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The Entropy of Polyatomic Molecules

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A general expression for the entropy of the polyatomic molecule, rigid in the sense that only one form with a given set of moments of inertia is possible, is tested by comparison of calculated and experimental values. The results are satisfactory for molecules with as many as seven rotational degrees of freedom.

THE entropy of the polyatomic molecule is expressed as the sum of three separable contributions, arising, respectively, from translation, rotation and internal vibration. The translational entropy, per mole, is expressed by the equation,

$$S_{tr} = R \ln \frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{5/2}, \quad (1)$$

in which R is the gas constant, V the molal volume, N is Avogadro's number, m is the mass of the molecule, k the Boltzmann constant, T is the absolute temperature, h is Planck's constant and e is the natural logarithmic base. At low pressures, such that the ideal gas laws are approximately obeyed, this expression is highly accurate regardless of the complexity of the molecule.

It is the rotational contribution which presents the principal problem in the complex polyatomic molecule. Expressions have been derived from fundamental mechanical principles for rigid molecules with two and three rotational degrees of freedom, and for the type represented by ethane in which two entirely equivalent parts rotate independently about a common axis. This latter derivation, by Mayer, Brunauer and Mayer,¹ presents rather formidable mathematical difficulties, from which it would appear that the similar derivation for the molecule with n independently rotating parts oriented at various angles to one another, would be extremely difficult if not impossible. However, an examination of the several equations which have been quoted or derived in the above paper shows them to be of the following form:

$$S_{rot} = R \ln \frac{1}{\pi \sigma} \left\{ \frac{8\pi^3 (A^a B^b C^c \dots G^g)^{1/n} k T e}{h^2} \right\}^{n/2} \quad (2)$$

¹ Mayer, Brunauer and Mayer, *J. Am. Chem. Soc.* **55**, 37 (1933).

Here A , B , etc., are the moments of inertia of the molecule and its independently rotating parts; a , b , etc., are the rotational degrees of freedom associated with the corresponding moments of inertia; $a+b+c+\dots+g=n$ is total number of rotational degrees of freedom, and σ is the symmetry number, defined as the number of indistinguishable permutations produced by rotation of the molecule or its parts. It is not unreasonable to suppose that this equation may apply in the generalized form to molecules of different symmetry, and with more rotational degrees of freedom than those for which it was originally derived. It is the purpose of this paper to show that for such substances a satisfactory agreement with experimental entropies is obtained. The comparisons with experimental data have been restricted to cases in which the molecules are rigid in the sense that no "optically isomeric" forms are possible, such as the alternative forms of n -butane.

The vibrational entropy is expressed by the equation:

$$S_{vib} = R \sum_{i=1}^{i=3N-3-n} \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln (1 - e^{-h\nu/kT}), \quad (3)$$

a summation over i frequencies of numerical value ν . This function is at best only approximate, and its application is somewhat restricted by the arbitrary nature of the selection of fundamental frequencies and their degeneracy. Molecules of low molecular weight have almost negligible total vibrational entropy, while the typical complex organic molecule has a sufficient number of low fundamental frequencies to make the vibrational entropy a contribution of considerable magnitude. In other words, the magnitude increases rapidly with the molecular weight, and, with our present knowledge of molecular vibrations, the uncertainty of the estimate increases still more

rapidly. As a result, the examples selected for the present purpose, primarily a test of Eq. (2), must be such as to introduce through the vibrational terms a maximum error which is small by comparison with the contribution due to a single rotational degree of freedom.

The procedure by which the vibrational entropy of acetone has been estimated may be taken as an example. The frequencies are taken from the Raman spectrum by Dadieu and Kohlrausch.² The decision as to the single or multiple character of the frequencies requires an attempt to describe the motions. For this purpose, the approach described by Dennison³ and the considerations of three particle systems by Cross and Van Vleck⁴ are very helpful.

The contribution of the lower frequencies is most important according to Eq. (3), those above 1000 cm^{-1} contributing little to the entropy. The acetone frequencies, with the approximate description of the probable motions represented by them, the corresponding multiplicity (m), and the entropy contribution (S), are summarized in Table I. The accuracy of the

TABLE I. *Vibrational entropy of acetone.*

(cm^{-1})	Probable Motion	m	S
390	Central C, \perp to CCCO plane	1	1.00
520	Waving of methyl groups	1	0.60
770	Stretching of C—C bonds	2	0.45
1000	Twisting of molecule, mainly bending C=O bond	1	0.10
1200	{ Bending of CH bond }	5	0.20
1450		5	0.04
1700	Stretching of C=O bond	1	—
2900	Stretching of C—H bond	6	—
Totals		22	2.39

result turns upon the interpretation of the lowest three frequencies, requiring that the significant Raman lines should be present and that the correct weight should be assigned to each. The total 2.4 E.U., should not be in error by more than 0.5 E.U. For other molecules, for which Raman data are not available, the vibrational contribution may be based upon estimated frequencies of probable fundamental vibrations, in this case of course with somewhat higher probable error. Eventually, as our knowledge of internal vibra-

tions increases, and the number of accurately known entropies becomes sufficiently large, it should be possible to make rapid estimates of vibrational entropy from the size and general shape of the molecule.

