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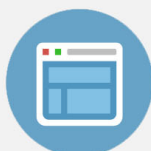
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The Effect of Rotational Distortion on the Thermodynamic Properties of Water and Other Polyatomic Molecules

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The classical mechanical expression for the energy of a non-vibrating, rotating polyatomic molecule is obtained which includes a correction term arising from the centrifugal distortion of the molecule caused by the rotation. Since the rotational partition function closely approaches the classical phase integral for room temperatures or higher, the latter is used to calculate the effect of centrifugal distortion on the entropy, heat capacity and free energy.

The correction terms $-\rho RT^2$, $2\rho RT$ and $2\rho RT$ must be added to F , S and C_v , respectively. ρ is a constant characteristic of each molecule. The values of ρ calculated are: H_2O , $2.04 \cdot 10^{-5}$; H_2S , $1.62 \cdot 10^{-5}$; NH_3 , $1.45 \cdot 10^{-5}$; CH_4 , $1.72 \cdot 10^{-5}$; C_2H_4 , 0.79×10^{-5} . For water this correction amounts to approximately $\frac{1}{2}$ percent of the heat capacity at the boiling point, or $+0.032$ entropy unit.

It is customary in calculating the thermodynamic properties of polyatomic molecules from spectral data to assume that the partition function can be separated into three factors, corresponding to the separation of the energy into the translational, rotational, and vibrational parts. Furthermore, it has been found to be a good approximation to use the classical limiting values for the translational and rotational factors for room temperature or above. Ordinarily, the rotational partition function is computed for a rigid rotator, neglecting any effect due to the distortion caused by rotation. It is the purpose of this paper to show how this distortional effect can be included in the calculations and to point out that it is not a negligible correction for certain light molecules with weak bending restoring forces. Classical mechanics will be used throughout.

THE PHASE INTEGRAL FOR THE RIGID ROTATOR

The classical limiting expression for the rotational partition function is the phase integral¹

$$Q_R = (1/h^3) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} e^{-W_R/kT} \times d\varphi d\theta d\chi dp_\varphi dp_\theta dp_\chi, \quad (1)$$

in which the Eulerian angles φ , θ and χ and their conjugate momenta p_φ , p_θ and p_χ have been used. h is Planck's constant, and W_R the rotational energy. For our purposes, it is more convenient to express W_R in terms of P_x , P_y and

P_z , the components of the angular momentum along a set of Cartesian axes x , y and z moving with the molecule. The relations between P_x , P_y , P_z and p_φ , p_θ , p_χ are²

$$\begin{aligned} p_\theta &= \sin \chi P_x + \cos \chi P_y, \quad p_\chi = P_z, \\ p_\varphi &= -\sin \theta \cos \chi P_x \\ &\quad + \sin \theta \sin \chi P_y + \cos \theta P_z. \end{aligned} \quad (2)$$

The Jacobian of this transformation is $\sin \theta$. Consequently, the phase integral becomes

$$Q_R = (8\pi^2/h^3) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-W_R/kT} dP_x dP_y dP_z, \quad (3)$$

where the new set of variables φ , θ , χ , P_x , P_y , P_z has been introduced and the integration carried out over $d\varphi d\theta d\chi$, since in terms of the new variables W_R is independent of the angles.

The energy of a rigid rotator is given by

$$W_R^0 = \frac{1}{2}(P_x^2/A_0 + P_y^2/B_0 + P_z^2/C_0), \quad (4)$$

in which A_0 , B_0 , C_0 are the principal moments of inertia. On inserting this in the integral for Q_R , the result is obtained that

$$Q_R^0 = (8\pi^2/h^3)(2\pi kT)^{\frac{3}{2}}(A_0 B_0 C_0)^{\frac{1}{2}}, \quad (5)$$

which is the usual result. From it one obtains the well-known expressions for the contribution of the rotation to the free energy F , entropy S , and heat capacity C_v , by using the relations

$$\begin{aligned} F &= -RT \log Q; \quad S = R \log Q \\ &\quad + RT(d \log Q/dT) \\ C_v &= 2RT(d \log Q/dT) + RT^2(d^2 \log Q/dT^2), \end{aligned} \quad (6)$$

in which R is the gas constant.

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¹ See R. H. Fowler, *Statistical Mechanics*, p. 44.

² See for example, E. B. Wilson, Jr. and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936), Eq. (30).

