quantum number index \mathcal{R} for E/V_0 from zero to 0.5 will outline a curve applicable to the valley between the n th and first maxima. When V_0/RT and $1/Q_f$ are chosen, the values of \mathcal{R} at which the energy levels may be placed are determined and E/V_0 can be found for each level by reference to the curve. If $1/Q_f(V_0/RT)^{\frac{1}{2}}$ is 0.0698, the first and second excited vibrational states will be placed at $0.0698(1 \pm \frac{1}{2})$ or at $\mathcal{R}=0.0524$ and 0.0873 , and the ground state will appear at $0.0698/4=0.0175$. Each energy ratio E/V_0 is decreased by E_0/V_0 and the result is multiplied by V_0/RT to give $\Delta E/RT$. Then,

$$Q = \sum e^{-\Delta E/RT}, \quad -F/T = R \ln Q,$$

$$H/T = (R/Q) \sum (\Delta E/RT) e^{-\Delta E/RT}$$

and

$$S = H/T - F/T.$$

OPTICAL ISOMERS

In this section the method outlined above will be applied to a double minimum system with the minima at the zero of energies and the maxima at different positions, V_1 and V_2 , on the energy scale. In the limit for high potential barriers, the populated states will be oscillations about the positions of the minima and the system will consist of two optically isomeric compounds in equilibrium. Such a system could occur only with repulsive forces between the rotating parts, such as would be found in an *ortho*-substituted diphenyl separable or nearly separable into stable isomeric forms. The results should be accurate for this type of molecule with its high moment of inertia and low $1/Q_f$, which would set the states close together and decrease the uncertainty arising in this method of calculation from the arbitrary location of the individual states comprising the pairs obtained in the quantization. If a principal axis of one of the

rings coincided with the 1-4 carbon-carbon line, a second source of uncertainty would be minimized, namely, that due to interaction with vibrations of low frequency.

Five potential energy curves will be considered, for which, respectively, V_2/V_1 is 1, $\frac{3}{4}$, $\frac{1}{2}$, $\frac{1}{4}$, and zero. Values of the free energy, heat content, and entropy are calculated for each of these situations at a number of positions in the range of the variables $1/Q_f$ and V_1/RT .

I. $V_2=V_1$. This is the limiting case of equal potential barriers for which $V=V_1(1-\cos 2\theta)/2$. The two valleys are exactly alike, with the minima at $\theta=0$ and π and the maxima at $\theta=\pi/2$ and $3\pi/2$. The required properties are obtained from the tables of Pitzer and Gwinn. For the unsymmetrical rotator at $1/Q_f$, V_1/RT , the

TABLE II. Index ρ as a function of E/V .

