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Maxwell L. Eidinoff and J. G. Aston

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The Rotational Entropy of Nonrigid Polyatomic Molecules

MAXWELL L. EIDINOFF AND J. G. ASTON, *School of Chemistry and Physics, The Pennsylvania State College*

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An expression is derived for the rotational entropy of nonrigid polyatomic molecules with zero potential and apart from nuclear spin and symmetry number corrections. Previous empirical formulae are derived as special simplified cases of the general formula. Applications are made to several important types of molecular models.

I. INTRODUCTION

THE theoretical calculation of the rotational entropy of molecules, apart from nuclear spin and symmetry number corrections, depends on the evaluation of the partition function¹ $\sum_{\alpha} \sum_{\beta} \cdots \sum_{\lambda} e^{-\epsilon_{\alpha, \beta, \dots, \lambda} / kT}$ where the summation is extended over all values of all the quantum numbers $\alpha, \beta, \dots, \lambda$ and where $\epsilon_{\alpha, \beta, \dots, \lambda}$ are the corresponding energy levels, obtained as the characteristic values of the quantum-mechanical rotational problem. In the field of nonrigid molecules, these levels have been solved exactly for the ethane top² and for spherically symmetric tops such as tetramethylmethane.³ No solutions of nonrigid asymmetric tops have been obtained. An empirical formula has been presented and tested by Halford.⁴ This formula, although useful, cannot be applied without uncertainty (Section III). Expressions will be derived for this sum, assuming limiting classical rotation. These formulae, together with vibration spectrum data, make possible comparisons of theoretical entropies with those obtained from heat capacity measurements down to 11°K, which are being conducted in this laboratory and elsewhere. Even at very low temperatures these expressions agree very well with the summations over the quantum levels (Section IV). In the application of the expressions to be derived to a specific model, it is unnecessary to obtain the Hamiltonian form of the rotational energy, and to perform the laborious integration over the momentum space associated with the rotational assembly.

II. EXPRESSIONS FOR THE ROTATIONAL PARTITION FUNCTION AND ROTATIONAL ENTROPY

The molecule under consideration is an M particle body, consisting of a rigid skeletal frame to which are attached N rotating (zero potential) tops, which, apart from their spins relative to the frame, have angular velocity components due to the motion of the frame. The center of gravity O of the molecule is considered fixed. The kinetic energy of rotation about the center of gravity may be derived in different ways depending on the specific nature of the problem. A general one is: The usual Eulerian angles (see Fig. 1), θ, ψ, φ , refer three \perp axes, origin at O , and fixed in the frame to three reference axes fixed in space. Angular coordinates, $\alpha_1, \alpha_2, \dots, \alpha_n$ are used to define the orientations of the tops relative to the frame. Components of angular velocity due to rotating frame and spinning tops are resolved along N sets of three \perp axes (x_i, y_i, z_i for the i th top), which are the principal axes for the N tops at O . If I_{x1}, I_{y1}, I_{z1}

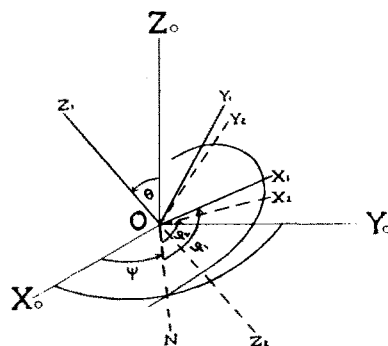


FIG. 1.

¹ Fowler, *Statistical Mechanics*, Chapter II.

² Mayer, Brunauer and Mayer, *J. Am. Chem. Soc.* **55**, 37 (1933).

³ Lacoste, *Phys. Rev.* **46**, 718 (1934).

