THE CALCULATION OF CHEMICAL EQUILIBRIUM FROM SPECTROSCOPIC DATA[1]

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On account of the high accuracy with which spectroscopic data are obtained, thermodynamic quantities calculated from these data are far more reliable than those obtained by direct thermal measurements. It may be predicted that in the future thermodynamic quantities will be calculated from spectroscopic data, whenever they are available. The band spectra of most diatomic molecules have been analyzed completely. Little progress has been made with polyatomic molecules because of their complexity, although there is reason to believe that the Raman spectrum may furnish sufficient data for approximate thermodynamic calculations, at least. The discussion of this article[2] will be limited to monatomic and diatomic molecules. The calculation

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[2] The symbols used in this article are as follows:

T = absolute temperature.

k = molecular gas constant = 1.37×10^{-16} ergs/degree.

N = total number of molecules.

N_0 = 6.06×10^{23}, the number in one molecule.

R = $N_0 k$ the molal gas constant.

m = the mass of one molecule.

h = Planck's constant = 6.55×10^{-27} ergs/second.

N_n = the number of molecules in the nth energy level.

ϵ_n = the energy of one molecule in the nth energy level.

e = the base of the system of natural logarithms.

I = the moment of inertia of a molecule.

ω = the frequency of vibration of the molecule.

p_n = the multiplicity of the nth level.

i = the quantum number n in a summation.

Σ = sign of summation to be taken over all energy levels from zero to infinity. The limits of the summation need not always be printed.

of heats of dissociation will not be discussed in this paper, since it belongs to the theory of spectroscopy rather than to statistical mechanics.

The ultimate goal in the analysis of the band spectrum of a molecule is the determination of the possible energy states of the molecule. From the conventional method of representing these energy states graphically (figure 1) they have come to be known as energy "levels." In the case of the diatomic molecule these levels are somewhat arbitrarily classified as rotational, vibrational or electronic levels. This classification has the ad-
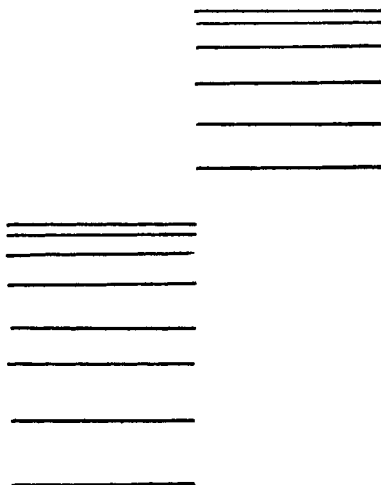

FIG. 1. ENERGY LEVELS OF A MOLECULE

vantage that the formulas for the spacing of the different kinds of levels are given for the simpler cases by the quantum mechanics, and in the more complex cases may be represented by empirical formulas. These formulas all contain a quantum number which, usually, begins with zero and takes on successive integral values.

Both diatomic and monatomic molecules in the gaseous stage possess kinetic energy of translation. This kinetic energy of translation is usually supposed to vary continuously, but in this paper we shall assume that translational energy also is quantized, and we shall proceed later to derive an expression for the trans-

lational energy levels. Consequently the possible energies of any gaseous molecule are given by a set of discrete energy levels, which are often very numerous and very close together, but which never become a continuum. When a molecule has a certain energy we shall say that it lies on a certain energy level.   ·

THE DISTRIBUTION LAW

The Maxwell-Boltzmann distribution law states that N_n, the number of molecules in the nth energy state or level, is given by the expression,

$$N_n = NKe^{-\frac{\epsilon_n}{kT}} \tag{1}$$

where N is the total number of molecules, K is a constant, e is the base of the system of natural logarithms, ϵ_n is the energy of the nth level, k is the molecular gas constant and T is the absolute temperature. Equation 1 has been tested by experiment and shown to hold rigorously under ordinary conditions, but recent theoretical developments have shown that this is more or less accidental. Equation 1 is derived by the use of the statistics of Boltzmann. We now know that the correct statistics for neutral molecules are those of Bose and Einstein. Both methods of calculation lead to the same limiting form of the distribution law, equation 1, for a gas at high temperatures and low pressures, but the Bose-Einstein method gives the correct result under all conditions and is free from certain inconsistencies that mar the Boltzmann statistics.