CALCULATION OF THE ROTATIONAL DISTORTION

For semi-rigid polyatomic molecules the classical energy of rotation and vibration is given by³

$$W = \frac{1}{2} \sum_{\alpha, \beta} \mu_{\alpha\beta} (P_\alpha - p_\alpha)(P_\beta - p_\beta) + \frac{1}{2} \sum p_k^2 + V, \quad (7)$$

in which $\alpha, \beta = x, y, \text{ or } z$, p_α is the α component of the vibrational angular momentum, P_α is the corresponding component of the total angular momentum, and p_k is the momentum conjugate to the normal coordinate Q_k . The coefficients $\mu_{\alpha\beta}$ are the elements of the matrix reciprocal to the matrix

$$\begin{pmatrix} A' & -D' & -F' \\ -D' & B' & -E' \\ -F' & -E' & C' \end{pmatrix},$$

in which A', B', C' are equal (up to quadratic terms in Q_k) to the instantaneous moments of inertia, while D', E', F' are similarly related to the instantaneous products of inertia. All these quantities are functions of the normal coordinates. V is the potential energy.

If we assume that the molecule is not vibrating, so that \dot{p}_k and \dot{p}_α are zero, then it is found that p_α and $\partial p_\alpha / \partial Q_k$ are zero. Consequently, one of Hamilton's equations can be written in the form

$$\frac{\partial H}{\partial Q_k} = \frac{1}{2} \sum_{\alpha, \beta} \frac{\partial \mu_{\alpha\beta}}{\partial Q_k} P_\alpha P_\beta + \frac{\partial V}{\partial Q_k} = -\dot{p}_k = 0. \quad (8)$$

For harmonic forces (an approximation) the potential energy can be written

$$V = \frac{1}{2} \sum_k \lambda_k Q_k^2, \quad (\lambda_k = 4\pi^2 \nu_k^2), \quad (9)$$

with ν_k signifying the frequency of the normal vibration Q_k . Furthermore, the quantity $\mu_{\alpha\beta}$ can be expanded into the form

$$\mu_{\alpha\beta} = \mu_{\alpha\beta}^0 + \sum_k \mu_{\alpha\beta}^{(k)} Q_k + \dots, \quad (10)$$

in which $\mu_{\alpha\beta}^0$ is the equilibrium value and

$$\mu_{\alpha\beta}^{(k)} = (\partial \mu_{\alpha\beta} / \partial Q_k)_0. \quad (11)$$

³ Ref. 2, Eq. (13).

Consequently, if higher powers of Q_k are neglected, Eq. (8) gives

$$Q_k = - (1/2\lambda_k) \sum_{\gamma, \delta} \mu_{\gamma\delta}^{(k)} P_\gamma P_\delta \quad (k=1, 2, \dots, 3N-6), \quad (12)$$

so that

$$\mu_{\alpha\beta} = \mu_{\alpha\beta}^0 - \frac{1}{2} \sum_{\gamma, \delta, k} \mu_{\alpha\beta}^{(k)} \mu_{\gamma\delta}^{(k)} P_\gamma P_\delta / \lambda_k. \quad (13)$$

These expressions for $\mu_{\alpha\beta}$, Q_k and V , when inserted into Eq. (7) yield

$$W_R = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta}^0 P_\alpha P_\beta - (1/8) \sum_{\alpha, \beta, \gamma, \delta, k} \times (\mu_{\alpha\beta}^{(k)} \mu_{\gamma\delta}^{(k)} / \lambda_k) P_\alpha P_\beta P_\gamma P_\delta \quad (14)$$

for the rotational energy, including a correction for the rotational distortion. The coefficient $-1/8$ is made up of a contribution $-1/4$ from the kinetic energy and $+1/8$ from the increased potential energy.

It is not necessary to use normal coordinates to get the above results, and in actual applications other coordinates are frequently more convenient. In terms of the $3N-6$ internal coordinates q_i , the potential energy is

$$V = \frac{1}{2} \sum b_{ij} q_i q_j, \quad (15)$$

to the same approximation as before. The constants b_{ij} are the force constants. The coefficients $\mu_{\alpha\beta}$ can be expanded in terms of the q_i 's, with the result that

$$\mu_{\alpha\beta} = \mu_{\alpha\beta}^0 + \sum \bar{\mu}_{\alpha\beta}^{(i)} q_i + \dots \quad (16)$$

Consequently the analogue of Eq. (12) is

$$\frac{1}{2} \sum \bar{\mu}_{\gamma\delta}^{(i)} P_\gamma P_\delta + \sum_i b_{ij} q_j = 0, \quad (i=1, 2, \dots, 3N-6). \quad (17)$$

These may be solved for q_i , the values obtained substituted in Eq. (16), and the resulting expression for $\mu_{\alpha\beta}$ used in the equation for W_R . An equation corresponding to Eq. (14) but expressed in terms of $\bar{\mu}_{\alpha\beta}^{(i)}$ and b_{ij} rather than $\mu_{\alpha\beta}^{(k)}$ and λ_k will result.

