The Entropy of Polyatomic Molecules and the Symmetry Number

BY JOSEPH E. MAYER, STEPHEN BRUNAUER AND MARIA GOEPPERT MAYER

Introduction

The calculation of the entropy of organic gases from molecular structure data promises considerable aid to the physical chemistry of organic compounds. Vapor pressure data and heats of vaporization are usually available and accurate estimations of the entropies of the gases may be used easily to calculate the entropies of the solid and liquid states. With heats of combustion these data can be used to calculate free energies and to estimate equilibria.

Calculations of the specific heats and entropies of diatomic molecules from spectral data have long been made, and have yielded results of great accuracy.[1]

More recently Villars and Schultze,[2] Villars,[3] Giauque and his students,[4,5] and Sterne[6] have used similar methods to calculate the entropies of some polyatomic molecules.

The method depends on the empirical fact that the energy of the single molecule may be fairly accurately accounted for as the sum of several independent terms. These terms are the translational energy, the energy due to rotation with constant moments of inertia, and the energies of one or more harmonic vibrational degrees of freedom. In the language of the quantum mechanics this condition is that the correct function necessary to represent any state of the molecule at low energies ($\epsilon/kT \sim 1$) be given to a good approximation as a product of independent functions of the various coördinates, and, further, that the potential energy be a sum of squares of the vibrational coördinates. If the above conditions hold, the entropy may be separated into additive terms due to translation, rotation, vibration, nuclear spin and to electron degeneracy. It is assumed that the lowest electron excitation has a high energy compared to kT and contributes nothing to entropy or specific heat. It is also convenient to make use of the fact that, with the possible exception of hydrogen, the moments of inertia of all actual molecules are so large that the entropy of rotation is given accurately by the classical equation at temperatures of about 200–300°K.

[1] See for instance Giauque, THIS JOURNAL, 52, 4816 (1930); 53, 507 (1931).
[2] Villars and Schultze, *Phys. Rev.*, 38, 998 (1931).
[3] Villars, *ibid.*, 38, 1552 (1931).
[4] Giauque, Blue and Overstreet, *ibid.*, 38, 196 (1931).
[5] MacDougall, *ibid.*, 38, 2074 (1931).
[6] Sterne, *Phys. Rev.*, 39, 993 (1932).

The fundamental equations for the more general case are given by Giauque.[7] If the above conditions hold the molar entropy of a diatomic gas of unlike atoms may be expressed as

$$S = R \left[\ln \frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{5/2} \left(\frac{8\pi^2 IkT}{h^2} \right) e\, p_e p_n + \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln (1 - e^{-h\nu/kT}) \right]$$

(1)

where R is the gas constant, V is molar volume, N is Avogadro's number, m is $m_1 + m_2$, the mass per molecule, $k = R/N$, the Boltzmann constant, h is Planck's constant, $e = 2.7183$, base of natural logarithms, $I = \mu r^2$ [$\mu = m_1 m_2/(m_1 + m_2)$], the moment of inertia, ν is the frequency of vibration, p_e is the degeneracy of the lowest electronic level, p_n is the degeneracy due to nuclear spin

$$p_n = (2s_1 + 1)(2s_2 + 1)$$

where s_1 and s_2 are the spins of atoms 1 and 2. We express the entropy divided by R at temperature T of the harmonic vibrator of frequency ν as

$$S_{\text{Ein}}(\nu, T) = \frac{h\nu/kT}{e^{h\nu/kT} - 1} - \ln (1 - e^{-h\nu/kT})$$

(2)

which, when $h\nu/kT$ is equal to about four or greater, becomes approximately

$$S_{\text{Ein}}(\nu, T) \cong (h\nu/kT + 1)e^{-h\nu/kT}$$

(3)

Equation (1) can then be written for 1 atm. pressure

$$S = R \left[0.769 + \frac{7}{2} \ln T + \frac{3}{2} \ln W + \ln A' + \ln p_e + \ln p_n + S_{\text{Ein}}(\nu, T) \right]$$

(4)

where W is molecular weight and $A' = I \times 10^{38}$.

The nuclear spin entropy $R \ln p_n$ may in practice be omitted. Gibson and Heitler[8] have shown that it does not alter in any reaction involving diatomic molecules, and it is usually assumed that this is also true for polyatomic molecules. The results of this paper prove that this is actually the case.

If the two atoms of the diatomic molecule are identical, or if we deal with a polyatomic molecule with two or more identical atoms, a new difficulty arises. Certain rotation states may not occur, or may occur only for molecules with a definite nuclear spin. Essentially the same problem has been handled with the methods of the classical statistics by Ehrenfest and Trkal.[9] They showed that $R \ln \sigma$ must be subtracted from any entropy equation like the above, in which σ, the symmetry number, represents the number of permutations of like atoms which can be carried out by changes in the coördinates of rotation alone (nuclear spin neglected). That is, σ is the number of ways in which the molecule can be rotated and still look identical. The argument is essentially the same as that which

[7] Giauque, THIS JOURNAL, **52**, 4808 (1931).

[8] Gibson and Heitler, Z. Physik, **49**, 465 (1928).

[9] Ehrenfest and Trkal, Proc. Sect. Sci. Amsterdam, **23**, 169 (1920).

justified the division of the total phase space of a gas of N identical molecules by $N!$, the number of permutations which left the system unchanged.

Hund[10] has discussed the quantum mechanical method by which one can determine the allowed rotational states for a molecule of definite nuclear spin type. Elert[11] has applied Hund's method to methane, and Villars and Schultze,[2] and Villars[3] have used the results of Hund and Elert to make detailed calculations of the entropies of methane and ammonia. Giauque[4] has correctly pointed out that at room temperatures the entropies of these gases must be given by the usual formulas with terms for classical rotational entropies minus $R \ln \sigma$.

There exists, however, no proof consistent with the formal quantum mechanical derivation of statistics which shows that such a procedure may be universally applied. This is proved here for all molecules with one σ'-fold axis and a perpendicular plane of symmetry or lower symmetry. Since probably the only molecules of higher symmetry are tetrahedral (methane like), and it follows from the work of Elert that the symmetry number may be used for these, the procedure can be used generally.

