

Partition Function for Internal Rotation in Methanol and Similar Molecular Models*

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Methanol falls outside the range of variables within which the internal rotator partition function and its required derivatives have been dependably calculated by the relatively simple methods of Pitzer and Gwinn. For such cases, Ivash, Li, and Pitzer have proposed a detailed, general formulation of potential extreme accuracy.

It is shown here that their partition function, obtained by integration over functions which are not unique for the model, can have two formally different values. Elimination of an ambiguity from their derivation leads back to an earlier and simpler method developed empirically by Halford, without, however, establishing this method for the general case.

A very simple derivation, which obviously gives answers of readily determined accuracy for a widely distributed set of special cases, is presented. It is shown that the Ivash-Li-Pitzer formulation gives accurate answers under specifiable conditions. It is also deduced that a considerable extension of the Pitzer-Gwinn Tables, at a high level of accuracy, sufficient to cover all likely cases of interest, is possible without serious increase in the detail of calculation.

Such an extension would solve the general case in a practical sense.

IN their excellent recent paper on the thermodynamic properties of ideal gaseous methanol, Ivash, Li, and Pitzer¹ have again considered the calculation of the partition function for internal rotation when the relatively simple methods of Pitzer and Gwinn² are not sufficiently detailed.

This problem was originally solved by the present writer³ for methanol in a manner which reduced the detail of calculation to exactly the same level as the original methods of Pitzer and Gwinn. Ivash, Li, and Pitzer have developed a formulation which calls for an extensively more detailed calculation. This formulation is claimed to be more general and to provide for increased accuracy by the inclusion of additional terms in the computations. They find, however, that at all temperatures of practical interest, there are no significant differences between Halford's "empirical approximation" and the results of their new and far more detailed formulation.

Since both calculations give the same answers for methanol, and methanol is the only presently known compound which requires these methods, the question of generality will remain trivial until some other molecule is found for which the tables of Pitzer and Gwinn are not adequate.

It can be inferred that Ivash, Li, and Pitzer regard their formulation as general in the sense that it can be applied equally readily to any two chosen rotator models. Their finding that their results for methanol are at all temperatures of practical interest equal to those given

by the simpler Halford formulation suggests, in addition, that there may be extensive groups or sets of models for which the partition function and its temperature derivatives are substantially the same.

In this connection, it is convenient to call attention to a family of rotator models for all of which the energy within any one band of levels can be expressed as the same function of a quantity KC_1/SC , or σ/S . K is any integer and can be called the quantum number for external rotation, S is the symmetry number, C_1 is the moment of inertia of one of the two opposed coaxial rotating parts, and, if C_2 is the moment of inertia of the other, $C=C_1+C_2$. σ is KC_1/C . The Ivash, Li, Pitzer formulation expresses the partition function in terms of integrals over curves which are identical for all members of this family, and thereby implies that the function is the same for all the models included. In applying their formulation, however, they substitute ordinate sums for their integrals, which may vary the results with the spacing of the ordinates. It will be shown here that their formulation, with correctly weighted ordinates at a properly chosen interval, can give a very accurate answer for any representative models of the family. For this purpose, the Simpson's rule sum which they recommend, however, is not formally correct, although it will probably yield accurate answers.

The family of models with a common periodic curve of energy against σ/S will also have a common potential barrier (v in ergs/molecule). According to Koehler and Dennison,⁴ the system of energy levels is determined by selecting α , σ , S , and v , where

$$\alpha = 2\pi^2 C_1 C_2 v / (h^2 C). \quad (1)$$

It is evident, from their recursion formula and the corresponding determinants, that, for all rotator models with the same α/S^2 , the ratio of total energy to v , as a

* After this paper was submitted for editorial review an extension of the tables of thermodynamic properties into the region of variables under consideration here was published (J. C. M. Li and K. S. Pitzer, *J. Phys. Chem.* **60**, 466 (1956)). Since their formulations agree with those of Ivash, Li, and Pitzer the range of accurate applicability of their tables is not clear. A study of the accuracy and probable utility of the new tables is now in progress.