If we introduce the symbol $\tau_{\alpha\beta\gamma\delta}$, W_R becomes

$$W_R = W_R^0 + \frac{1}{4} \sum_{\alpha, \beta, \gamma, \delta} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta. \quad (18)$$

In terms of $\mu_{\alpha\beta}^{(k)}$ and λ_k , $\tau_{\alpha\beta\gamma\delta}$ is given by

$$\tau_{\alpha\beta\gamma\delta} = -\frac{1}{2} \sum_k \mu_{\alpha\beta}^{(k)} \mu_{\gamma\delta}^{(k)} / \lambda_k. \quad (19)$$

THE PHASE INTEGRAL FOR THE SEMI-RIGID ROTATOR *

The second term of Eq. (18) is a correction term, consequently its contribution to the exponential $e^{-W_R/kT}$ will be expanded as a power series.

$$e^{-W_R/kT} = e^{-W_R^0/kT} [1 - (1/4kT) \sum_{\alpha, \beta, \gamma, \delta} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta + \dots]. \quad (20)$$

It will be found sufficient to take the first two terms only. The phase integral, Eq. (3), then becomes

$$Q_R = Q_R^0 - (2\pi^2/h^3 kT) \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} \int \int \int P_\alpha P_\beta P_\gamma P_\delta e^{-W_R^0/kT} dP_x dP_y dP_z. \quad (21)$$

For each set of values of $\alpha\beta\gamma\delta$, the integral factors, becoming

$$\int_{-\infty}^{\infty} P_x^r e^{-P_x^2/2A_0 kT} dP_x \cdot \int_{-\infty}^{\infty} P_y^s e^{-P_y^2/2B_0 kT} dP_y \cdot \int_{-\infty}^{\infty} P_z^t e^{-P_z^2/2C_0 kT} dP_z \quad (22)$$

in which $r, s, t = 0, 1, 2, 3$ or 4 with the condition that $r+s+t=4$. However, if r, s , or t is an odd integer, the corresponding integral vanishes. With r, s and t all even the integrals can be evaluated, with the result that

$$Q_R = Q_R^0 (1 + \rho T), \quad (23)$$

in which

$$\rho = -\frac{1}{4} k (3\tau_{xxxx} A_0^2 + 3\tau_{yyyy} B_0^2 + 3\tau_{zzzz} C_0^2 + 2\tau_{xxyy} A_0 B_0 + 2\tau_{yyzz} B_0 C_0 + 2\tau_{zzxx} C_0 A_0 + 4\tau_{xyzy} A_0 B_0 + 4\tau_{yzxz} B_0 C_0 + 4\tau_{zxzx} C_0 A_0). \quad (24)$$

* In these computations it is assumed that the vibrational and rotational partition functions can be treated as independent, which is not, of course, strictly true.

The relations $\tau_{xyxy} = \tau_{yxxy} = \tau_{xyyx} = \tau_{yxyx}$, etc., have been used.

Consequently, the corrected expressions for F , S and C_v are

$$F = F' - \rho RT^2, \quad (25)$$

$$S = S' + 2\rho RT, \quad (26)$$

$$C_v = C_v' + 2\rho RT, \quad (27)$$

in which higher powers of ρT have been dropped. F' , S' and C_v' represent the quantities calculated for the rigid rotator, plus the translational and vibrational contributions.

NUMERICAL RESULTS AND DISCUSSION

Table I shows the numerical values of ρ for several light molecules. These have all been

TABLE I. Values of ρ for several molecules.⁴

	H ₂ O	H ₂ S	NH ₃	CH ₄	C ₂ H ₄	
ρ	2.04	1.62	1.45	1.72	0.79	($\times 10^{-6}$)

calculated with the assumption of valence forces. It is seen from these results that the distortional correction is not entirely negligible in these light molecules, but that it may contribute a correction of as much as half a percent to the heat capacity in certain cases. For heavier molecules, however, the effect will be quite small.

Considerable experimental data exist on the heat capacity of steam, a summary of which is given by Keyes.⁵ When the above correction is applied to Gordon's⁶ calculated values of C_p^0 , the agreement with the average of the experimental values is somewhat improved.

⁴ The experimental data used were: for H₂O, the force constants were taken from L. G. Bonner, Phys. Rev. **46**, 458 (1934); for H₂S, from P. C. Cross, Phys. Rev. **47**, 7 (1935); for NH₃, from J. B. Howard, J. Chem. Phys. **3**, 207 (1935); for CH₄, the fundamental frequencies listed by N. Ginsburg and E. F. Barker, J. Chem. Phys. **3**, 668 (1935); for C₂H₄, the force constants were taken from L. G. Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

⁵ F. G. Keyes, L. B. Smith and H. T. Gerry, Proc. Am. Acad. Arts and Sciences, **70**, 319 (1936). These results have been multiplied by 18.0154/4.1833 to yield 15° cal./mole.

⁶ A. R. Gordon, J. Chem. Phys. **2**, 65 (1934). These results have been corrected to $R=1.9863$.