

Thermodynamic Functions of Tetramethylmethane

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interesting to note that if the two bending frequencies arising from translational terms are stiff enough so that the system lies almost entirely in the corresponding lowest states, the reaction diameter as just defined will be less than the kinetic diameter by the factor $8\pi^2IkT/h^2$ which may reach value of the order of 100 for heavy atoms and moderately high temperatures.

The present formulation of the calculation of absolute rates of chemical reactions has certain features in common with a number of more intuitive previous treatments,¹¹ but has more in common with the treatment of Pelzer and Wigner. It goes beyond these in formulating the general problem in a way susceptible to treatment with our present potential energy surfaces and in pointing out the consequences of quantization on the temperature coefficient and the difference in rate for isotopes. The fact that the activated complex is much like any other molecule except in the degree of freedom in which it is flying to pieces makes possible our comparatively simple formulation. A number of investigations are now in progress in which the absolute rate of reaction is being calculated.

I want particularly to thank Dr. Bryan Topley for valuable discussions as it was with him the present calculations of absolute rates were begun. I also want to thank Professors Taylor and Webb for helpful discussions.

¹¹ W. H. Rodebush, *J. Chem. Phys.* **1**, 440 (1933); V. K. La Mer, *ibid.* **1**, 289 (1933); O. K. Rice and H. Gershinowitz, *ibid.* **2**, 853 (1934).

Thermodynamic Functions of Tetramethylmethane¹

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The Q -sum corresponding to La Coste's eigenvalues for the rotational levels of tetramethylmethane has been expressed by the usual asymptotic expansion. The relatively large coupling terms between the various rotations cancel almost exactly in the Q -sum, so that the thermodynamic functions are scarcely affected by the coupling.

LA COSTE³ has given an exact solution for the rotational wave equation of tetramethylmethane with zero potential energy. The energy levels are

$$E = (h^2/8\pi^2 I_0) [j(j+1) + (I_0/I_s)(m_1^2 + m_2^2 + m_3^2 + m_4^2) + q^2 - 2qm_\phi], \quad (1)$$

where I is the moment of inertia of the molecule with methyl groups fixed, I_s the moment of a methyl group about the $C-C$ axis, $I_0 = I - (4/3)I_s$ and

$$q^2 = m_1^2 + m_2^2 + m_3^2 + m_4^2 - (2/3)(m_1m_2 + m_1m_3 + m_1m_4 + m_2m_3 + m_2m_4 + m_3m_4). \quad (2)$$

The quantum numbers m_1, m_2, m_3 and m_4 of the single methyl groups take integral positive and negative values, while j, m_ϕ and m_x are the ordinary quantum numbers for a symmetrical top. The term q^2 within the bracket represents a coupling between the various internal rotations which raises the energy levels and thus decreases the Q -sum. The term $-2qm_\phi$ splits the levels without shift in their center of gravity and hence raises the Q -sum. Each of these effects is quite large, but the two will be found to cancel almost exactly.

With the notation

$$\sigma = h^2/8\pi^2 I_0 kT, \quad (3); \quad \rho = I_0/I_s, \quad (4)$$

the Q -sum is

$$Q = \sum_i \sum_{m_\phi} \sum_{m_x} \sum_{m_1} \sum_{m_2} \sum_{m_3} \sum_{m_4} \exp [-j(j+1)\sigma - \rho\sigma(m_1^2 + m_2^2 + m_3^2 + m_4^2) - q^2\sigma + 2qm_\phi\sigma]. \quad (5)$$

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³ La Coste, *Phys. Rev.* **46**, 718 (1934).

The term $e^{2qm_\varphi\sigma}$ may then be expanded as a power series, and each term replaced by its mean value over the range $m_\varphi = -j$ to $+j$, by the exact relations

$$\overline{m^2} = (1/3)j(j+1), \quad (6)$$

$$\overline{m^4} = (1/5)j^2(j+1)^2 - (1/15)j(j+1), \quad (7)$$

$$\overline{m^6} = (1/7)j^3(j+1)^3 - (1/7)j^2(j+1)^2 + (1/21)j(j+1). \quad (8)$$

Averages over odd powers naturally vanish. The sums over j , m_φ and m_x may now be executed at once, using Eqs. (34), (36), (39) and (43) of a previous paper.⁴ At this stage the result is