¹ Ivash, Li, and Pitzer, *J. Chem. Phys.* **23**, 1814 (1955).

² K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428 (1942).

³ J. O. Halford, *J. Chem. Phys.* **18**, 1051 (1950).

⁴ J. S. Koehler and D. M. Dennison, *Phys. Rev.* **57**, 1006 (1940).

function of σ/S , is represented by S curves of identical shape in each band of levels. These curves have the period unity and are displaced laterally at intervals $1/S$ on the scale σ/S . To make the internal energy curves the same for all models of the family requires selection of a single ν which will cause C to vary with C_1 , C_2 and S . Since, however, the partition function for external rotation is factored out as an independent quantity, this will not make the result less general. It will be permissible to adjust a result from one C to another without loss of accuracy. Insistence upon a fixed C would require adjustment of ν and would lead to partition functions for the various models which were the same at different temperatures. The α of Eq. 1, from Koehler and Dennison, is not the same as the α of Ivash, Li and Pitzer.

Since σ is proportional to K , a pattern of S energy levels in each band will occur at any chosen K . If the net energy/ kT ratios are represented as $F_{K\tau n}$, with τ designating a particular periodic curve in each band and n identifying the band, the contributions at constant K to the over-all partition function can be summed over τ and n in either order. The sum over τ at constant n and K is the Q_τ of Ivash, Li, and Pitzer, while the sum over n at constant K and τ is the q_K of the original Halford development. The over-all partition function for rotation about the internal rotator axis can therefore be expressed as

$$SQ_{K\tau n} = \sum_{K\tau} q_{K\tau} \exp(-\delta K^2) \quad (2)$$

$$= \sum_K \sum_n Q_\tau \exp(-\delta K^2). \quad (3)$$

The notation q_K implies that each $q_{K\tau}$ for $\tau=2, 3$, etc., has been replaced by an equal q_{K1} from the first periodic curve in each band. The value of δ is given in Eq. (4).

$$\delta = \hbar^2 C / (8\pi^2 C_1 C_2 kT). \quad (4)$$

It is clear by inspection that the pattern of S levels found at a chosen value of σ or K must repeat itself whenever σ is increased by any integer. This is the conclusion reached by Ivash, Li, and Pitzer about the periodicity of Q_τ in terms of a defined coordinate z . Their next step is to substitute K for z or σ according to the definition $\sigma = \pm KC_1/C$, thereby expressing $Q_{K\tau n}$ as a continuous function of K . The required partition sum is then replaced by an integral which is readily evaluated. The result is an infinite sum in which the value of every term but the leading term is dependent upon the ratio C_1/C . In application, all terms depending upon C_1/C are dropped as negligible under conditions of practical interest. However, at very low C_1/C , the neglected terms could contribute appreciably and might be required for adequate accuracy.

Unfortunately for the integration process in the present problem there are, for the general model, two distinct equally acceptable substitutions for σ/K , namely, C_1/C , and C_2/C . For the more usual definition

C_1/C , there is nothing in the theory which limits C_1 to one of the opposed rotators, regardless of their relative size. This duality makes ambiguous all the terms in the Ivash, Li, Pitzer final sum which depend asymmetrically upon C_1 . If C_2 had been used, and it had been assumed that $C_2 > C_1$, all of the neglected terms of their sum would have been smaller. The larger the corrections in one representation, the smaller they will be in the alternative equation. The proposed improvement of accuracy by the inclusion of neglected terms has not therefore been formulated in a unique manner.

Prior to the integration, however, the dual nature of σ has introduced no ambiguity. At every integral K both expressions lead to the same energy levels in the same symmetry classes. Since $C_2/C = 1 - C_1/C$, every energy level, $E_{K\tau n}$, will be duplicated, when the alternative σ is used, by a level $E_{-K\tau n}$, and each $E_{K\tau n}$ will be reproduced by another level at the same K but sometimes a different τ . If, following Ivash, Li, and Pitzer, Q_τ is expressed as a general periodic function of K , there are now two functions with different periods. At all integral K , these functions are readily shown to yield equivalent patterns, but the functions and patterns are different, for the two representations, if K is not an integer. The inconsistent asymmetric terms obtained by integration are the result of this difference.