⁴ Halford, *J. Chem. Phys.* **2**, 694 (1934).

are the moments of inertia, and ω_{xi} , ω_{yi} , ω_{zi} are the corresponding angular velocities about these axes, (and similarly for the other tops), then the rotational kinetic energy may be written:

$$\Phi_1 = \text{K.E.} = \frac{1}{2} \left\{ \sum_{i=1}^n (I_{xi}\omega_{xi}^2 + I_{yi}\omega_{yi}^2 + I_{zi}\omega_{zi}^2) \right\}. \quad (1)$$

The number of independent degrees of freedom will be determined by the original constraints of the problem. If the number of these be r , and corresponding coordinates x_1, x_2, \dots, x_r , and velocities $\dot{x}_1, \dot{x}_2, \dots, \dot{x}_r$, it is possible to bring Φ_1 to the positive definite symmetric quadratic form,

$$\Phi_2 = 2\text{K.E.} = \sum_{i,j=1}^r A_{ij}\dot{x}_i\dot{x}_j \quad (2)$$

of matrix (A) and determinant $[A]$ where

$$\Omega = \frac{1}{h^r} \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \int_{\alpha_r}^{\beta_r} \dots \int_{\alpha_1}^{\beta_1} e^{-1/2kT \sum_{i,j=1}^r B_{ij}P_iP_j} dP_1 \dots dP_r dx_1 \dots dx_r, \quad (4)$$

where h is Planck's constant, k is the Boltzmann constant, x_i varies from α_i to β_i , P_i from $-\infty$ to $+\infty$. It will be proven that in general, the integral with respect to the momenta is: $(2\pi kT)^{r/2} [A]^{1/2} / h^r$. $[A]$ is readily obtained from (2). The problem is then reduced to the evaluation of:

$$\Omega = [(2\pi kT)^{r/2} / h^r] \int_{\alpha_r}^{\beta_r} \dots \int_{\alpha_1}^{\beta_1} [A]^{1/2} dx_1 \dots dx_r. \quad (5)$$

This expression may be integrated to furnish the complete solution of the problem. Examples will be given in IV.

Proof:

Let $\Phi_3 = \sum_{i,j=1}^r B_{ij}P_iP_j$ be a real positive definite quadratic form with nonsingular matrix (B) and determinant $[B]$. If the P 's are subjected to a homogeneous linear transformation with the matrix (C) the new quadratic form in, say, the P'' 's, has the matrix $(C)'(B)(C)$ where $(C)'$ is the transposed matrix of (C) . In particular Φ_3 may be reduced by a real orthogonal transformation in r variables of determinant 1 to the normal form: $\sum_{i=1}^r D_iP_i'^2$. Because of the positive definiteness of the form, none of the D_i 's may be identically zero.** The Jacobian of the transformation is 1. The integrand is positive and the limits of integration are from $-\infty$ to $+\infty$. (4) becomes:

$$\Omega = \frac{1}{h^r} \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} \int_{\alpha_r}^{\beta_r} \dots \int_{\alpha_1}^{\beta_1} e^{-1/2kT \sum_{i=1}^r D_iP_i'^2} dP_1' \dots dP_r' dx_1 \dots dx_r. \quad (4a)$$

The integration with respect to the momenta gives at once:

* The symbols for a matrix $()$, and determinant $[]$, enclosing capital letters are adhered to throughout.

** The theorems from the theory of real quadratic forms

$A_{ij} = f_{ij}(x_1, x_2, \dots, x_r)$.* If the matrix is nonsingular, the transformation to Hamiltonian form gives:

$$\Phi_3 = 2\text{K.E.} = \sum_{i,j=1}^r B_{ij}P_iP_j \quad (3)$$

of matrix (B) and determinant $[B]$ where $P_i = \partial \text{K.E.} / \partial \dot{x}_i$;

$$B_{ij} = (\text{cofactor of } A_{ij}) / [A] = f_{ij}'(x_1, \dots, x_r);$$

$$(B) \times (A) = (1); \quad [B] \times [A] = 1.$$

It is necessary to integrate over the momentum and configuration space the following definite integral, which is the limiting value approached by $\sum_a \Sigma_\beta \dots \Sigma_\lambda e^{-\epsilon_a, \beta, \dots, \lambda / kT}$ with increasing temperature and especially rapidly for molecules with large moments of inertia.

are stated explicitly here. Reference: Bocher's *Higher Algebra*, or Hilton's *Linear Substitutions*.

$$\Omega = \frac{(2\pi kT)^{r/2}}{h^r} \int_{\alpha_r}^{\beta_r} \cdots \int_{\alpha_1}^{\beta_1} \left(\frac{1}{D_1 D_2 \cdots D_r} \right)^{1/2} dx_1 \cdots dx_r. \quad (4b)$$