E/V	00	01	02	03	04	05	06	07	08	09
0	.0000	.0028	.0056	.0085	.0113	.0142	.0170	.0199	.0228	.0257
0.1	.0286	.0315	.0344	.0373	.0402	.0432	.0461	.0491	.0520	.0550
0.2	.0580	.0610	.0639	.0669	.0699	.0730	.0760	.0791	.0821	.0852
0.3	.0882	.0913	.0944	.0975	.1006	.1038	.1069	.1100	.1132	.1164
0.4	.1195	.1227	.1259	.1292	.1324	.1357	.1389	.1422	.1455	.1488
0.5	.1521	.1555	.1588	.1622	.1656	.1690	.1724	.1758	.1793	.1828
0.6	.1863	.1898	.1933	.1969	.2005	.2041	.2077	.2113	.2150	.2187
0.7	.2224	.2262	.2299	.2337	.2375	.2414	.2453	.2492	.2532	.2572
0.8	.2612	.2652	.2694	.2735	.2777	.2820	.2863	.2907	.2951	.2996
0.9	.3042	.3088	.3136	.3186	.3238	.3291	.3345	.3400	.3457	.3517
1.0	.3592	.3666	.3730	.3788	.3842	.3894	.3945	.3993	.4041	.4088
1.1	.4134	.4178	.4222	.4265	.4307	.4348	.4389	.4429	.4469	.4508
1.2	.4546	.4584	.4622	.4669	.4696	.4732	.4768	.4804	.4840	.4875
1.3	.4909	.4944	.4978	.5011	.5045	.5078	.5111	.5144	.5176	.5209
1.4	.5241	.5272	.5304	.5335	.5366	.5397	.5428	.5458	.5488	.5518
1.5	.5548	.5578	.5607	.5636	.5665	.5694	.5723	.5752	.5780	.5808
1.6	.5837	.5864	.5892	.5920	.5948	.5975	.6002	.6030	.6057	.6084
1.7	.6110	.6137	.6164	.6190	.6216	.6242	.6268	.6294	.6320	.6346
1.8	.6371	.6396	.6422	.6447	.6472	.6497	.6522	.6547	.6571	.6596
1.9	.6620	.6645	.6669	.6693	.6718	.6742	.6765	.6789	.6813	.6837
2.0	.6861	.6884	.6907	.6931	.6954	.6977	.7000	.7023	.7046	.7069
2.1	.7092	.7115	.7137	.7160	.7182	.7205	.7227	.7249	.7271	.7294
2.2	.7315	.7337	.7359	.7381	.7403	.7425	.7446	.7468	.7489	.7511
2.3	.7532	.7554	.7575	.7596	.7617	.7638	.7659	.7680	.7701	.7722
2.4	.7743	.7763	.7784	.7805	.7825	.7846	.7866	.7886	.7907	.7927
2.5	.7947	.7967	.7987	.8007	.8027	.8047	.8067	.8087	.8107	.8127
2.6	.8146	.8166	.8186	.8205	.8225	.8244	.8264	.8283	.8302	.8322
2.7	.8341	.8360	.8379	.8398	.8417	.8436	.8455	.8474	.8493	.8512
2.8	.8531	.8550	.8569	.8587	.8606	.8624	.8643	.8661	.8680	.8698
2.9	.8716	.8735	.8753	.8771	.8790	.8808	.8826	.8844	.8862	.8880
3.0	.8898	.8916	.8934	.8952	.8970	.8988	.9005	.9023	.9041	.9059
3.1	.9076	.9094	.9111	.9129	.9146	.9164	.9181	.9199	.9216	.9233

	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.0
3	.8898	.9076	.9251	.9422	.9590	.9755	.9917	1.0077	1.0234	1.0389
4	1.0542	1.0692	1.0840	1.0986	1.1130	1.1273	1.1413	1.1552	1.1689	1.1825
5	1.1959	1.2091	1.2222	1.2352	1.2480	1.2607	1.2733	1.2857	1.2981	1.3104
6	1.3225	1.3345	1.3464	1.3582	1.3698	1.3814	1.3929	1.4043	1.4156	1.4268
7	1.4379	1.4489	1.4599	1.4708	1.4816	1.4923	1.5029	1.5135	1.5240	1.5344
8	1.5447	1.5550	1.5652	1.5753	1.5854	1.5954	1.6054	1.6153	1.6251	1.6349
9	1.6446	1.6542	1.6638	1.6734	1.6829	1.6923	1.7017	1.7110	1.7203	1.7295
10	1.7387	1.7479	1.7570	1.7660	1.7750	1.7839	1.7928	1.8017	1.8105	1.8193
11	1.8280	1.8367	1.8453	1.8539	1.8625	1.8710	1.8795	1.8880	1.8964	1.9048
12	1.9131	1.9207	1.9282	1.9357	1.9432	1.9507	1.9582	1.9657	1.9732	1.9807
13	1.9945	2.0014	2.0082	2.0150	2.0218	2.0286	2.0354	2.0422	2.0490	2.0558
14	2.0729	2.0802	2.0874	2.0946	2.1018	2.1090	2.1162	2.1234	2.1306	2.1378
15	2.1432	2.1504	2.1576	2.1648	2.1720	2.1792	2.1864	2.1936	2.2008	2.2080
16	2.2211	2.2283	2.2355	2.2427	2.2499	2.2571	2.2643	2.2715	2.2787	2.2859
17	2.2916	2.3000	2.3084	2.3168	2.3252	2.3336	2.3420	2.3504	2.3588	2.3672
18	2.3801	2.3897	2.3993	2.4089	2.4185	2.4281	2.4377	2.4473	2.4569	2.4665
19	2.4266	2.4397	2.4527	2.4658	2.4789	2.4920	2.5051	2.5182	2.5313	2.5444
20	2.4913	2.5041	2.5169	2.5297	2.5425	2.5553	2.5681	2.5809	2.5937	2.6065
21	2.5544	2.5668	2.5792	2.5916	2.6040	2.6164	2.6288	2.6412	2.6536	2.6660
22	2.6160	2.6281	2.6402	2.6523	2.6644	2.6765	2.6886	2.7007	2.7128	2.7249
23	2.6762	2.6880	2.6998	2.7116	2.7234	2.7352	2.7470	2.7588	2.7706	2.7824
24	2.7350	—	—	—	—	—	—	—	—	—

