

METHOD FOR CALCULATION OF ROTATIONAL PARTITION FUNCTION

A. MARTIN and G. VARSÁNYI

Department of Physical Chemistry, Technical University, H-1521 Budapest

Received May 10, 1982

Summary

A new approximative method is suggested for the determination of the rotational partition function. The proposed formula combines the advantages of other methods used and its error is less than 1%.

One of the fundamental problems of calculations based on statistical mechanics is the evaluation of the partition function q :

$$q = \sum_{i=1}^{\infty} g_i \exp(-\varepsilon_i/kT) \quad (1)$$

where ε_i are the energy values of the g_i -fold degenerated characteristic rotational levels, T is the temperature and k is the Boltzmann constant.

The allowed energy states of molecules can be given as the sum of the translational, rotational, vibrational and electron energies and the quantum theory gives expressions for the calculation of these energy members. Accordingly, the partition function can be given as a product of the corresponding contributions. The rotational partition function contribution can be calculated only approximately. A simple but very exact approximative calculation is suggested here for the determination of the rotational partition function.

The quantization of the rotational energy levels of linear molecules with small moment of inertia is not sufficiently fine for a summation replaced by integral formula. The usual integral approximation [1] is very inaccurate especially for molecules of small moment of inertia at low temperature. For this reason a new approximative function is proposed instead of integral calculation.

The rotational partition function is given by the following equation

$$q_r = \sum_{J=0}^{\infty} (2J+1) \exp\left(-\frac{J(J+1)h^2}{8\pi^2IkT}\right) \quad (2)$$

In this equation the allowed values of the rotational quantum number J are $0, s, 2s, \dots$ where s is the symmetry number (for symmetric linear molecules is

equal to 2, otherwise to 1), I is the moment of inertia and h is the Planck's constant. Replacing the sum on the right-hand side of (2) by the corresponding integral a very simple equation can be obtained:

$$q_r = \frac{8\pi^2 IkT}{sh^2} \quad (3)$$

For a more accurate formula, Mulholland [1] proposed an improved approximation:

$$q_r = \frac{8\pi^2 IkT}{sh^2} \left[1 + \frac{1}{3} \frac{h^2}{8\pi^2 IkT} + \frac{1}{15} \left(\frac{h^2}{8\pi^2 IkT} \right)^2 + \frac{4}{315} \left(\frac{h^2}{8\pi^2 IkT} \right)^3 + \dots \right] \quad (4)$$

Our suggested formula combines the advantages of both methods: the simplicity of the integral approximation and the accuracy of Mulholland's equation. Our equation was obtained by the analysis of the error function of the integral approximation. A universal error function has been derived, introducing the so-called characteristic rotational temperature ($\Theta_r = h^2/8\pi^2 Ik$). Using this temperature unit, the function becomes independent of any material property, except the symmetry number. This universal error function has been examined in the intervals of $1 < T/\Theta_r < 30$ for $s=1$ and 2 , $8 < T/\Theta_r < 30$ for $s=2$ only, as for greater T/Θ_r values the error of the simple integral approximation is negligible (less than 1%) and for smaller T/Θ_r , the first two terms of the original infinite series give already satisfactory approximation. The analytical form of the error function in this interval has been determined by hyperbolic fitting and the following formulae were obtained:

$$q_r = \frac{A^2}{A-0.30} \quad (s=1) \quad (5)$$

$$q_r = \frac{A^2}{2A-0.68} \quad (s=2)$$

where $A = T/\Theta_r$. The validity of these equations exceeds the above intervals. They have no upper limit in A , while its lower limit is 1 for $s=1$ and 2.4 for $s=2$. The committed error is less than 1%. Below this limits the Mulholland's formula is not suitable either, but in this case already the third term of (2) is negligible.

Accordingly, the suggested rotational partition function formulae for linear molecules:

$$\text{for } s=1: \quad q_r = \frac{(T/\Theta_r)^2}{(T/\Theta_r) - 0.30} \quad T/\Theta_r > 1$$

$$q_r = 1 + 3 \exp(-2\Theta_r/T) \quad T/\Theta_r \leq 1$$

$$\text{for } s=2: \quad q_r = \frac{(T/\Theta_r)^2}{2(T/\Theta_r) - 0.68} \quad T/\Theta_r > 2.4$$

$$q_r = 1 + 5 \exp(-6\Theta_r/T) \quad T/\Theta_r \leq 2.4$$

The error of the rotational partition function calculated by these equations is less than 1% in the whole interval. This is illustrated in Table 1, where the different rows represent some rotational partition functions (q_r) calculated by summation (a), by integration (b), by the first two terms of (2) (c), by Mulholland's formula (d) and by the suggested formula (e) and the errors in (b), (c), (d), (e).

Table 1

Some rotational partition functions (q_r) calculated by summation (a), by integration (b), by the first two terms of formula (2) (c), by Mulholland's formula (d) and by the suggested formula (e) and the errors in (b), (c), (d), (e)

T/Θ_r		0.5	0.8	1.0	1.5	2.4	3.0	5.0	10.0
$s=1$	a	1.055	1.249	1.418	1.885	2.764	3.357	5.347	10.340
	b	0.500	0.800	1.000	1.500	2.400	3.000	5.000	10.000
	c	1.055	1.246	1.406	1.791	2.304	2.540	3.011	3.456
	d	1.017	1.237	1.413	1.883	2.763	3.357	5.347	10.340
	e	1.250	1.280	1.429	1.875	2.743	3.333	5.319	10.309
$s=2$	a	1.000	1.003	1.012	1.092	1.413	1.688	2.674	5.170
	b	0.250	0.400	0.500	0.750	1.200	1.500	2.500	5.000
	c	1.000	1.003	1.012	1.092	1.410	1.677	2.506	3.744
	d	0.509	0.618	0.706	0.942	1.382	1.678	2.674	5.170
	e	0.781	0.696	0.758	0.970	1.398	1.692	2.682	5.176
error %	b	52.6	35.9	29.5	20.4	13.2	10.6	6.5	3.3
	c	0.0	0.2	0.8	5.0	16.6	24.3	43.7	66.6
	d	3.6	1.0	0.4	0.1	0.0	0.0	0.0	0.0
	e	-18.5	-2.5	-0.7	0.5	0.8	0.7	0.5	0.3
$s=2$	b	75.0	60.1	50.6	31.3	15.0	11.1	6.5	3.3
	c	0.0	0.0	0.0	0.0	0.2	0.7	6.3	27.6
	d	49.1	38.3	30.2	13.7	2.2	0.6	0.0	0.0
	e	21.9	30.6	25.2	11.2	1.0	-0.2	-0.3	-0.1

References

1. EVERDELL, M. H.: Statistical Mechanics and its Chemical Applications Academic Press, London 1957

Dr. Antal MARTIN }
Prof. Dr. György VARSÁNYI } H-1521 Budapest