If the functions are modified to eliminate the inconsistency, the new one may represent an over-simplification which leads to a result which is still not dependably accurate. The correct result will have to be verified independently. It is fortunate, for the present problem, that this can be done, as shown below, for enough models to outline the result for the general case.

Although the claim cannot be made that the answer is rigorously accurate, it is still interesting to outline an attempt to eliminate the effect of the ambiguity in σ from the development of Ivash, Li, and Pitzer.

The partition sum Q_τ , which they express as a general periodic function of K , can be consistently single-valued for all possible combinations of C_1 and C_2 only if it is a constant independent of K and σ . An ordinate Q_τ is the sum of S terms, $\exp(-F_{K\tau n})$, or $\exp(-F_{\sigma\tau n})$, for τ unity to S , taken from the S identical but displaced curves of energy against σ . If F_{K1n} is regarded for the moment as a general periodic function of σ with period S , this will require that

$$\exp(-F_{\sigma 1n}) = \sum a_p \cos(2\pi p\sigma/S). \quad (5)$$

Each $Q_\tau(\sigma)$ will be expressible as the sum of S ordinates from this one curve and the function will require adjustment, at each S , so that all sums of appropriate ordinates will be equal. For this to be true for symmetry number S , it is necessary that a_S and some higher coefficients be zero. Since the same function must apply at all values of S , this will eliminate most of the periodic terms. When S is unity, however, the result is an obviously unacceptable oversimplification. If the argument is accepted for all higher symmetry numbers, the

result is

$$\exp(-F_{\sigma 1n}) = a_0 + a_1 \cos(2\pi\sigma/S). \quad (6)$$

When this function is summed over n , it follows that

$$q_{\sigma} = A_0 + A_1 \cos(2\pi\sigma/S). \quad (7)$$

Equation (7) is the original empirical sinusoidal relation which Halford found by numerical trial to be highly accurate for the then current methanol model.

Although the argument yields an obviously oversimplified and unacceptable conclusion for unit symmetry number, it is interesting that both Halford and later Ivash, Li, and Pitzer have found that the resulting Eqs. (6) and (7) give accurate results for methanol models. The meaning of the surprisingly simple Halford representation in relation to the general solution is thus somewhat clarified.

The possible constancy of Q_{τ} would be consistent with several other relatively simple formulations for $Q_{\tau n}$ (or for \bar{q} in the Halford notation). If the cycle of F or q in σ is divided into twelve uniform intervals, seven ordinates, $q_0 \cdots q_6$, will appear in each half cycle. This is the scale represented by Ivash, Li, and Pitzer at unit intervals in a defined coordinate x . Constant Q_{τ} (or $q_{K\tau}$) will then require

$$\bar{q} = q_3 = (q_0 + q_6)/2 \quad \text{for } S=2,$$

$$\bar{q} = (q_0 + 2q_4)/3 = (2q_2 + q_6)/3 = (q_1 + q_3 + q_5)/3 \quad \text{for } S=3, \quad (8)$$

etc.

It is evident that the Ivash, Li, Pitzer derivation must lead to two formally different results according to the chosen definition of σ and that a simplification of the derivation chosen to eliminate the ambiguity leads back to the original Halford method. While all of these formulations will undoubtedly give substantially equal results under conditions of practical interest, none of them can be defended as the general, wholly accurate rigorous answer to the problem.

An answer of readily determined accuracy can be obtained in a very simple manner for a number of the models of the related family with a common potential barrier and common curves of energy against σ/S . These models can be spread out on a scale determined by the spacing of the energy levels on the common curve, in terms of either permissible definition of σ . This spacing is C_1/SC (or C_2/SC). When the number of energy levels in a cycle or half cycle is an integral multiple of the symmetry number, it is possible in many cases to factor the combined partition function by inspection, without integrating over τ . Integration is required only to evaluate certain systematic parts of the one-dimensional rotator partition function. For this function the relation of the integrals to the corresponding sums is well known and is in general highly accurate. The inaccuracy of the integrals is readily determined.