$\rho = (E/V - 0.5)^{\frac{1}{2}} - 0.025/(E/V)^{\frac{1}{2}}$

TABLE III. Quantum number index in terms of E/V_1 for $V_2=3V_1/4$.

E/V_1	ρ_1	$4\rho_1/7$	E/V_2	ρ_2	$3\rho_2(V_2/V_1)^{1/2}$	\mathcal{R} (or $2\mathcal{R}$)
0.1	0.0286	0.0163	0.1333	0.0383	0.0142	0.0306
0.2	0.0580	0.0331	0.2667	0.0781	0.0290	0.0621
0.3	0.0882	0.0504	0.4000	0.1195	0.0444	0.0948
0.4	0.1195	0.0683	0.5333	0.1633	0.0606	0.1289
0.5	0.1521	0.0869	0.6667	0.2101	0.0780	0.1649
0.6	0.1863	0.1065	0.8000	0.2612	0.0969	0.2034
0.7	0.2224	0.1271	0.9333	0.3203	0.1189	0.2460
0.8	0.2612	0.1493	1.0667	0.3977	0.1476	0.2969
0.9	0.3040	0.1798	1.2000	0.4546	0.1687	0.3426
1.0	0.3592	0.2053	1.3333	0.5022	0.1864	0.3917
2.0	0.6861	0.3921	2.6667	0.8277	0.3072	0.6993

properties are taken from the tables at $2/Q_f$, V_1/RT and the entropy and the quantity $-F/T$ are increased by $R \ln 2$. If the properties are calculated by the method outlined here for the unsymmetrical rotator, they will involve twice as many energy levels as the number of regions entering into the method of Pitzer and Gwinn or the equal number of energy levels laid out by the old quantum theory for the symmetrical rotator. If, however, the tables for the symmetrical rotator are generally applicable to systems of all symmetry numbers, the same partition function should be obtained, within narrow limits, as the sum from each n th state or the sum for all possible states divided by n . For example, if $n=3$, each region or level found for the symmetrical case is the mean position of a triplet whose components may have varying probabilities according to the particular molecular species under consideration. The average weight of the three components in the symmetrical system will be that of a single state, and, if it makes any difference how the weight is divided among the components, it is to be supposed that the properties are not susceptible to accurate general tabulation.

This point has been checked in the more

TABLE IV. Thermodynamic properties, $V_2=3V_1/4$, $1/Q_f=0.4$, $V_1=16RT$.

r	\mathcal{R}	E/V_1	$\Delta E/RT$	p_e	pe	$-\Delta E/RT$	$(\Delta E/RT)p_e$	$-\Delta E/RT$
0	0.05	0.161	0	2.0000	0			
1	0.15	0.460	4.784	0.01673	0.08004			
2	0.25	0.708	8.752	0.00032	0.00280			
3	0.35	0.916	12.080	0.000006	0.00007			
4	0.3569	0.930	12.304	0.000005	0.00006			
	0.4431	1.112	15.216					
			$Q=2.01706$				0.08297	$\log Q=0.30472$
			$-F/T=1.394$				$H/T=0.082$	$S=1.476$

sensitive regions at $1/Q_f=0.2$, $V/RT=1$ and at $1/Q_f=0.4$, $V/RT=4$, where the states are widely separated and where significant contributions to the partition function are made by the rotational states. Within limits considerably less than 0.01 cal./mole/degree, the same results are obtained for systems with symmetry numbers 2 and 3 either by direct addition of terms from single states or by summation over all states divided by 2 or 3. In addition, the result is not sensitive to the degree of arbitrary splitting from the mean doublet positions whose location has been outlined in the method proposed here. Even when the rotational states are taken as unseparated doublets at integral values of the quantum number the partition functions are not materially changed.