In addition the quantum mechanical solution is given for a symmetric top with two rigid bodies of equal moments of inertia independently rotating about the unique axis. This probably represents the best zeroth order approximation for the ethane molecule, in which it seems likely that there is nearly free rotation about the C–C bond. The equation for the energy levels is derived. The classical entropy of rotation of a gas composed of such molecules is calculated.

The Symmetry Number

We wish first to consider a system composed of N independent similar particles, that is, a system the energy function of which has no terms containing the coördinates or momenta of more than one particle. The functions Ψ giving the state of the system may be expressed as products $\Pi_{i=1}^{i=N} \psi_k(i)$. $\psi_k(i)$ is then a function of the coördinates (i) (including spin) of the i'th particle, k represents the value of all of the quantum numbers of the i'th particle. For any single function Ψ_l in which k for each particle is given, we shall introduce the integers λ_k giving the number of particles in the completely defined quantum state k. There will be $N!/\Pi_k \lambda_k!$ different functions having the same values of the λ_k's obtainable from each other by carrying out all of the permutations of particles which have different values of k. All these functions will be solutions to the original differential equations which, with the spin and boundary conditions, determined our system. They will be orthogonal to each other and we will assume them to be normalized. Therefore, any linear combination of these functions will be a solution.

[10] Hund, *Z. Physik*, **43**, 788; **43**, 805 (1927).

[11] Elert, *ibid.*, **51**, 6 (1928).

There is one other condition which any function expressing the state of the system must fulfil to be acceptable. If the particles contain an odd number of fundamental units, protons, electrons and probably neutrons, that is, if the particles have half integer spins, the function must be completely antisymmetric. This means that it must become multiplied by minus one by a single transposition of two particles, that is, a transposition of two identical groups of electrons and protons. If the particles contain an even number of units, have zero or integer spins, the function must be completely symmetric, it must be unchanged by a transposition. (A function antisymmetric in transpositions of electrons, protons (and neutrons) would be symmetric in the transposition of two identical groups of an even number of such units, for example, two carbon nuclei.)

There is only one linear combination of all the $N!/\Pi_k\lambda_k!$ functions having the same λ_k values which is perfectly symmetric and normalized, namely, the sum of all the functions. There is only one linear combination which is antisymmetric, the sum of all $N!$ possible permutations, the even permutations taken with positive, the odd with negative signs. This antisymmetric function will be identically zero if any λ_k is greater than 1. These two cases of symmetric and antisymmetric functions correspond to the Bose–Einstein and Fermi–Dirac statistics, respectively. In each case a single state is defined by the integers λ_k, and in the second case only values 1 or 0 are allowed.

We are interested in a molecule composed of several atoms of which a certain number may be identical. Since in this case the potential energy is not independent of the relative positions of the atoms (indeed it depends only on the relative positions), we cannot make even an approximate solution in terms of products of functions of the atomic coördinates. We can, however, transform to such coördinates that, to a good approximation, the complete function Ψ of the molecule may be expressed as a product of functions of these coördinates. These coördinates which have no interaction terms are the familiar natural coördinates of translation, rotation and the classical normal coördinates of vibration, as well as the coördinates of nuclear spin which remain untransformed.

The nuclear position coördinates and the natural coördinates must be connected by transformation equations such that the values of one set completely define all the values of the other set. We will find in general that there are several values of the relative positions of the atoms which will have identical minimum values of the potential energy. These will correspond to what will be called here different "optical isomers," according to the terminology of Hund. It is to be understood that among these optical isomers may occur members that differ only in the permutation of identical atoms and will not differ in light rotating power. These positions of minimum energy will all correspond to the same zero value of all

the vibrational coördinates.   It is necessary, then, to add an extra coördinate to our natural system, the value of which tells us in what optically isomeric form our system is.   This coördinate i, by definition, may take only a finite number of discrete values a, b, ... n, corresponding to the n isomers.   The eigenfunctions of this coördinate will be $\psi_c(i) = \delta(ci)$, $\delta(ci) = 1$ when $i = c$, $\delta(ci) = 0$ when $i \neq c$, in which c designates the isomeric state of the molecule.

The complete function Ψ of the molecule may be expressed as a product of the type

$$\Psi = \psi \text{ (electron)} \times \psi \text{ (isomer)} \times \psi \text{ (vibration)} \times \psi \text{ (rotation)} \times \psi \text{ (nuclear spin)} \times \psi \text{ (translation)}$$

We shall assume that the function ψ (electron) has been completely solved, and that it is symmetrical to transpositions of identical nuclei, which is usually the case with stable chemical compounds.   The following argument is made simpler by this assumption, although the conclusions are independent of it. ψ (translation) depends only on the coördinates of the center of gravity which are unaffected by transpositions of like nuclei and it is therefore perfectly symmetrical.   The normal coördinates of vibration may be so selected that they are either unaffected, or change sign, when two like nuclei are transposed.   The lowest energy eigenfunction of a harmonic oscillator is symmetric to a change of sign of the coördinate, as are all states with even quantum numbers.   In the lowest vibrational energy level ψ (vibration) is then symmetrical.   As in the case of ψ (electron) the conclusions we draw will also hold for higher non-symmetric vibration states, but the language of the discussion is simplified if we deal only with the symmetrical case.

The product of the three symmetrical functions ψ (electron) $\times \psi$ (vibration) $\times \psi$ (translation) will be symmetrical and therefore the complete function ψ will have the symmetry character of the remaining product, (or linear combination of the product), ψ (isomer) $\times \psi$ (rotation) $\times \psi$ (nuclear spin).   This product must be antisymmetrical to transposition of atoms with half integer spins, and symmetrical to transpositions of atoms with integer or zero spins.

The symmetry number σ of a molecule is defined as the number of permutations of identical particles in the molecule which can be carried out by changes in the coördinates of rotation and spin alone.