Equation 1 is often written:

$$N_n = NKp_ne^{-\frac{\epsilon_n}{kT}} \tag{2}$$

where p_n is the weight factor of the nth energy level. If p_n has a value different from unity it means that the level is degenerate, that is, that under a perturbing field, the molecules will be separated into classes which differ from each other slightly in energy. In other words, p_n is the multiplicity of the nth level. It will often be simpler for our purposes to assign to a level with the multiplicity p_n the designations n, $n+1$, etc., with the understanding that the energies ϵ_n, ϵ_{n+1}, etc., become equal to each other in the absence of a perturbing field.

THE BOSE-EINSTEIN STATISTICS

Let p_i be the multiplicity of a level with energy ϵ_i. Then the number of different ways in which N_i molecules may be distributed among the p_i levels is

$$\frac{(N_i + p_i)!}{N_i! \, p_i!}$$

$N_i!$ appears in the denominator because in the Bose-Einstein statistics the interchange of like molecules is without significance, and p_i appears in the denominator, because the interchange of levels can have no physical meaning. The total number of possible arrangements of N molecules among a series of energy levels is given by the continued product of terms

$$P = \prod_{i=0}^{\infty} \left[\frac{(N_i + p_i)!}{N_i! \, p_i!} \right] \tag{3}$$

The most probable values for N_0, N_1, etc., are those which will make P a maximum. This condition may be stated for our purposes most conveniently,

$$\delta \ln P = 0 \tag{4}$$

Expanding equation 3 and remembering that p_i is a constant, we have[3]

$$\sum_{i=0}^{\infty} \ln \left(1 + \frac{p_i}{N_i} \right) \delta N_i = 0 \tag{5}$$

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[3] When N is a large number

$$N! = N^N e^{-N} \sqrt{2\pi N}.$$

For the calculations in this paper a sufficient approximation is obtained by writing

$$N! = N^N e^{-N}$$

Taking logarithms, equation 3 becomes

$$\ln P = \Sigma \ln \frac{(N_i + p_i)^{N_i + p_i} e^{-(N_i + p_i)}}{N_i^{N_i} p_i^{p_i} e^{-N_i} e^{-p_i}}$$

This becomes

$$\delta \ln P = \Sigma (N_i + p_i) \ln (N_i + p_i) - \Sigma N_i \ln N_i - \Sigma p_i \ln p_i$$

Since the total number of molecules and the total energy is constant, we have two further conditions

$$\Sigma N_i = N \tag{6}$$
$$\Sigma \epsilon_i N_i = E \tag{7}$$

which may be written

$$\Sigma \delta N_i = 0 \tag{8}$$
$$\Sigma \epsilon_i \delta N_i = 0 \tag{9}$$

If, following the custom of the mathematician, we multiply equations 8 and 9 by undetermined multipliers, α and β, and add them to equation 5 we have

$$\sum \left[\ln \left(1 + \frac{p_i}{N_i} \right) + \alpha + \beta \epsilon_i \right] \delta N_i = 0 \tag{10}$$

Since for the maximum value of P the δN's are arbitrary we may choose values for the δN's, α, and β so that all terms vanish except the one which contains N_n.

$$\ln \left(1 + \frac{p_n}{N_n} \right) + \alpha + \beta \epsilon_n = 0 \tag{11}$$

This may be rewritten

$$1 + \frac{p_n}{N_n} = e^{\alpha + \beta \epsilon_n} \tag{12}$$

or

$$N_n = e^{\frac{p_n}{\alpha + \beta \epsilon_n}} - 1 \tag{13}$$

It turns out that for a gas at ordinary temperature and pressure e^α is very large compared to unity so that we may write

$$N_n = p_n e^{-\alpha} e^{-\beta \epsilon_n} \tag{14}$$

Remembering that N_i is varied and p_i is constant we get

$$\delta \ln P = 0 = \Sigma \delta N_i + \Sigma \ln (N_i + p_i) \delta N_i - \Sigma \delta N_i - \Sigma \ln N_i \delta N_i$$

This leads to equation 5 above.

A given set of values for N_0, N_1, N_2, etc., is called a distribution. The number of ways in which this distribution may be obtained, counting as one those which differ only by permutations of like molecules, will be referred to as the number of arrangements.