For the moment of inertia of the methyl group, the value 0.0517×10^{-38} has been employed. Other moments are estimated, based upon the following interatomic distances (in Angstrom units): C—C, 1.52; C—H, 1.08; C—O, 1.4; C=O, 1.3; C=C, 1.4. The angle between the oxygen valences in methyl alcohol is taken as 100° , and between single carbon valences as 110° . Since the moments enter as the square roots into the rotational entropy, considerable errors could be made without too large effects upon the final results. In estimating the moments of the molecule as a whole, the hydrogens of the methyl group have been taken arbitrarily as a mass of three at a point 0.37 Angstrom units from the carbon atom. The principal axes are evident by inspection in the more symmetrical molecules. For methyl alcohol they were estimated to be inclined at $1^\circ 23'$ and $91^\circ 23'$ to the CO bond. The angle of inclination to the C=C bond in trimethylethylene was calculated to be $28^\circ 20'$. An error of a few degrees in the inclination of the axes produces little error in the result.

The entropies for comparison with experimental data have been calculated for the gaseous state at one atmosphere pressure and 25°C . Introducing these quantities into Eqs. (1) and (2) and combining, we obtain for the total practical entropy,

$$S_{298}(\text{g}) = 23.75 + \frac{3}{2}R \ln M + \frac{1}{2}R \ln A^a B^b C^c \dots G^g + 8.70n - R \ln \sigma + S \text{ vib.} \quad (4)$$

In this equation M is the molecular weight, and A , B , etc., now represent the moments of inertia multiplied by 10^{38} .

The results of the calculations are shown in Table II, in which the first column gives the substance, the second the number of rotational degrees of freedom, the third the moments of inertia ($\times 10^{38}$) the fourth the symmetry number, the fifth the sum of the translational and rotational contributions, the sixth the estimated vibrational entropy, and the seventh the total calculated entropy according to Eq. (4). In the eighth col-

² Dadieu and Kohlrausch, Ber. 63, 251 (1930).

³ Dennison, Rev. Mod. Phys. 3, 280 (1931).

⁴ Cross and Van Vleck, J. Chem. Phys. 1, 350 (1933).

TABLE II. *Entropy of polyatomic molecules.*

Substance	<i>n</i>	<i>A, B, etc.</i>	σ	$S_{tr} + S_{rot}$	<i>S</i> vib	<i>S</i> (g) 298	<i>S</i> (l) exp.	<i>S</i> _{vap.}	<i>S</i> (g) exp.
Methyl alcohol	4	0.301, 0.016, 0.317, 0.0517	3	57.3	0.3	57.6	30.3	26.4	56.9
Toluene	4	1.593, 3.423, 4.977, 0.0517	6	68.8	7.5	76.3	52.4	23.3	75.7
Dimethyl ether	5	0.636, 0.159, 0.795, 0.0517	18	64.5	1.1	65.6			
Acetone	5	0.846, 0.851, 1.697, 0.0517	18	67.9	2.4	70.3	47.9	21.2	70.1
Isobutane	6	1.71, 0.298, 0.0517	81	68.9	3.0	71.9	(51.5)	19.8	71.3
Trimethylethylene	6	2.364, 0.905, 3.269, 0.0517	27	75.2	3.9	79.1	59.5	20.2	79.7
Neopentane	7	1.71, 0.0517	729	74.1	4.4	78.5	(57.)	19.9	76.9

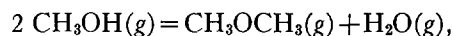
umn is shown the experimental entropy of the liquid, in the ninth, the estimated entropy of vaporization, and in the tenth the total entropy of the gas, based on the experimental data.

The experimental entropies shown in the eighth column have been taken from Parks and Huffman.⁵ Those in parentheses are estimates from the measured values for closely related compounds. The entropies of vaporization of methyl alcohol and toluene are obtained from the heats of vaporization used by these authors. The heat of vaporization of acetone is taken from *International Critical Tables*.⁶ The values for the vaporization of the hydrocarbons have been calculated by means of the Kistiakowsky equation. The vapor pressure data of Whitmore and Fleming⁷ on neopentane give a value about one entropy unit lower than the one in column nine of the table. In view of the large variation in heats of vaporization from different sources, apparently equally reliable, it is difficult to fix the entropy of vaporization within two entropy units. For this reason, in order to be consistent, the Kistiakowsky equation was employed. The probable

error in the calculated value is of the order of one entropy unit, that of the "experimental" value two entropy units.

The effect of the rotating methyl groups may be seen by comparing the result for acetone (70.3 E.U.) with a calculation which assumes that no such rotation occurs, and predicts the value 63.0.

A check on the dimethyl ether calculation, for which no experimental data are available, is obtained by means of the reaction,



for which Parks and Huffman find $\Delta S = 5.1$. From the calculated entropy values of Table II, together with the entropy of water vapor as given by Giaque and Ashley⁸ (45.17), we obtain for the above reaction, $\Delta S = 4.4$.

With the exception of trimethylethylene, the calculation leads in every case to a value slightly higher than the corresponding experimental or estimated value. It is possible, but improbable, that this might be the result of omitting some factor from Eq. (4). It is more probable that it arises from the low temperature extrapolation employed with the experimental data. For practical purposes, the agreement is well within the limits of error.

⁵ Parks and Huffman, *Free Energies of Some Organic Compounds*. Chemical Catalog Co., Inc., 1932.

⁶ International Critical Tables, Vol. 5, p. 137.

⁷ Whitmore and Fleming, J. Am. Chem. Soc. 55, 806 (1933).

⁸ Giaque and Ashley, Phys. Rev. 43, 81 (1933).