The Unsymmetrical Molecule.—If $\sigma = 1$ the rotational coördinates will be unaffected by permutations and the rotational function ψ (rotation) will be perfectly symmetrical.   If the molecule contains only N like atoms there will be $N!$ isomer functions.   If the molecule contains several of each of two kinds of atoms or in general more kinds of atoms, there may exist physically distinguishable (light rotating) isomers of the same potential energy.   We may then arbitrarily use two coördinates, one of

which defines the physically indistinguishable optical isomer resulting from permutation of the like atoms, the other defines the physically distinguishable isomeric state. The complete isomer function will then be a product of functions of each of these two coördinates. The functions of the coördinate of distinguishable isomers, which do not contain the coördinate of the like atom permutations, will be symmetric to these permutations, and may be omitted from the discussion. The number of the other isomer functions will be $N!$

Not only simple products of isomer and spin functions will be solutions of the problem. Linear combinations of the isomer functions multiplied by linear combinations of the spin functions will also be solutions, and any linear combinations of permutations of these products. We seek the number of such orthogonal functions which fulfil the conditions of perfect symmetry (/antisymmetry). The *exact* solution of the complete function Ψ is not a product of functions of the different coördinates, since there are actually small interaction terms. Nevertheless, the true Ψ may be determined by the method of perturbations from such a product. It will have the same symmetry character as the product, provided we use the correct zeroth order function of the many possible linear combinations which satisfy the degenerate problem. For any physical perturbation, since it must be symmetrical in identical particles, the correct linear combinations of isomer and spin functions are a complete set of representatives of all the possible symmetry characters.

Using the group theory Wigner[12] has discussed this general problem, Hund[13] has recapitulated the discussion and the results without the use of the group theory.

A function of N identical particles is said to belong to the symmetry character $S(\lambda_1 + \lambda_2 + \ldots + \lambda_j + \ldots + \lambda_n)$ with $\Sigma_j\lambda_j = N$ and $\lambda_j \geq \lambda_{j+1}$ if it cannot be made by permutation and linear combination symmetric in more than λ_1 particles, and by permutation of the remaining $N - \lambda_1$ particles symmetric in more than λ_2 particles, etc. A *representative* of this symmetry character is symmetric in one group of λ_1 particles, and in another of λ_2 particles, etc.

Any function of symmetry character $\tau = S(\lambda_1 + \lambda_2 + \ldots + \lambda_j + \ldots + \lambda_n)$ has a degeneracy n_τ where $n_\tau = N! \, \Pi_{j>l}(\lambda_l - \lambda_j + j - l)/\Pi_j(\lambda_j + n - j)!$ If the system has no degeneracy besides that due to the identity of the particles, there are n_τ different functions of character τ each having a degeneracy n_τ making in all n_τ^2 orthogonal functions, with $\Sigma_\tau n_\tau^2 = N!$

To every symmetry character τ there corresponds another character τ^* called the reciprocal character[14] and $n_{\tau^*} = n_\tau$. The degeneracy of a

[12] Wigner, *Z. Physik*, **40**, 492 (1926); **40**, 883 (1927).

[13] Hund, *ibid.*, **43**, 788 (1927); **43**, 805 (1927).

[14] The definition of the reciprocal character is given by Hund.[13]

product of functions of character τ and τ' is $n_\tau \times n_{\tau'}$. A symmetric (/anti-symmetric) function can only be formed by permutation and linear combination from the product of two functions of characters τ and τ' if $\tau' = \tau(/\tau' = \tau^*)$, and then only the fraction $1/n_\tau^2$ of all the linear combinations leads to a symmetric (/antisymmetric) function.

Spin functions are generally degenerate because there are only $2s + 1$ possible functions per particle. The number of functions of character τ is not in general n_τ and may be zero, although the degeneracy of each existing function must be n_τ.

If the molecule is composed of N identical atoms of spin s there will be $(2s + 1)^N$ spin functions, from which linear combinations may be formed that can be classified into non-combining groups of different symmetry character. The $N!$ orthogonal isomer functions may also be formed into non-combining groups of different character, n_τ^2 functions of the character τ. Only products of isomer and spin functions belonging to the same (/reciprocal) character, may by permutation and linear combination lead to functions completely symmetric (/antisymmetric) to transpositions of identical atoms. From the product of n_s spin functions of character τ with all the n_τ^2 isomer functions of character τ (/τ^*) only the fraction $1/n_\tau^2$ or n_s completely symmetric (/antisymmetric) functions can be formed. If we sum the symmetric (/antisymmetric) products over all the different nuclear spin symmetry characters, we obtain as many functions as the total number of nuclear spin functions, $(2s + 1)^N$.

The conclusion is that a molecule of symmetry number $\sigma = 1$, composed of N identical atoms of spin s will have $(2s + 1)^N$ orthogonal functions representing $(2s + 1)^N$ degenerate states for every value of the usual quantum numbers of the molecule. To the simple entropy expression for such a molecule must be added $RN \ln (2s + 1)$, or $R \ln (2s + 1)$ nuclear spin entropy for every atom of spin s.

Had the molecule contained other unlike atoms i, j of spin s_i, s_j the preceding argument could have followed in detail for each of the $\Pi_i(2s_i + 1)$ spin states of these atoms. To the entropy should then be added $R \ln (2s_i + 1)$ for every atom of spin s_i.

Had the number of unlike atoms been greater than 3 there may have been a number I of physically distinguishable isomers and the argument would lead to an additional entropy $R \ln I$.

If the molecule contained an additional N_k identical atoms k of spin s_k a similar grouping of functions with respect to the isomers obtained by permuting the atoms k, for every one of the preceding functions, would lead to an additional $RN_k \ln (2s_k + 1)$ in the entropy.

The total nuclear spin entropy $R \ln (2s_i + 1)$ for every atom of spin s_i is the same expression as that in monatomic and diatomic gases, and as will later be shown in symmetrical polyatomic molecules. This entropy

will cancel in all chemical reactions and need not be included in any practical values. The entropy due to the I physically distinguishable isomers, $R \ln I$, will not cancel, and must always be included.