$D_1 D_2 \cdots D_r = [C]' [B] [C] = [B]$, since for a real orthogonal matrix $[C]' = [C]^{-1} = 1$. Thus (4b) becomes:

$$\Omega = [(2\pi kT)^{r/2}/h^r] \int_{\alpha_r}^{\beta_r} \cdots \int_{\alpha_1}^{\beta_1} [A]^{1/2} dx_1 \cdots dx_r. \quad (5)$$

If the coefficient of the integral in (5) is called λ and the integral itself Λ , then the rotational partition function

$$\Omega = \lambda \Lambda \quad (6a)$$

and the rotational contribution to the entropy (for the gaseous state and excluding nuclear spin and symmetry number corrections), is, by well-known methods:

$$S_R = R \ln \{ \lambda \Lambda e^{r/2} \}. \quad (6b)$$

III. A SPECIAL CASE; DERIVATION OF A PREVIOUSLY SUGGESTED EMPIRICAL FORMULA

In the special case that $[A]$ has a form closely related to $\sin^2 \theta \prod_{i=1}^r I_i$, where $\prod_{i=1}^r I_i$ is the product of moments of inertia and where θ , the angle of inclination of the frame, varies from 0 to π , the other angular coordinates from 0 to 2π , then (5) may be integrated at once to give*

$$\Omega' = 2^{3r/2} \pi^{3r/2-1} (kT)^{r/2} \left\{ \prod_{i=1}^r I_i \right\}^{1/2} / h^r \quad (7)$$

and $S_R = R \ln e^{r/2} \Omega'$ which is exactly the empirical formula proposed and tested by Halford.⁴ It is now possible to discuss this formula theoretically: (a) There is an uncertainty in the correct moments⁵ to be substituted in (7), because of the nonrigidity of the molecule. The correct moments are always in $[A]$ of (6a, b). (b) Because of the free rotation of the tops, the so-called

* An example of the special case for which $[A]$ has the form $\sin^2 \theta \prod_{i=1}^r I_i$ is the asymmetric top of moments of inertia A, B, C , for which $[A] = ABC \sin^2 \theta$. Formula (7) will apply because formulae (5), (6a, 6b) reduce to (7) in this case.

⁴ Kassel, J. Chem. Phys. 3, 115 (1935).

"reduced" moments³ must be used. In certain cases, the magnitude of these reduced moments may be easily found. In general, however, the proper reduced moment will not appear in (2) but in its determinant $[A]$. This is precisely what is necessary for the application of (6a, b). (See Section IV, (9) for example.) (c) In asymmetric molecules, where the coupling between spins does not vanish, $[A]$ will contain the spin coordinates explicitly, and expressions of the form (7) are obtained only as a first approximation, depending on the asymmetry of the molecule. A specific example of this is given in (11), (12).

IV. APPLICATIONS

(A) As a first illustration of the direct applicability of (5), (6a, b), the limiting rotational partition function and entropy of tetramethylmethane will be obtained and compared with the summation over the quantum levels.

The model for this molecule consists of four freely spinning gyroscopes located at the corners of a rigid tetrahedral frame. Seven coordinates are used; three, the usual Eulerian angles, refer the frame to axes fixed in space, while the other four refer the spin of the tops relative to the frame. Details will be found in Lacoste's paper.³ The kinetic energy is given in form (2). Its determinant $[A]$ is a symmetric 7th order determinant, which after rearrangement, is simply evaluated to be: $I_0^3 I_4^4 \sin^2 \theta$

where I_0 refers to the reduced moment considered in III, I_4 is the moment of inertia of a methyl top about the spin axis.