For a hypothetical model with symmetry number unity and $C_1=C_2$, there is one characteristic curve in each band of levels. Since C_1/SC is $\frac{1}{2}$, the levels occur at the maxima and minima. The K values are even at the minima and odd at the maxima, and the corresponding q_K can be called q_0 and q_6 to align them with the Ivash-Li-Pitzer x scale. Obviously,

$$\begin{aligned} Q_{K\tau n} &= q_0(1 + 2e^{-4\delta} + 2e^{-16\delta} + \dots) \\ &\quad + q_6(2e^{-\delta} + 2e^{-9\delta} + 2e^{-25\delta} + \dots) \\ &= (q_0 + q_6)Q_K/2. \end{aligned} \quad (9)$$

It follows that

$$\bar{q} = Q_{\tau n} = (q_0 + q_6)/2. \quad (10)$$

For a second example the model is chosen with $S=3$ and $C_1/C=1/4$, which corresponds to the x spacing of Ivash, Li, and Pitzer. If the q_K are systematically charted against K , each $\exp(-\delta K^2)$ is multiplied by one of three combinations of q 's, and:

$$\begin{aligned} 3Q_{K\tau n} &= (q_0 + 2q_4)(1 + 2e^{-16\delta} + 2e^{-64\delta} + \dots) \\ &\quad + (q_1 + q_3 + q_6)(2e^{-\delta} + 2e^{-9\delta} + 2e^{-25\delta} + 2e^{-49\delta} + \dots) \\ &\quad + (2q_2 + q_5)(2e^{-4\delta} + 2e^{-36\delta} + 2e^{-100\delta} + \dots). \end{aligned} \quad (11)$$

Therefore,

$$\bar{q} = (q_0 + 2q_1 + 2q_2 + 2q_3 + 2q_4 + 2q_5 + q_6)/12, \quad (12)$$

since the parenthesized infinite sums are, in order, by inspection, $Q_K/4$, $Q_K/2$ and $Q_K/4$.

The factoring operation illustrated by Eqs. (9), (10), (11), and (12) cannot be used to simplify the general case for all S and C_1/C without introducing assumptions about the functional dependence of Q_{τ} or q_{τ} upon σ . For useful simplification it is necessary that the number of levels on the cycle or half-cycle of one characteristic curve, in terms of the smaller definable σ , be an integral multiple of the symmetry number. In these cases only a few different q_K can occur, while in the general case, which is merely the original sum, there is an individual q_K for each K .

Simplification of the general case is effected by inference from the special cases for which extensive simplification is possible. As long as the integration over the appropriate subdivisions of the one dimensional free rotator function continues to represent the corresponding sums accurately, the evaluation of \bar{q} for the favorable special cases can be continued to successively higher values of C/C_1 . It is this factor, independent of the symmetry number, which determines the pertinent subdivisions of the rotator series. Application of the illustrated factoring method depends upon the integral

$$\int_{-\infty}^{+\infty} \exp[-\delta(aK+m)^2] dK = [\pi/(\delta a^2)]^{1/2} = Q_K/a. \quad (13)$$

When the integration is acceptable, Eq. (13) yields the

same total, with a and m integers, for all sums consisting of every a th term of the rotator series, when this series is written with the positive and negative K terms expressed separately. For some values of m this will not go beyond evaluating the $[2/a]$ th part of the series. For example, if a is 8 and m is 1 or 7, the positive $aK+m$ are 1, 9, 17, etc., and the negatives are 7, 15, 23, etc., or vice versa. The series is divided into five parts, $\frac{1}{8}, \frac{1}{4}, \frac{1}{2}, \frac{1}{4}$ and $\frac{1}{8}$, which will, however, serve to complete the factoring operation.