Those isomers that are not physically distinguishable, that is, the isomers corresponding to different permutations of identical atoms, occur in the complete function of the molecule in the form of linear combinations. Due to the symmetry demands of the Pauli principle no molecule can be said to be composed of only one isomeric type. On those isomers which are physically distinguishable there are no such limitations. As far as present knowledge goes we may write a molecular function which contains only one isomer. Professor G. N. Lewis has suggested to one of us that even in the exact solution the different isomer functions may not combine. This certainly appears reasonable to the prejudice of the chemist, for otherwise not only would the two states have slightly differing energies, but a gas of one isomer cooled to such a temperature that excitation in a given time had low probability, would in finite time be transformed 100% into the other isomer! The mathematical reason for this probable intrinsic degeneracy is, however, not obvious.

The Symmetric Molecule.—In order to investigate the case of a molecule $\sigma > 1$, ψ (rotation) must be considered. Only molecules having no higher symmetry than a σ'-fold axis of symmetry, and with or without a plane of symmetry perpendicular to this axis will be considered. For these cases $\sigma = 2\sigma'$ or $\sigma = \sigma'$, respectively. Since probably tetrahedral molecules are the only actual cases of $\sigma > 1$ not falling into these classes the case is quite general. There will be $N!/\sigma$ different isomer functions, and σ rotational functions, which latter we shall show differ only by a phase factor. All such molecules will either be symmetric top types, or sufficiently close to it to allow symmetric top eigenfunctions to be used as a first approximation. Higher approximations will show the same number of states, and the same symmetry characters as the zeroth.

The rotational eigenfunctions of the symmetrical top problem have been solved in the usual Eulerian angles, θ, ψ and φ.[15,16]

The form of equation here used is given by Hund. The solutions may be written

$$\psi \text{ (rotation)} = \begin{cases} v_{j,m,\lambda} \left(\sin \dfrac{\theta}{2} \right) e^{\pm i(m\psi + \lambda\varphi)} \\[2em] v_{j,m,\lambda} \left(\cos \dfrac{\theta}{2} \right) e^{\pm i(m\psi - \lambda\varphi)} \end{cases} \tag{5}$$

where $j \geq m \geq 0, j \geq \lambda \geq 0$

$$v_{j,m,\lambda} \left(\sin \frac{\theta}{2} \right) = \cos^s \frac{\theta}{2} \sin^d \frac{\theta}{2} F \left(\frac{s+d}{2} - j, 1 + s + d, 1 + d, \sin^2 \frac{\theta}{2} \right)$$

[15] Dennison, *Phys. Rev.*, **28**, 318 (1926).
[16] Reiche, *Z. Physik*, **39**, 444 (1926).

and $s = m + \lambda$, $d = |m - \lambda|$. F is the Jacobi polynomial. The energy, if C is the moment of inertia about the unique axis and A is the moment about the other two axes, has the form

$$E = \frac{h^2}{8\pi^2}\left[\frac{1}{A}j(j+1) + \left(\frac{1}{C} - \frac{1}{A}\right)\lambda^2\right] \qquad (6)$$

Of the permutations of identical atoms σ' lead only to a different phase of rotation about the axis of symmetry, the unique axis of the top, differences which in the natural coördinates correspond only to shift of the type in which φ changes to $\varphi + q2\pi/\sigma'$ where q is an integer. The only change in the complete function of the natural coördinates, without the spin coördinates, is multiplication by a complex number, $(\exp.)i\lambda q2\pi/\sigma'$.

If the molecule has a plane of symmetry perpendicular to the unique axis the function is further degenerate. States differing in the substitution of $\cos(\theta/2)$ for $\sin(\theta/2)$ and simultaneously $-\varphi$ for φ will have identical energies even in the presence of a magnetic field, and even if the top is not perfectly symmetric. We may then rewrite and form the linear combinations

$$\psi \text{ (rotation) } = \begin{cases} \left[v_{j,m,\lambda}\left(\sin\frac{\theta}{2}\right)e^{\pm i\lambda\varphi} + v_{j,m,\lambda}\left(\cos\frac{\theta}{2}\right)e^{\mp i\lambda\varphi}\right]e^{\pm im\psi} \\ \\ \left[v_{j,m,\lambda}\left(\sin\frac{\theta}{2}\right)e^{\pm i\lambda\varphi} - v_{j,m,\lambda}\left(\cos\frac{\theta}{2}\right)e^{\mp i\lambda\varphi}\right]e^{\pm im\psi} \end{cases} \qquad (7)$$

An end to end transformation of the unique axis corresponds to the following changes: θ to $\pi - \theta$, ψ to $\pi + \psi$, and φ to $-\varphi$. The first of the equations is multiplied by $(\exp.) \pm im\pi$ by this change, the second by $-(\exp.) \pm im\pi$, that is, since m is an integer, by ± 1 and ∓ 1.

The molecule of symmetry number σ greater than one has then no longer $N!$ orthogonal products of isomer and rotation functions corresponding to the $N!$ permutations. The permutations fall into $N!/\sigma$ groups, each containing σ permutations; the isomer times rotation functions for any of one group can be obtained from any of the other of that group by multiplication by a (complex) factor. There are only $N!/\sigma$ orthogonal functions for every value of the usual quantum numbers. The question is, can every symmetry character be formed out of these $N!/\sigma$ orthogonal functions as the quantum numbers change their values, and, if so, what will be the number of functions of the various symmetry characters?