Applying formulae (5), (6a, b)

$$\Omega = \frac{(2\pi kT)^{7/2} (I_0^3 I_s^4)^{1/2}}{h^7} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \int_{\theta=0}^{\pi} \sin \theta d\theta d\psi d\varphi d\alpha_1 d\alpha_2 d\alpha_3 d\alpha_4$$

$$\text{and} \quad S_R = R \ln e^{7/2} 2^{21/2} \pi^{19/2} (kT)^{7/2} (I_0^3 I_s^4)^{1/2} / h^7. \quad (8)$$

The summation over the quantum states:

$$\Omega' = \sum_{j\theta} \sum_{m_\varphi} \sum_{m_\psi} \sum_{m_1} \sum_{m_2} \sum_{m_3} \sum_{m_4} e^{-f(j, m_\varphi, m_1, m_2, m_3, m_4)}$$

has been carried out by Kassel,⁵ whose result is:

$$S_R' = R \ln \frac{e^{7/2} 2^{21/2} \pi^{19/2} (kT)^{7/2} (I_0^3 I_s^4)^{1/2}}{h^7} + \frac{R\sigma}{4} \\ + \text{terms negligible even at } 100^\circ\text{K}, \quad (9)$$

where $\sigma = 0.0022$ at 100°K and is inversely proportional to T . Neglecting $R\sigma/4$ which, even as low as 100°K produces an error of less than 0.005 cal./deg. (9) becomes identical with (8).

(B) As a second illustration, the method will be applied to a general class of molecules, for only Case V of which (see below) has a quantum mechanical solution been attempted.

The model (Fig. 1) is a molecule consisting

of two freely spinning asymmetric tops subject to the restriction that a line from the center of gravity of one top through the center of gravity of the molecule be the common principal axis, and also spin axis of each top. Molecular examples will be given below. The usual Eulerian angles refer three axes fixed in each top at the center of gravity of the molecule, O , to a reference frame fixed in space, origin at O . θ is the angle of inclination of $Z_1 Z_2$ to OZ_0 ; ψ is the angle between the fixed axis X_0 and the nodal line ON ; φ_1 is the angle between ON and X_1 ; φ_2 is the angle between ON and X_2 where X_1, Y_1, X_2, Y_2 lie in the equatorial plane. Let A, B, C be the moments of inertia of top 1 about X_1, Y_1 and Z_1 ; and D, E, F , be the moments of inertia of top 2 about X_2, Y_2 and Z_2 .

The kinetic energy of rotation is expressible in the form:

$$2K.E. = A(\dot{\theta} \cos \varphi_1 + \dot{\psi} \sin \theta \sin \varphi_1)^2 + B(-\dot{\theta} \sin \varphi_1 + \dot{\psi} \sin \theta \cos \varphi_1)^2 \\ + D(\dot{\theta} \cos \varphi_2 + \dot{\psi} \sin \theta \sin \varphi_2)^2 + E(-\dot{\theta} \sin \varphi_2 + \dot{\psi} \sin \theta \cos \varphi_2)^2 \\ + C(\dot{\varphi}_1 + \dot{\psi} \cos \theta)^2 + F(\dot{\varphi}_2 - \dot{\psi} \cos \theta)^2. \quad (10)$$

The determinant $[A]$ of (10) is readily found to be:

$$[A] = CF \sin^2 \theta [AB + DE + (AD + BE) \sin^2 (\varphi_1 - \varphi_2) + (AE + BD) \cos^2 (\varphi_1 - \varphi_2)]. \quad (11)$$

Formulae (5), (6a, b) may now be applied, by using (11) to give the rotational partition function and the rotational entropy. The integral required is:

$$\frac{(2\pi kT)^2}{h^4} (CF)^{1/2} \int_{\varphi_2=0}^{2\pi} \int_{\varphi_1=0}^{2\pi} \int_{\psi=0}^{2\pi} \int_{\theta=0}^{\pi} \\ \times \sin \theta [AB + DE + (AD + BE) \sin^2 (\varphi_1 - \varphi_2) + (AE + BD) \cos^2 (\varphi_1 - \varphi_2)]^{1/2} d\theta d\psi d\varphi_1 d\varphi_2. \quad (12)$$

Integrating with respect to θ and ψ , and after a slight change of variables, (12) may be brought to the form:*

$$\Omega = 2\pi \lambda m \int_0^{2\pi} (1 - k^2 \sin^2 u)^{1/2} du, \quad (13a)$$

* In order to bring (12) to the form (13a), it is required that $A > B$; $E > D$. Interchanging the magnitudes of A and B , or of D and E in (12) will interchange the mag-

nitudes of the coefficients of the $\sin^2 (\varphi_1 - \varphi_2)$ and $\cos^2 (\varphi_1 - \varphi_2)$ terms, but will not alter the value of the integral.