β is to be identified with $\dfrac{1}{kT}$ so that we have the general form of equation 1

$$N_n = p_n e^{-\alpha} e^{-\frac{\epsilon_n}{kT}} \qquad (15)$$

THE ENERGY LEVELS OF A MONATOMIC GAS

The experiments of Stern on the reflection of molecules from crystal surfaces show that the motion of a free particle may be represented by a DeBroglie wave of wave length $\lambda = \dfrac{h}{mv}$. Just as there is a limitation on the number of stationary acoustical waves that can exist in a box so is there a precisely analogous limitation on the number of possible DeBroglie waves in an enclosure. The effect of this is to limit the momentum and hence the translational energy of the molecule to certain discrete values. The result is most easily obtained from the Schroedinger equation

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - W) \psi = 0 \qquad (16)$$

W, the potential energy, is zero throughout the box containing the gas and ψ must vanish at the walls. The solution of the above differential equation is

$$\psi = \sin \frac{n_1 \pi x}{l} \sin \frac{n_2 \pi y}{l} \sin \frac{n_3 \pi z}{l} \qquad (17)$$

where l is the length of one edge of the cubical box. On substitution of equation 17 in equation 16 it is seen that the permitted values of E are

$$E = \epsilon_n = \frac{h^2}{8ml} (n_1^2 + n_2^2 + n_3^2) \qquad (18)$$

Here h is Planck's constant, m is the mass of the molecule and n_1, n_2 and n_3 are three quantum numbers corresponding to the three degrees of freedom of the molecule. These numbers are restricted to integral values. The factor p_n in equation 15 represents the number of possible ways in which a given value

ϵ_n may be obtained by using different integral values for n_1, n_2 and n_3. For the simple form, equation 15, it is possible to evaluate $e^{-\alpha}$.

In order to do this it is necessary to note the significance of p_n. p_n is the number of different ways that a given energy

$$\epsilon_n = \frac{h^2}{8ml^2}(n_1^2 + n_2^2 + n_3^2) \tag{19}$$

may be represented as a sum of the squares n_1^2, n_2^2, n_3^2. Physically these different representations correspond to the different directions of velocity possible for a molecule of kinetic energy, ϵ_n, inside the box.

It is not possible to express p_n as a simple function of ϵ_n, and it is not necessary to do this to obtain e^α. If we sum equation 15 over all values of n we only need to remember that the exponential term is to be summed over all integral values of n_1, n_2, n_3, and p_i drops out. We have

$$\sum N_i = N = e^{-\alpha} \sum_{n_1} \sum_{n_2} \sum_{n_3} e^{-\frac{h^2(n_1^2 + n_2^2 + n_3^2)}{8ml^2kT}} \tag{20}$$

This may be written

$$Ne^\alpha = \sum_{n_1} e^{-\frac{h^2 n_1^2}{8ml^2kT}} \sum_{n_2} e^{-\frac{h^2 n_2^2}{8ml^2kT}} \sum_{n_3} e^{-\frac{h^2 n_3^2}{8ml^2kT}} \tag{21}$$

As

$$\frac{h^2}{8ml^2kT}$$

approaches zero the value of

$$\sum_n e^{-\frac{h^2 n^2}{8mlkT}}$$

approaches

$$\sqrt{\frac{2\pi ml^2kT}{h^2}}$$

and equation 21 becomes

$$Ne^\alpha = \left(\frac{2\pi ml^2kT}{h^2}\right)^{\frac{3}{2}} \tag{22}$$

But

$$l^3 = V \tag{23}$$

where V is the volume of the box.   Hence[4]

$$e^\alpha = \left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} \tag{24}$$

Equation 13 may be written in the form of equation 15 when e^α is large compared to unity, and by reference to equation 24 we see that this is the case for a gas at ordinary temperatures and pressures.

The general form of the distribution law for a monatomic gas may therefore be written

$$N_n = \frac{N p_n e^{-\frac{\epsilon_n}{kT}}}{\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}} V} \tag{25}$$

which is the standard form in which we shall write all distribution laws.[5]

THE DISTRIBUTION LAW FOR DIATOMIC GASES

The general form of the distribution for diatomic gases must take account of the internal energy of the molecule.   Actually

[4] The author is indebted to Mr. R. H. Ewart for this method of evaluating e^α.

[5] In the sketchy derivation given above, we have only indicated that equation 25 represents the most probable distribution of molecules. It can be shown mathematically that the number of arrangements which gives the distribution of equation 25 is so much greater than the number of arrangements corresponding to any distribution differing appreciably from equation 25, that the total number of all other arrangements is negligible when compared with the number of arrangements corresponding to the distribution of equation 25.