We may write in a purely formal manner a complete set of orthogonal representatives of the symmetry characters as linear combinations of the various permutations. For each of these permutations must now be substituted the appropriate product of an isomer function and a rotational phase factor. The permutations belonging to each isomer may be grouped and the phases factored out as a sum, which, for instance, in the perfectly symmetrical case will have the form $\Sigma_{q=0}^{q=\sigma'-1}(\exp.)i\lambda q2\pi/\sigma'$. The complete

function may then be multiplied by a complex factor containing λ, such as $(\exp.) - i\lambda q 2\pi/\sigma'$, if necessary, to assure that at least one of the phase factors contains 1 in the sum (in the symmetrical case the term with $q = 0$ is already 1). These functions are assuredly orthogonal and are representatives of various symmetry characters. Any one may, however, be identically equal to zero for any given value of the quantum numbers m and λ. The zero value will evidence itself by the fact that each of the phase factors, functions of m and λ, will be zero. For every value of m and λ (and for each function of (7) and each j) there will be only $N!/\sigma$ functions which are other than zero.

The sum of all of the phase factors over all values of λ between $a + 1$ and $a + \sigma'$ inclusive, and if the molecule contains a plane of symmetry, over an even and an odd value of m, may now be made for each function. Since at least one phase factor contains 1 the sum will not be zero because $\Sigma_{\lambda=a+1}^{\lambda=a+\sigma'}(\exp.)\lambda 2\pi i q/\sigma' = 0$, unless $q = 0$ or $q = \sigma'$. Every function exists at least once in these values of the quantum numbers m and λ. Since the total number of orthogonal functions which can exist is $\sigma \times N!/\sigma = N!$, and this is the number of all of our functions, every function exists exactly once. Over a range of σ' consecutive values of λ and two adjacent values of m the same functions exist, and the same number of them, as exist for every quantum state of a completely unsymmetric molecule.

Within the range of the quantum number λ between $a + 1$ and $a + \sigma'$ (and for two consecutive values of m if the molecule has a plane of symmetry) there are n_τ^2 isomer times rotation functions of character τ. We may then proceed as for the case when $\sigma = 1$ to multiply each of these functions with the spin functions of the same (/reciprocal) symmetry character, and find $(2s + 1)^N$ completely symmetric (/antisymmetric) linear combinations of the products. We obtain for the above σ rotation states just as many acceptable orthogonal normalized functions as were previously obtained for every single rotation state of the unsymmetric molecule.

The result allows us to make the following statement. For temperatures high enough that $(\exp.)\delta\epsilon/kT$ is about equal to 1, where $\delta\epsilon$ is the energy difference between states having values of λ differing by σ', the molar entropy of a molecule having a symmetry number σ is $R \ln \sigma$ less than the entropy of the same molecule were it entirely non-symmetrical.

It is also a corollary that every nuclear spin state exists in the same proportion as in a non-symmetrical molecule, and the entropy due to nuclear spin will be $R \ln (2s + 1)$ for every atom of spin s.

The Ethane Like Top

It appears to be probable that single valence bonds show no potential energy changes in rotation. The opposite rotation of the two CH_3 groups

in ethane about the C–C axis, for instance, would cause potential energy changes only due to the varying distances between hydrogen atoms. This effect cannot be very great. It seems reasonable to choose as the zeroth approximation for such a molecule the solutions for absolutely free rotation. Probably the states most numerously present in the gas at 200–300°K. will be given fairly accurately by functions obtained on the basis of this assumption. As model for the problem is then chosen a symmetrical top with two equal moments of inertia A about two perpendicular axes x' and y', and consisting of two similar rigid bodies of equal moments of inertia C. Each of the bodies can be independently rotated about the unique axis of the top z'. z' is then the axis of the C–C bond in ethane.

If p and q are the angular velocities about x' and y', and r_1 and r_2 the angular velocities of the bodies 1 and 2, respectively, about z', the kinetic energy will be

$$T = \frac{1}{2} \left[A(p^2 + q^2) + C(r_1^2 + r_2^2) \right]$$

Angles similar to the Eulerian angles are introduced. θ is the angle between the fixed z axis in space and z', ψ the angle between the nodal line of the xy and $x'y'$ planes and the fixed x axis, φ_1 and φ_2 the angles between the nodal line and two fixed axes in the two rigid bodies 1 and 2, respectively. Defining p_θ, p_ψ, p_{φ_1} and p_{φ_2} as the momenta conjugate to the respective coördinates, the equation for the kinetic energy may be written

$$T = \frac{1}{2} \left[\frac{p_\theta^2}{A} + \left(\frac{A}{C} + \cot^2 \theta \right) \frac{p_{\varphi_1}^2 + p_{\varphi_2}^2}{A} + 2 \cot^2 \theta \frac{p_{\varphi_1} p_{\varphi_2}}{A} + \right.$$
$$\left. \frac{1}{\sin^2 \theta} \frac{p_\psi^2}{A} - \frac{2 \cos \theta}{\sin^2 \theta} \frac{p_\psi}{A} \left(p_{\varphi_1} + p_{\varphi_2} \right) \right] \qquad (8)$$

Transformation by the usual method yields the Schrödinger equation for ψ (rotation), which is here written U. The equation is

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial U}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 U}{\partial \psi^2} + \left(\frac{A}{C} + \cot^2 \theta \right) \left(\frac{\partial^2 U}{\partial \varphi_1^2} + \frac{\partial^2 U}{\partial \varphi_2^2} \right) +$$
$$2 \cot^2 \theta \frac{\partial^2 U}{\partial \varphi_1 \partial \varphi_2} - \frac{2 \cos \theta}{\sin^2 \theta} \left(\frac{\partial^2 U}{\partial \varphi_1 \partial \psi} + \frac{\partial^2 U}{\partial \varphi_2 \partial \psi} \right) + \frac{8\pi^2 A}{h^2} E U = 0 \qquad (9)$$

when the potential energy V is set equal to zero. Using the following substitution

$$\psi(\text{rotation}) = U = \Theta(\theta) \, e^{i(\lambda_1 \varphi_1 + \lambda_2 \varphi_2 + m\psi)} \qquad (10)$$

one obtains the differential equation for $\Theta(\theta)$

$$\frac{\partial^2 \Theta}{\partial \theta^2} + \cot \theta \frac{\partial \Theta}{\partial \theta} - \frac{(m - \lambda \cos \theta)^2}{\sin^2 \theta} \Theta + \left[\frac{8\pi^2 A}{h^2} E - \frac{A}{C} (\lambda_1^2 + \lambda_2^2) \right] \Theta = 0 \qquad (11)$$

in which $\lambda = \lambda_1 + \lambda_2$, and λ_1 and λ_2 are integers. This is the same equation that was obtained in the solution of the simple symmetrical top problem, and yields functions such as are given in equation (5).