$$\begin{aligned} Q = & \sum_{m_1} \sum_{m_2} \sum_{m_3} \sum_{m_4} \pi^{1/2} \sigma^{-3/2} e^{\sigma/4} [1 + (\sigma - \sigma^2/6)q^2 \\ & + (\sigma^2/2 - \sigma^3/6 + 7\sigma^4/360)q^4 + (\sigma^3/6 - \sigma^4/12 \\ & + 7\sigma^5/360 - 31\sigma^6/15120)q^6 + \dots] \\ & \times \exp [-\rho\sigma(m_1^2 + m_2^2 + m_3^2 + m_4^2) - q^2\sigma] \\ = & \sum_{m_1} \sum_{m_2} \sum_{m_3} \sum_{m_4} \pi^{1/2} \sigma^{-3/2} e^{\sigma/4} [1 - (1/6)\sigma^2 q^2 \\ & + (7/360)\sigma^4 q^4 - (31/15120)\sigma^6 q^6 + \dots] \\ & \times \exp [-\rho\sigma(m_1^2 + m_2^2 + m_3^2 + m_4^2)]. \quad (9) \end{aligned}$$

The final sums are quite readily obtained, using the asymptotic expansion

$$\sum_{-\infty}^{\infty} e^{-am^2} = \pi^{1/2} \alpha^{-1/2} \quad (10)$$

and its derivatives with respect to α . All sums of the type $\sum_{-\infty}^{\infty} m^{2n+1} e^{-am^2}$ vanish identically. The result is

$$\begin{aligned} Q = & \pi^{5/2} \rho^{-2} \sigma^{-7/2} e^{\sigma/4} [1 - (1/3)\rho^{-1}\sigma \\ & + (7/54)\rho^{-2}\sigma^2 - (62/945)\rho^{-3}\sigma^3 + \dots]. \quad (11) \end{aligned}$$

⁴ Kassel, J. Chem. Phys. 1, 576 (1933).

Since $\rho = 31.54$,⁵ the factor in brackets is approximately $1 - 0.01\sigma + 0.001\sigma^2$ and is thus much less important than $e^{\sigma/4}$, the correction term which carries over from the ordinary rigid top. Both factors may be discarded above 100°K, where $\sigma = 0.00220$. The limiting high-temperature value is then

$$Q = \pi^{-1} (8\pi^3 kT/h^2)^{7/2} I_0^{3/2} I_s^2 \quad (12)$$

and, apart from symmetry and nuclear spin corrections,

$$S = R[(7/2) + \ln \pi^{-1} (8\pi^3 kT/h^2)^{7/2} I_0^{3/2} I_s^2]. \quad (13)$$

$$\text{Also, of course, } H = (7/2)RT \quad (14)$$

$$\text{and } C_p = (7/2)R. \quad (15)$$

When symmetry and nuclear spin are taken into account, the limiting high-temperature value of Q is multiplied by $2^{12}/3^4 \times 12 = 1024/243$.⁶ The effect on the asymptotic expansion is not in all cases quite this simple and cannot very easily be calculated. It is quite certain that the use of this factor is justified above 100°K. Deviations of the rotational specific heat from $(7/2)R$ will then be due to a potential energy associated with the internal rotation, and might be used as an experimental approach to the problem of determining this potential.

The limiting equation (13) agrees with the general equation tentatively proposed by Halford⁷ except for the occurrence of I_0 instead of I , the slightly large total moment of the rigid molecule. For ethane, Halford's equation agrees with the calculation of Mayer, Brunauer and Mayer⁸ only if the external moments are taken to be A , A and C , where the moments of the rigid molecule are A , A and $2C$. A correction of this nature to the external moments will always be necessary, but ethane is perhaps the only case in which it is not small.

⁵ This is calculated with $d_{CC} = 1.54 \times 10^{-8}$ cm and $d_{CH} = 1.08 \times 10^{-8}$ cm.

⁶ Cf. Ludloff, Zeits. f. Physik 57, 227 (1929).

⁷ Halford, J. Chem. Phys. 2, 694 (1934).

⁸ Mayer, Brunauer and Mayer, J. A. C. S. 55, 37 (1934).