The fundamental postulate of the Bose-Einstein statistics is that the permutation of like molecules does not produce a new arrangement of molecules.   In the Boltzmann statistics each permutation of molecules is counted as a new arrangement.   The fact that the two kinds of statistics give the same limiting form of the distribution law must be regarded as a coincidence.   The distribution law (7) is derived for a constant total energy.   It remains to show that the total energy is related in some simple way to the absolute temperature.   This may be done either by use of the laws of thermodynamics or by an arbitrary definition of absolute temperature in terms of the average translational energy of a gas molecule at higher temperatures.

of course at any instant a molecule possesses a certain discrete energy, but this energy may be represented as a sum of translational, rotational, vibrational and electronic terms. Thus,

$$\epsilon_n = \epsilon_{n(tr)} + \epsilon_{n(r)} + \epsilon_{n(v)} + \epsilon_{n(e)} \tag{26}$$

For example, in addition to possessing a certain discrete translational energy a molecule may at a given instant exist in particular rotational, vibrational and electronic states.

Corresponding to the multiplicity of each state or level there will be an integral weight factor. The general distribution law for a diatomic molecule thus becomes

$$N_n = NK p_{n(tr)} p_{n(r)} p_{n(v)} p_{n(e)} e^{- \frac{\epsilon_{n(tr)} + \epsilon_{n(r)} + \epsilon_{n(v)} + \epsilon_{n(e)}}{kT}} \tag{27}$$

In so far as the distributions of these energies are independent of one another, distribution equations may be written for particular forms of the energies. Thus,

$$N_n = NK p_{n(r)} e^{- \frac{\epsilon_{n(r)}}{kT}} \tag{28}$$

represents the distribution of diatomic molecules among the various rotational levels. The internal energy of the molecule is quite independent of the translational energy, but the distribution of the various rotational, vibrational and electronic energies may only be considered independent as a first approximation. The reasons for this will be noted later.

GENERAL PROPERTIES OF THE DISTRIBUTION EQUATION

The partition function

By summing equation 2 over all energy levels we obtain

$$\sum_{i=0}^{\infty} N_i = N = NK \sum_{i=0}^{\infty} p_i e^{- \frac{\epsilon_i}{kT}} \tag{29}$$

From this equation we see that

$$K = \frac{1}{\displaystyle\sum_{i=0}^{\infty} p_i e^{- \frac{\epsilon_i}{kT}}} \tag{30}$$

and equation 2 becomes

$$N_n = \frac{N p_n e^{-\frac{\epsilon_n}{kT}}}{\sum\limits_{i=0}^{\infty} p_i e^{-\frac{\epsilon_i}{kT}}} \tag{31}$$

The summation

$$\sum_{i=0}^{\infty} p_i e^{-\frac{\epsilon_i}{kT}}$$

has been called by Planck the "Zustandsumme." This is not a convenient word for an English-speaking person and it has no satisfactory translation, but R. H. Fowler has suggested that it
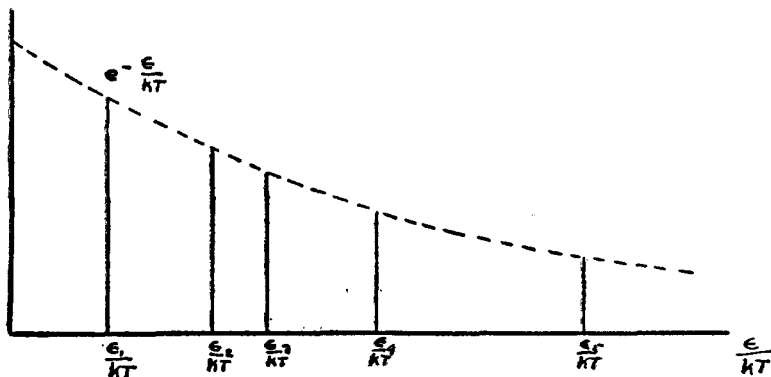

FIG. 2. GRAPHICAL REPRESENTATION OF THE DISTRIBUTION LAW

be called the "partition function" and we shall use this term for this very important expression to which we shall be constantly referring in this paper.

The graphical representation of the partition function

In figure 2 is a graphical representation of a partition function. The various terms of the summation $e^{-\frac{\epsilon_i}{kT}}$ are plotted as ordinates against the energy divided by kT, as abscissas. The partition function is obviously the sum of the lengths of the ordinates to infinity. This is a very convenient graphical representation.