II. $V_2=3V_1/4$. In this case the second maximum has been somewhat lowered relative to the first and the minima have been moved to a separation different from π on the rotational coordinate. The values of a for the successive half-valleys are $7/3$, $7/3$, $7/4$, and $7/4$, the higher numbers being associated with the lower maximum. If the maxima are placed at $\pi/2$ and $3\pi/2$, the minima will have been moved to $\pi(1/2 \pm 4/7)$ or $\pi(3/2 \pm 3/7)$.

This case may be used for a more detailed illustration of the method. Table III shows how the relation between E/V_1 and \mathcal{R} has been set up.

For E/V_1 (first column), the second column shows ρ_1 taken directly from Table II. This is multiplied by $4/7$, or $1/a_1$, to give the entry in the third column. The fourth column contains E/V_2 corresponding to the E/V_1 of the first column, the fifth shows ρ_2 corresponding to E/V_2 from Table II, and in the sixth column ρ_2 has been multiplied by $(3/7)(V_2/V_1)^{1/2}$ as required by Eq. (8). Because there are four half-valleys, in two like pairs, one-half the summation of the contributions of the half-valleys is in this case the sum of the entries in the third and sixth columns. This sum is shown in the seventh column as \mathcal{R} or $2\mathcal{R}$.

The general method outlined here would use this quantity as $2\mathcal{R}$ in the individual valleys and as \mathcal{R} in the energy region above the lower maximum. The states are placed at values of E/V_1 corresponding to $(2\mathcal{R})=2(r \pm \frac{1}{2})/Q_f(V_1/RT)^{1/2}$ within the valleys, at $\mathcal{R}=[r \pm (\frac{1}{4} + V_2/4E)]/$

$Q_f(V_1/RT)^{\frac{1}{2}}$ for states between the two maxima and at $\mathcal{R} = [r \pm (V_1/4E + V_2/4E)]/Q_f(V_1/RT)^{\frac{1}{2}}$ in the rotational region.

In the actual solution for the energy levels, Table III was extended in sufficient detail to $E/V_1=12$, more than far enough for calculation at $V_1=RT$. The index \mathcal{R} (or $2\mathcal{R}$) was plotted against E/V_1 and the energy ratios E/V_1 at the selected quantum numbers were found graphically up to $E=3V_1$ and by linear interpolation at higher levels.

The calculation of thermodynamic properties at $1/Q_f=0.4$ and $V_1=16RT$ is illustrated in Table IV. Since $1/Q_f(V_1/RT)^{\frac{1}{2}}=0.1$, the pairs are placed at $\mathcal{R}=0.1r$ above the lower maximum and at $(2\mathcal{R})=0.2r$ within the valleys, in which the required positions for the quantum numbers $r \pm \frac{1}{4}$ are at $(2\mathcal{R})=0.05, 0.15, 0.25$. Since these assignments are made separately in the two valleys, these levels enter the sum over states as doublets. Above the lower maximum the first pair occurs at the average position $\mathcal{R}=0.30$, but one component of the $2r+1$ states at this level and below has already been placed at $\mathcal{R}=0.25$. The other component is therefore set at $\mathcal{R}=0.35$ to maintain the average at 0.30.

The first column shows the mean quantum number of a pair of states referred to the limiting free rotator, the second the position of the component on the \mathcal{R} scale, the third the ratio E/V_1 from the graph based upon Table III, the fourth $\Delta E/RT$ for the excess of energy above the ground state, the fifth the exponential $e^{-\Delta E/RT}$ multiplied by p , the number of states at the level ΔE , and the last the product of the fifth column entry by the fourth column entry, to be used in finding the heat content. H/T is obtained by multiplying the sum of the entries in the last column by R/Q , where R has been taken as 1.9869 as previously used by Pitzer and Gwinn and by the writer.