The solution of the problem may then be written

$$\psi \text{ (rotation)} = \begin{cases} v_{j,\,m,\,\lambda} \left(\sin \dfrac{\theta}{2} \right) e^{\pm i(\lambda_1\varphi_1 + \lambda_2\varphi_2 + m\psi)} \\[2ex] v'_{j,\,m,\,\lambda} \left(\cos \dfrac{\theta}{2} \right) e^{\pm i(\lambda_1\varphi_1 + \lambda_2\varphi_2 - m\psi)} \end{cases} \tag{12}$$

with $j \geq \lambda = \lambda_1 + \lambda_2 \geq 0$; $j \geq m \geq 0$. The meaning of the function $v_{i,\,m,\,\lambda}$ is given under equation (5). The equation for the energy is

$$E = \frac{h^2}{8\pi^2} \left[\frac{1}{A} j(j+1) + \left(\frac{1}{C} - \frac{1}{A} \right) \lambda^2 - \frac{2\lambda_1\lambda_2}{C} \right] \tag{13}$$

Although the equation is most easily solved in the coördinates φ_1 and φ_2 it would appear natural to transform to coördinates $\varphi = (\varphi_1 + \varphi_2)/2$ and $\varphi' = (\varphi_1 - \varphi_2)/2$, the "average" angle φ, and the angular displacement φ' of one CH$_3$ group from this average angle. The displacement of the other group is of course equal to $-\varphi'$. In all higher approximations the potential energy will depend only on φ'. The equations then become

$$\psi \text{ (rotation)} = \begin{cases} v_{j,\,m,\,\lambda} \left(\sin \dfrac{\theta}{2} \right) e^{\pm i(\lambda\varphi + m\psi + \lambda'\varphi')} \\[2ex] v_{j,\,m,\,\lambda} \left(\cos \dfrac{\theta}{2} \right) e^{\pm i(\lambda\varphi - m\psi + \lambda'\varphi')} \end{cases} \tag{14}$$

with $\lambda = \lambda_1 + \lambda_2$ and $\lambda' = \lambda_1 - \lambda_2$. The quantum numbers must obey the relations $j \geq \lambda \geq 0$; $j \geq m \geq 0$; $\lambda' = \lambda \pm 2\,n$, where n is an integer, that is, λ and λ' are both odd, or both even. The energy expressed in terms of the new quantum numbers becomes

$$E = \frac{h^2}{8\pi^2} \left[\frac{1}{A} j(j+1) + \left(\frac{1}{2C} - \frac{1}{A} \right) \lambda^2 + \frac{(\lambda')^2}{2C} \right] \tag{15}$$

While this paper was being prepared for publication, there has appeared an article by Nielson[17] in which the ethane-like molecule is handled in a much more elaborate manner. His equations, when the potential energy of rotation within the molecule is set equal to zero, reduce to equation (14).

The entropy of a mole of such rotators may be calculated for high temperatures, in which case it becomes identical to the entropy of a mole of similar classical rotators with appropriate constants. The condition for the temperature is that $h^2/8\pi^2CkT$ and $h^2/8\pi^2AkT$ shall both be considerably smaller than 1. Actually values of about one fourth suffice for this condition. The equation for the entropy is

$$S_{\text{rotation}} = R \left[\ln 64\pi^5 \left(\frac{kT}{h^2} \right)^2 AC + 2 \right] \tag{16}$$

For ethane, could the two CH$_3$ groups not rotate separately around the C–C bond, the symmetry number would be 6; with free rotation, however, 18 permutations of the identical atoms can be carried out by changes in the angle coördinates. It is obvious further that the argument of the previous section applies as well to rotations of the angle φ' as to rotations

[17] Nielson, *Phys. Rev.*, 40, 445 (1932).

of φ, and that the entropy will be reduced by subtraction of $R \ln \sigma$, with $\sigma = 18$.

The Entropy Equations

Equations (1) or (4) give the entropy of a diatomic molecule of two unlike atoms at temperatures above about 200°K. but not high enough to produce any appreciable electronic excitation. Ordinarily one can safely use the equations up to 1000°K.

A diatomic molecule of two identical atoms will have the symmetry number $\sigma = 2$ and to equation (1) or (4) must be added $-R \ln \sigma = -R \ln 2$.

A linear polyatomic molecule will have an entropy given by an equation that differs from (1) or (4) only in that there will be more terms S_{Ein} (ν, T). In a triatomic linear molecule there are four vibrational degrees of freedom and four terms $S_{\text{Ein}}(\nu, T)$, two of the frequencies usually the two lowest, those due to bending, will in most cases be identical. This means that spectroscopically only one (degenerate) frequency will be found, but two entropy terms must be used for this frequency. The symmetry number may be 1 or 2.

For non-linear rigid polyatomic molecules the entropy of rotation will be greater due to the greater number of degrees of freedom. There will also be at least three frequencies of vibration. In general if there are N atoms in the molecule, one must account for $3N-6$ vibrational degrees of freedom. Some observed frequencies may be degenerate, the assignment of the number of degrees of freedom to any frequency is a problem which may be solved by mathematical[18] or by mechanical[19] means.