As C/C_1 increases, a progressively more severe strain is placed upon the accuracy of summation by integration. If S is also high, this should cause no trouble, since, with a large number of $q_{K\tau}$ and $Q_{K\tau}$ occurring at each K , the sum of these functions over τ must become practically invariant with K or σ , making \bar{q} equal to the average $q_{K\tau}$ at any one K . If, however, S is low while C/C_1 is high, the accuracy of the integration will fail. In the limit for very high C/C_1 only the initial part of a cycle of each characteristic curve will be involved and the result for \bar{q} must approach the average $q_{K\tau}$ for K equal to zero. A suitable if not totally accurate answer should be obtainable from a study of the variation of $\bar{q}\sigma$ with σ . This situation was discussed in qualitative terms in the original paper by Halford.

In the limit, for symmetry number 3, on the chosen x scale, the correct answer must be $(q_0+2q_4)/3$, where q_4 is obtained by summation over n from the symmetrical curves at any integral value of σ except a multiple of 3. Since, for the symmetrical curves, summed over n ,

$$q_\sigma = \sum_m a_m \cos(2\pi\sigma m/S), \quad (14)$$

the limiting q is a_0+a_3 , if higher terms are neglected. This is the mean partition function given by the Ivash-Li-Pitzer Eq. (15) after summation over n , provided that the smaller moment of inertia has been used for C_1 . With the larger moment, the equation would demand the answer a_0 . For other symmetry numbers, the corresponding results from the two integrations are a_0+a_S and a_0 .

At the limit for low C_1 , then, the integration over the function of the longer period SC/C_1 is formally more accurate than the alternative one. Since the a_m must decrease rapidly with increasing m , the deviation from a_0 should always be practically negligible, except for symmetry number 1 and possibly for symmetry number 2. The integration is probably highly accurate under all conditions of practical interest regardless of which moment of inertia is used.

It is also evident that a simple average like $(q_0+2q_4)/3$ or $(q_0+q_6)/2$ is a good practical approximation to the partition function.

At constant low C/C_1 the factoring operation will tolerate indefinite increase in S without loss of accuracy. In the limit for high S , \bar{q} approaches the integrated

average of q_K over a cycle or half-cycle of the first characteristic curve. This limit is the result expressed in Eq. (18) of the Ivash-Li-Pitzer theory, obtained after the asymmetric corrective terms in C_1/C had been neglected.

In application, Ivash, Li, and Pitzer have come very close to the correct answer for low C/C_1 by substituting for their integrals Simpson's rule sums with an ordinate spacing near or coinciding with the K spacing of the model. Equation (12), which is obviously correct for the model implied by their ordinate spacing, is not, however, a Simpson's rule sum, but is instead a simpler trapezoidal sum. Simpson's rule therefore introduces a formally incorrect relative weight of the energy levels, but should, nevertheless, give a very accurate partition function.

By means of the method proposed here or the equivalent modified Ivash-Li-Pitzer equation, the partition function can be obtained with any desired accuracy for some model close to the model of interest. The procedure is general in being equally applicable to all symmetry numbers. No general answer applicable to all C/C_1 , however, has been verified.

The practical general answer, valid for all conceivable reasonable molecular models, can nevertheless be readily outlined. The situation is logically just like the one encountered by Pitzer and Gwinn in making up their tables of thermodynamic properties, which they tabulated only when the extreme values of q_K and its temperature derivatives were close enough together to permit a simple accurate estimate of the effective average.

It is now evident that it is not q_K but $\sum_\tau q_{K\tau}$ which limits this procedure. There must be a broad region, beyond the limits of the Pitzer and Gwinn tables, in which the extreme values of $(\sum q_{K\tau})/S$, are close together, regardless of the value of S , but not for S equal to unity. In other words, the amplitude of the function $\sum q_{K\tau}(\sigma)$ must be very much less for such cases than that of $q_K(\sigma)$.

Where $\sum q_{K\tau}$ is nearly invariant with K and σ at all symmetry numbers except unity, this quantity at some one K for any symmetry number will give a quite accurate general answer. This explains the success of the Halford approximation for methanol, which is merely one of the extreme values of $(\sum q_{K\tau})/S$ for a model with the same curve of q_{K1} against σ/S as methanol, but with symmetry number 2. On the presently chosen scale, this is $(q_0+q_6)/2$. The other extreme would be simply q_3 . The success of the approximation shows that the two extremes are negligibly different from each other and from the corresponding extremes for symmetry number 3, which appear in Eq. (8).