III. $V_2=V_1/2$. For this case $a_1=3/2$ and $a_2=3$. The potential minima therefore appear at $\theta=\pi(1/2 \pm 2/3)$ or $\pi(3/2 \pm 1/3)$.

IV. $V_2=V_1/4$; $a_1=5/4$, $a_2=5$. Minima at $\theta=\pi(1/2 \pm 4/5)$ or $\pi(3/2 \pm 1/5)$. For this barrier ratio, when $1/Q_f$ is high, the potential valleys have become too shallow to hold the three states required for the symmetrical rotator to avoid the necessity of a downward adjustment of the ground state. With the symmetrical rotator it

was found that the accepted values of the free energy were obtained closely enough if the zero state was adjusted according to the empirical equation:

$$7.7 \times 10^6 \rho_0^9 + \rho_0 = \rho_1/4. \quad (9)$$

The adjustment, contained in the first term, is enough to cause the disappearance of the zero point energy as the n potential maxima are simultaneously reduced to zero.

In the case now under consideration, only one of the two maxima is being lowered and the limiting position of the zero state as this maximum approaches zero is not zero but $\mathcal{R}_1/8$. This limit will be approached if the lowest state is placed at the mean of the two positions calculated separately by Eq. (9) for the two sides of the potential valley. To find these positions, the uncorrected position $\mathcal{R}_1/4$ is first found and the corresponding ratios E/V_1 and E/V_2 are determined from the curve of \mathcal{R} against E/V_1 . For each of these energy ratios ρ is taken from Table II and adjusted downward according to Eq. (9). This will give two values of ρ_0 corresponding to known values of E/V_1 and E/V_2 in Table II. From each of these a value of \mathcal{R}_0 can be calculated and the mean of two such values of \mathcal{R}_0 is taken in conjunction with the curve of E/V against \mathcal{R}_0 to find the usable position of the zero state. This state, however, is a doublet, with one component for each valley, and only one of the components will reach the limit $\mathcal{R}_1/8$, which is required for the single minimum case if the assignment here is to be consistent with experience gained with the symmetrical rotator. The other component will be at $3\mathcal{R}_1/8$ in the limit, and the method is not capable of dictating its position during the transition. Consequently, an uncertainty is introduced into the thermodynamic properties which affects the free energy appreciably in one direction and the heat content somewhat more in the opposite direction. The entropy is relatively insensitive to the choice of positions under these conditions.

For the cases $1/Q_f=0.4$, $V_1/RT=16$; $1/Q_f=0.3$, $V_1/RT=9$; $1/Q_f=0.2$, $V_1/RT=4$ and $1/Q_f=0.1$, $V_1/RT=1$, the preliminary value of \mathcal{R}_0 is 0.05, for which E/V_1 is 0.142 and $E/V_2=0.568$. The adjustment is negligible on the higher side of the potential valley. On the lower

TABLE V. Thermodynamic properties of the double minimum internal rotator (cal./mole/degree) as function of $1/Q_f$, V_1/RT and V_2/V_1 .