The equation for the entropy of a rigid non-linear polyatomic molecule is

$$S = R \left[\ln \frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{5/2} \left(\frac{8\pi^{7/2}(ABC)^{1/2}kT)^{3/2}}{h^2} \right)^{3/2} e^{3/2} \, p_e p_n \cdot \frac{1}{\sigma} I + \sum_{i=1}^{i=3N-6} S_{\text{Ein}} (\nu_i, T) \right] \qquad (17)$$

in which I is the number of physically distinguishable optical isomers, and with A, B and C the three moments of inertia. The explanation of the other symbols is given under equation (1). This may be written, at 1 atm. pressure

$$S = R \left[2.307 + 4 \ln T + 3/2 \ln W + 1/2 \ln A'B'C' + \ln p_e p_n I / \sigma + \sum_{i=1}^{i=3N-6} S_{\text{Ein}} (\nu_i, T) \right] \qquad (18)$$

in which $A' = A \times 10^{38}$, $B' = B \times 10^{38}$ and $C' = C \times 10^{38}$.

If two of the moments of inertia A and B are equal the molecule is a

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[18] See for instance Mulliken, *Rev. Modern Phys.*, **2**, 60, 506 (1930); **3**, 90 (1931).

[19] Kettering, Shutts and Andrews, *Phys. Rev.*, **36**, 531 (1930).

symmetrical top and the equations (17) or (18) may still be used with this substitution.

A molecule of the ethane type will have $3N-7$ vibrational degrees of freedom. The equation for the entropy may be written

$$S = R\left[\ln\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}e^{5/2}\left(\frac{8\pi^{3/2}(AC)^{1/2}kT}{h^2}\right)^2 e^2 p_e p_n\frac{1}{\sigma}I + \sum_{i=1}^{i=3N-7}S_{\text{Ein}}(v_i, T)\right] \quad (19)$$

which reduces at 1 atm. pressure to

$$S = R\left[3.841 + 9/2\ln T + 3/2\ln W + \ln A'C' + \ln p_e p_n I/\sigma + \sum_{i=1}^{i=3N-7}S_{\text{Ein}}(v_i, T)\right] \quad (20)$$

with $A' = A \times 10^{38}$, $C' = C \times 10^{38}$.

Accuracy

The accuracy with which the universal physical constants that enter the entropy equations are known is undoubtedly far greater than any practical use of the entropy demands. The molecular weight also introduces no error. The uncertainty in the use of these equations lies partly in the assumptions of their derivation and partly in the accuracy with which the moments of inertia and the frequencies are known.

The assumption that the moments of inertia in all states existing in appreciable quantities remain constant can be roughly tested by calculation of the stretching force constant from the frequencies. In most cases the average change in the moment of inertia up to 1000°K. is less than 8%, introducing about 0.1 Entropy Unit (cal. deg.$^{-1}$) error per rotational degree of freedom at this temperature. Failure of the vibrations to be linear harmonic probably introduces even less error. The assumption that ethane-like molecules rotate freely about the C–C bond is much more questionable. Ebert[20] and Wagner[21] have discussed the question of how "free" the rotation really is in ethane, basing their discussion largely on the specific heat measurements of Heuse[22] which were carried out in 1913–1914. The specific heat values appear to agree with those of a fully excited vibrator, rather than with the lower specific heat of a free rotator; it may be questioned, however, whether data of that date are sufficiently accurate to decide the question.

Although the calculations, if carried out for the constrained rotating oscillator, would use $\sigma = 6$ and correspondingly three times as many isomer functions as here used, the phase space would be constrained to one-third of the total angle 2π, instead of the full rotational angle, and the

[20] Ebert, "Leipziger Vorträge," 1929, p. 74.

[21] Carl Wagner, Z. physik. Chem., [B] 14, 166 (1931).

[22] Heuse, Ann. Physik, 59, 86 (1919).

entropy based on such an assumption would approach, with decreasing potential energy, that of the free rotator of equation (20). We believe that for ethane itself, at least, the entropy will be given fairly well by equation (20). More accurate measurements of the specific heat and entropy appear to be the only experimental method of decision.

The moments of inertia of some molecules can be obtained from spectroscopic data. Usually no values so obtained are available, but the spacing of the atoms can frequently be accurately estimated from x-ray data for the molecule in question or for some similar compound. With the usual assumptions for the geometrical structure these data probably allow calculations of the moments of inertia for the simpler organic compounds to within at least 10%, introducing 0.1 Entropy Unit error per rotational degree of freedom. The total entropy of one vibrational degree of freedom with frequency 200 cm.$^{-1}$ at 300°K. is 2.16 E. U., and for 1100 cm.$^{-1}$ at 300°K. it is only 0.03 E. U. An error of 10% in the value of the frequency introduces an error of 0.2 E. U. in the first case and no appreciable error in the second. Much more important is the correct assignment to each frequency of the number of degrees of freedom, and the certainty with which one can assume that all frequencies are known. Much progress has been made in the interpretation of the lower, and less numerous, frequencies[19] which are due to the mutual vibrations of the heavier atoms. In many cases one can feel quite confident that the interpretation is correct. Fortunately the less certain frequencies due to the motion of the hydrogen atoms appear to be all above 1100 cm.$^{-1}$ and introduce less than 0.03 E. U. at 300°K. per degree of freedom.

It appears not unreasonable to expect that we can calculate the entropies of many of the simpler organic compounds to within 0.5 cal. deg.$^{-1}$. This would introduce barely 30% error in an equilibrium constant prediction.

The Entropy of Some Simple Molecules

Ethane.—The moment of inertia C of the CH_3 group about the C–C bond will be equal to the moment of inertia of methane, if the tetrahedral angle for the hydrogen bonds is approximately maintained in ethane. The moment of inertia of methane is known from its band spectra.[23] x-Ray data show that the C–C distance in aliphatic hydrocarbons has a constant value, and this with the C–H distance calculated from the moment of inertia of methane gives the other moment A of the ethane molecule.

The Raman line at 990 cm.$^{-1}$ is undoubtedly due to the mutual vibration of the two methyl groups, and will have one degree of freedom. The assignment of the other frequencies, 4 at 1200 cm.$^{-1}$ and 6 at 1460 cm.$^{-1}$ both due to hydrogen "bending" is pure guess, especially since no line at 1200 is observed, but the total entropy which these contribute is so low (0.2 E. U.) that the assignment is unimportant.