It is thus evident that the factor which limited the tabulations of Pitzer and Gwinn is a significant limitation only for symmetry number unity. It would be permissible to calculate considerably extended tables applicable to higher symmetry numbers, limited only by

the extreme values of $\sum q_{K\tau}/S$. The nearly sinusoidal curve obtained by Halford for q_K against σ in the methanol case indicates that such tables would be accurate enough for $S=1$ in spite of the formal limitation to higher symmetry numbers. Such an extension of the tables, however, would not be widely useful.

Although the present discussion has been limited to \bar{q} , which determines the free energy, it is readily extended, without interfering complications, to \bar{q}' and \bar{q}'' , the sums proportional to the first and second temperature derivatives of q which are required for calculating the energy, entropy and heat capacity.

Potential Constants of Nitrous Acid*

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A normal coordinate treatment was carried out using a general quadratic potential function. Possible sets of force constants were evaluated on the basis of previously observed vibrational bands. The most probable range for the potential constants was established by means of bond order criteria and distributions of potential and kinetic energies among the internal coordinates.

ALTHOUGH the infrared spectrum of nitrous acid was studied recently,¹ a normal coordinate treatment for this molecule has not been reported in the literature. Such calculations have been made for a number of related molecules,² in particular for the various oxides of nitrogen.³ Since the fundamentals of HNO_2 and its deuterated analog, DNO_2 , have been determined, sufficient data are available to permit a normal coordinate treatment to be carried out for these molecules. The object of this investigation was to evaluate consistent sets of potential energy constants and to establish reasonable ranges for these quantities.

PREVIOUS SPECTRAL DATA AND MOLECULAR PARAMETERS

The infrared spectra of HNO_2 and DNO_2 which were reported by D'Or and Tarte^{1a} and by Jones, Badger, and Moore^{1b} have been obtained from equilibrium mixtures of gaseous $\text{NO}-\text{NO}_2-\text{H}_2\text{O}$ and $\text{NO}-\text{NO}_2-\text{D}_2\text{O}$, respectively. Both groups of investigators observed a

doubling of most bands which they attributed to the existence of rotational isomerism. They agree in their interpretation and assignments of the spectra, but each reported slightly different values for the fundamental vibrations, as may be seen from Table I. The major difference between the two sets of data appears in the NOH bending mode of *cis*- HNO_2 ; the present calculations favor the higher value of 1370 cm^{-1} . The bond torsional modes of *cis*- and *trans*- DNO_2 were not observed by D'Or and Tarte since this region was experimentally inaccessible to them. In general, the bands of *trans*- HNO_2 were considerably more intense than those of the *cis*-isomer. Jones, Badger, and Moore^{1b} observed rotational fine structure for the OH stretching fundamental and overtone bands, for the OD overtone of *cis*- DNO_2 and for the out-of-plane mode of the *trans*-isomer. From the rotational constants and estimated parameters, they calculated the probable values for the moments of inertia. The molecular constants, reported by Jones, Badger, and Moore,^{1a} which have been employed in the present computations are: $\text{O}-\text{H}=0.98\text{ \AA}$, $\text{N}-\text{O}=1.46\text{ \AA}$, $\text{N}=\text{O}=1.20\text{ \AA}$ for both *cis*- and *trans*-isomers and $\angle\text{NOH}=103^\circ$, $\angle\text{ONO}=114^\circ$ for the *cis*-form and $\angle\text{NOH}=105^\circ$ and $\angle\text{ONO}=118^\circ$ for the *trans*-form of nitrous acid.

Table II shows the results of the sum and product rules which have proved valuable in correlating fundamental vibrations of rotational isomers and isotopic molecules. The discrepancies arising from the application of the sum and product rules to HNO_2 may be due in part to the fact that the azimuthal angle differs from 180° , as has been assumed here. Another assumption that the potential constants are identical for both *cis*- and *trans*-isomers is not substantiated by the values presented in Table V. The isotopic ratios are satisfactory and indicate that the data are adequate for a first approxima-

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