V_1/RT	$1/Q_f$ V_2/V_1	0.05			0.10			0.20			0.30			0.40		
		$-F/T$	H/T	S	$-F/T$	H/T	S	$-F/T$	H/T	S	$-F/T$	H/T	S	$-F/T$	H/T	S
1	1	5.25	1.58	6.83	4.03	1.42	5.45									
	$\frac{3}{4}$	5.33	1.52	6.85	4.10	1.38	5.47									
	$\frac{1}{2}$	5.38	1.47	6.85	4.13	1.34	5.48									
	$\frac{1}{4}$	5.37	1.47	6.84	4.08	1.38	5.46									
	0	5.17	1.66	6.83	3.88	1.58	5.45									
4	1	3.96	1.86	5.82	2.90	1.58	4.48	2.09	1.12	3.21						
	$\frac{3}{4}$	4.09	1.88	5.98	3.02	1.61	4.62	2.17	1.16	3.34						
	$\frac{1}{2}$	4.23	1.86	6.04	3.14	1.60	4.73	2.26	1.17	3.43						
	$\frac{1}{4}$	4.29	1.76	6.06	3.18	1.52	4.70	2.17	1.14	3.31						
	0	3.79	2.02	5.81	2.58	1.86	4.44	1.51	1.58	3.09						
9	1	3.20	1.58	4.78	2.28	1.30	3.47	1.68	0.66	2.34	1.50	0.36	1.86			
	$\frac{3}{4}$	3.35	1.62	4.97	2.37	1.26	3.63	1.73	0.73	2.46	1.52	0.42	1.94			
	$\frac{1}{2}$	3.43	1.69	5.13	2.46	1.34	3.80	1.80	0.82	2.62	1.57	0.50	2.07			
	$\frac{1}{4}$	3.56	1.68	5.24	2.56	1.34	3.90	1.83	0.82	2.66	1.53	0.42	1.95			
	0	2.96	1.81	4.77	1.82	1.58	3.41	0.90	1.20	2.10	0.50	0.89	1.40			
16	1	2.76	1.40	4.16	1.96	0.94	2.90	1.52	0.39	1.91				1.39	0.06	1.45
	$\frac{3}{4}$	2.86	1.45	4.31	2.02	1.00	3.02	1.55	0.45	2.00				1.39	0.08	1.48
	$\frac{1}{2}$	2.94	1.50	4.44	2.09	1.07	3.16	1.59	0.52	2.11				1.41	0.12	1.53
	$\frac{1}{4}$	3.06	1.55	4.61	2.18	1.14	3.32	1.64	0.59	2.23				1.40	0.09	1.48
	0	2.44	1.69	4.13	1.38	1.41	2.79	0.58	0.94	1.52				0.14	0.39	0.53

side, ρ_2 is 0.1751 for the uncorrected level, and this is corrected by Eq. (9) to $\rho_2=0.1250$, for which $E/V_2=0.4172$, $E/V_1=0.1043$ and $\mathcal{R}_0=0.036$. The mean position is 0.043, $E/V_1=0.123$. This considerable adjustment has an appreciable effect upon the calculated thermodynamic properties and leaves the question open as to how accurate they are. The adjustment, however, is based upon the one used successfully with the symmetrical rotator, and the states approach the correct positions in the limits $V_2=V_1$ and $V_2=0$. Of the calculated properties tabulated below, only those at the four points listed at the beginning of this paragraph are appreciably affected by the adjustment of the zero state.

The uncertainty centered upon the question whether both components of the zero state should be kept together while inside the valley reaches its maximum when both $1/Q_f$ and V_1/RT are high. At the four points listed above, variations of the position of the second component of the ground state within reasonable limits introduce large uncertainties in $-F/T$ and H/T at $V_1/RT=9$ or 16, but produce negligible effect at $V_1/RT=1$ or 4. At $V_1/RT=16$, the variation in the entropy is about 0.05 cal./mole/degree.

V. $V_2=0$. This is the single minimum limit for which $V=V_1(1-\cos\theta)/2$. The thermodynamic

properties are taken directly from the tables of Pitzer and Gwinn.

Table V contains the calculated thermodynamic properties of the optical isomer system with the several selected ratios V_2/V_1 . For each combination of V_1/RT and $1/Q_f$ there are tabulated as a function of the barrier ratio five values of each of the three properties, free energy ($-F/T$), heat content (H/T), and entropy (S), in cal./mole/degree.

In the table the properties at $V_1/RT=9$, $1/Q_f=0.30$, and at $V_1/RT=16$, $1/Q_f=0.40$ which are seriously affected by the question whether both components of the zero level should be lowered empirically are shown in italics. The alternatives are lower values of $-F/T$ combined with higher values of H/T , producing small increases in the listed entropies.