where

$$\begin{aligned} u &= \varphi_1 - \varphi_2, & A > B; E > D, \\ \lambda &= (CF)^{\frac{1}{2}}(4\pi)(2\pi kT)^2/h^4, & K &= \left(\frac{(A-B)(E-D)}{(A+D)(B+E)} \right)^{\frac{1}{2}} < 1, \\ m &= ((A+D)(B+E))^{\frac{1}{2}}, \end{aligned}$$

This is a well-known elliptic integral of the second kind, and the result may be put in the form:

$$\Omega_1 = \frac{2^6 \pi^5 (kT)^2}{h^4} \{ (CF)(A+D)(B+E) \}^{\frac{1}{2}} \left[1 - \frac{K^2}{2^2} - \frac{1^2}{2^2} \frac{3}{4^2} K^4 - \dots \right], \quad (13b)$$

where the series in $[\dots]$ rapidly approaches 1 as $A \rightarrow B$ or $D \rightarrow E$.

Case I. $A > B; E > D; C \neq F$

Example: Derivatives of diphenyl, where atoms have been substituted symmetrically in either one or both of the phenyl groups. The partition function is (13b) and the rotational entropy is $R \ln e^2 \Omega_1$.

Case II. $A = E; B = D; C = F$

Two freely spinning equivalent asymmetric tops.

Example: Diphenyl.

$$\begin{aligned} \Omega_2 &= [2^6 \pi^5 (kT)^2 / h^4] \{ (CF)(A+D)^2 \}^{\frac{1}{2}} \\ &\quad \times \left[1 - \frac{K^2}{2^2} - \frac{1^2 \cdot 3K^4}{2^2 \cdot 4^2} - \dots \right]; \\ K^2 &= \frac{(A-D)^2}{(A+D)^2} \quad \text{and} \quad S_R = R \ln e^2 \Omega_2. \end{aligned} \quad (13c)$$

Case III. $A = B; E > D; C \neq F$

Top 1 symmetric.

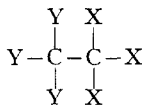
Example: Toluene

$$\begin{aligned} \Omega_3 &= [2^6 \pi^5 (kT)^2 / h^4] \{ (CF)(A+D)(A+E) \}^{\frac{1}{2}}; \\ K &= 0 \quad \text{and} \quad S_R = R \ln e^2 \Omega_3. \end{aligned} \quad (13d)$$

Case IV. $A = B; D = E; C \neq F$

Two freely spinning nonequivalent symmetric tops.

Example: All symmetrically substituted derivatives of ethane of the type:



$$\begin{aligned} \Omega_4 &= [2^6 \pi^5 (kT)^2 / h^4] \{ (CF)(A+D)^2 \}^{\frac{1}{2}}; \\ K &= 0 \quad \text{and} \quad S_R = R \ln e^2 \Omega_4. \end{aligned} \quad (13e)$$

Case V. $A = B = D = E; C = F; A' = 2A$

Two freely spinning equivalent symmetric tops.

Example: Ethane.

$$\begin{aligned} \Omega_5 &= 2^6 \pi^5 (kT)^2 (A'C) / h^4; \\ K &= 0 \quad \text{and} \quad S_R = R \ln e^2 \Omega_5. \end{aligned} \quad (13f)$$

SUMMARY

(1) A general formula is derived for the limiting rotational partition function and entropy of non-rigid polyatomic molecules (apart from nuclear spin and symmetry number corrections and assuming no potential). In order to apply the formula, it is unnecessary to obtain the Hamiltonian form of the rotational energy, and to perform the integration over the momentum space.

(2) A previous formula for the rotational entropy, suggested empirically, is derived as a special case of the general formula.

(3) Illustrations of the use of the formulae derived are made to:

(a) The spherically symmetric top with internal gyroscopes, such as tetramethylmethane, and compared with the summation using quantum-mechanical energy levels.

(b) The general case of a molecule consisting of two freely spinning asymmetric tops subject to the condition that a common principal axis through the center of gravity of one top and the center of gravity of the molecule be a spin axis for each top; rotational partition functions and entropies are obtained for five special cases of this model, and molecular examples given.