[23] Moorhead, *Phys. Rev.*, **39**, 83 (1932).

The following constants are then used for ethane in equation (20) to calculate the entropy at 1 atm. pressure, 298°K.: $W = 30$; $C' =$ moment of inertia of methane, $C \times 10^{38} = 0.0517$; A', calculated from C–C distance 1.55 Å. and C–H distance 1.08 Å., is 0.417; $p_n = 2^6 = 64$; $p_e = 1$; $\sigma = 18$; ν_1, 1 degree of freedom 990 cm.$^{-1}$; ν_2, 4 degrees of freedom 1200 cm.$^{-1}$; ν_3, 6 degrees of freedom 1460 cm.$^{-1}$; total vibrational entropy at 298°K. = 0.26 E. U. For ethane gas, 298°K., 1 atm., the total absolute molar entropy $S = 63.8$ cal. deg.$^{-1}$, of which $R \ln 64 = 8.3$ due to nuclear spin may be neglected, leaving for the practical entropy $S_p = 55.5$.

Acetylene.—A band in the infra-red spectrum of acetylene[24] at 730 cm.$^{-1}$ may possibly contribute 4 degrees of freedom and 0.5 E. U. at 298°K. It seems more probable that this band is not a fundamental and that the lowest fundamental, contributing 4 degrees of freedom due to hydrogen "bending," is at 1330 cm.$^{-1}$. The following entropy may be as much as 0.5 E. U. too low because of this assumption. The constants used in equation (4) with 4 of the total 7 frequencies contributing an appreciable entropy are: $W = 26$; $A' = 0.23$;[25] $p_e = 1$; $p_n = 2^2 = 4$; $\sigma = 2$; ν_1, 4 degrees of freedom, 1330 cm.$^{-1}$ contributing 0.1 E. U. at 298°K. For acetylene gas, 1 atm., 298°K. the total absolute entropy, $S = 49.9$ cal. deg.$^{-1}$, of which 2.7 E. U. are due to nuclear spin, leaving a practical entropy $S_p = 47.2$ E. U.

Benzene.—Andrews[19] has obtained excellent agreement between the Raman lines of benzene and his models, which enables us to assign the number of degrees of freedom to the frequencies with considerable certainty. x-Ray data on hexamethylbenzene and graphite,[26] and electron diffraction data on gaseous benzene,[27] allow us to estimate the C–C distance accurately. The C–H distance, which is unimportant in the moments of inertia, is assumed to be that of methane. The following constants are substituted in equation (18): $W = 78$; $A' = B'$, calculated from C–C = 1.42 Å. and C–H = 1.08 Å., is 1.508; $C' = 3.016$; $p_e = 1$; $p_n = 64$; $\sigma = 6$

ν_1, 2 degrees of freedom = 360 cm.$^{-1}$
ν_2, 1 degree of freedom = 605 cm.$^{-1}$
ν_3, 2 degrees of freedom = 805 cm.$^{-1}$
ν_4, 6 degrees of freedom = 990 cm.$^{-1}$
ν_5, 1 degree of freedom = 1170 cm.$^{-1}$
ν_6, 12 degrees of freedom = 1590 cm.$^{-1}$

other frequencies too high to contribute to the entropy. The total vibrational entropy at 298°K. is 3.8 E. U. For benzene gas, 1 atm., 298°K., the total absolute entropy $S = 73.4$ cal. deg.$^{-1}$, of which $R \ln 64 = 8.3$

[24] Levin and Meyer, *J. Opt. Soc. Am.*, **16**, 137 (1928).
[25] From infra-red measurements.[24]
[26] Ewald and Hermann, "Strukturbericht," 1913–1928.
[27] Wierl, *Ann. Physik*, **8**, 521 (1931).

E. U. are due to nuclear spin, leaving a practical entropy, S_p = 65.1 cal. deg.$^{-1}$.

The experimental entropy of the liquid at 298°K. is 41.9 E. U. and the entropy[28] of vaporization at the equilibrium vapor pressure at this temperature, 94 mm., is 27.5 E. U. To the sum of these must be added −4.3 E. U. to convert to 1 atm., making the experimental entropy of benzene gas at 1 atm., 298°K., 65.1 E. U.

The value of σ = 6 for benzene was calculated by Deitz[29] from measurements of the vapor pressure. The less structure sensitive methods of x-ray and electron diffraction have hitherto always indicated plane structure for the carbon atoms, which would lead one to assume σ = 12. An undetected transition in the solid state of benzene below the lowest temperatures of the specific heat determinations could only lead to a lower value of σ. The excellent constancy of the σ as calculated by Mr. Deitz over a wide range of temperatures (from 100°K. to 298°K. σ varied from 5.4 to 6.9) indicates, we believe, conclusively, that all twelve atoms of benzene do not lie in one plane.

Summary

It has been shown that any molecule will have among the additive terms in the entropy expression: $-R \ln \sigma$, with σ the symmetry number; $R \ln(2s_i + 1)$ for every atom i of spin s_i; $R \ln I$, with I the number of distinguishable optical isomers present in the gas.

The quantum mechanical wave functions and the energy values of an ethane-like molecule have been calculated under the assumption of free independent rotation of the two CH_3 groups about the C–C bond. The entropy of this type of molecule has also been calculated.

Convenient expressions have been given for the molal entropy of diatomic, rigid linear and non-linear polyatomic, and ethane-like molecules.

The data necessary for the entropy evaluations have been reviewed, and the accuracy which can be expected has been briefly discussed. It appears probable that for many of the simpler organic gases the entropy can be calculated with present data to within 0.5 E. U. (cal. deg.$^{-1}$).

The practical molar entropies (neglecting nuclear spin which cancels in all chemical reactions), of ethane, acetylene and benzene gases at 1 atm., 298°K., have been calculated to be 55.5, 47.2 and 65.1 E. U., respectively.

[28] Parks and Huffman, THIS JOURNAL, **52**, 1032 (1930).

[29] Victor Deitz, *J. Chem. Physics*, **1**, January, 1933.