DISCUSSION

As the ratio V_2/V_1 decreases from unity it is found, throughout the range of the calculations with respect to $1/Q_f$ and V_1/RT , that the entropy and free energy ($-F/T$) rise, pass through maxima, and drop again at the limit $V_2=0$. When $V_1=RT$, the maxima occur near $V_2=V_1/2$, and they tend to move toward lower values of V_2/V_1 as V_1/RT is increased or as $1/Q_f$ is decreased. For use with thermodynamic data,

interest centers on the entropy as a property susceptible to experimental determination. For the entropy the maximum calculated increase above that of the system of equal maxima is 0.46 unit, occurring at $V_1=9RT$ and $1/Q_f=0.05$. This increase can be taken as a good approximation to the maximum error which might be made in interpreting data for unsymmetrical systems with the aid of values tabulated for the symmetrical rotator. It would be close to the actual error if it had been assumed that the optical isomer system could be taken as equivalent to an equal mixture of two symmetrical rotators with a potential barrier equal to the higher one, V_1 .

The behavior of the heat function (H/T) with the changing barrier ratio is more variable with the quantities $1/Q_f$ and V_1/RT . When V_1/RT is small, the property appears to go through a simple minimum between the limits $V_2=V_1$ and $V_2=0$. In general, however, the curve of H/T against V_2/V_1 contains a maximum and minimum which may both disappear in the region of high V_1/RT at low $1/Q_f$.

Some of this behavior is predictable from a consideration of the limit of high potential barriers for which the deviations from the properties of the harmonic oscillator become negligible. The effect of lowering one of two equal high potential barriers is to decrease the restraint on the system, increasing the value of the integral sum in Eq. (5), and therefore to increase the value of the quantum number at any selected level of energy. Conversely, the energy level corresponding to a given quantum number is lowered and the states drop to lower levels and are brought closer together. The frequency of the equivalent harmonic oscillator is therefore lower and the properties ($-F/T$), H/T , and S must all increase. They will continue to increase with decreasing V_2 as long as both barriers remain high, regardless of their ratio.

If the second barrier is now lowered further, with the first remaining high, and is finally eliminated, the system will again be nearly harmonic, but with a frequency only half as large as it originally had when the barriers were equal. Two states, one for each valley, which had the same energy $(n+\frac{1}{2})\epsilon$ when the potential maxima were equal, will have dropped down, remaining together as the one barrier was

lowered, and will have finally emerged, as the second barrier disappeared, in the positions $(n+\frac{1}{2}\pm\frac{1}{4})\epsilon$. Exactly how they behave during the emergence from the valley and subsequent separation cannot be clearly determined by the method used here. The recommended method of calculation, based upon experience acquired with the symmetrical rotator, would cause the lower component of each pair, except possibly for the lowest state, to pass through a minimum as V_2/V_1 decreased, while the upper component would remain paired with the lower one until, at a low value of V_2 , they emerged from the valley. At this point the two would separate and rise, as V_2 went to zero, the one rapidly, the other more slowly, to their final positions at $(n+\frac{1}{2}\pm\frac{1}{4})\epsilon$ for $V_2=0$.

When V_1/RT is high, and $1/Q_f$ is low, the maxima in the entropy and the function $-F/T$ will occur at low values of V_2/V_1 , with the drop to the properties of the single minimum system occurring precipitously in a narrow range of low values of the barrier ratio.

The system of optical isomers considered here occurs as part of the system present in ethyl alcohol or isopropyl alcohol, which have been interpreted by the methods proposed by Aston, Szasz, Iserow, and Kennedy.³ It is the writer's intention, as soon as time permits, to attempt an interpretation for these compounds by the method proposed in the present paper. Before this is done, however, a further illustration of the method will be made by applying it to a double minimum system with attractive forces, for which the heights of the maxima remain fixed and equal while one minimum is raised relative to the other.

Calculations have been limited to cases for which there can be little doubt that the method is accurately applicable. As a result, the range of $1/Q_f$ covered is much less than that of the Pitzer-Gwinn tables for the symmetrical rotator. For a rotator of a given moment of inertia, however, $1/Q_f$ for the symmetrical system is twice as large as for the unsymmetrical one. Consequently, the range of values of $1/Q_f$ covered by the calculations would be twice as large if the rotator under consideration had the symmetry number two.

³ J. G. Aston, S. Iserow, G. J. Szasz, and R. M. Kennedy, *J. Chem. Phys.* 12, 336 (1944).