Since the spacing of the ordinates is proportional to the spacing of the energy levels it is convenient to turn the diagram (figure 2) around and plot it as in figure 3. The plot is now similar to figure 1. The spacings of the energy levels are multiplied by the
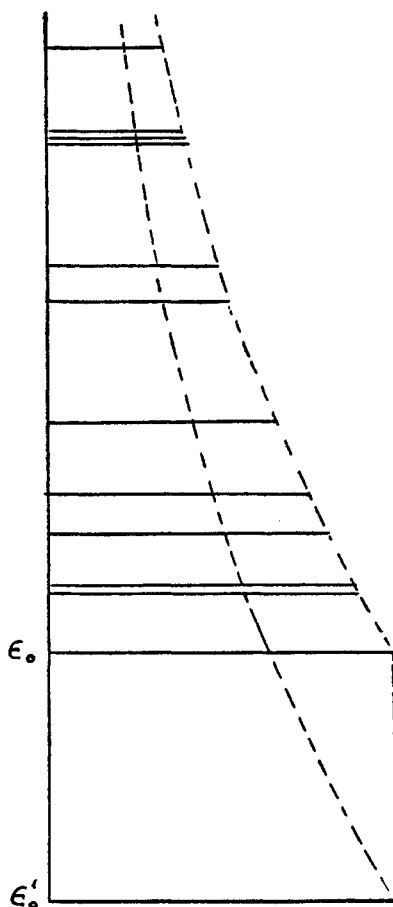

FIG. 3. GRAPHICAL REPRESENTATION OF THE PARTITION FUNCTION

constant factor $\frac{1}{kT}$, but this causes no difficulty since the scale is arbitrary. The distribution of the molecules among the various levels is easily visualized, since the number of molecules in any

level is proportional to the length of the level. Degenerate levels are represented simply as multiple levels, the lines being drawn very close together. The effect of temperature on the distribution is shown in figure 4, where the spacing of the levels
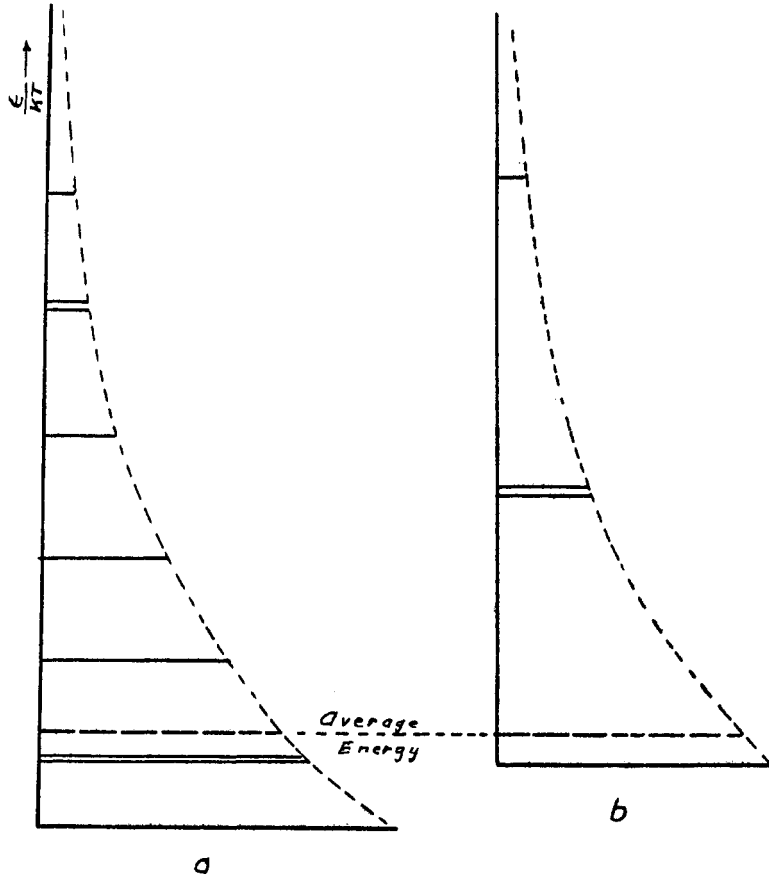

FIG. 4. GRAPHICAL REPRESENTATION OF PARTITION FUNCTIONS AT DIFFERENT TEMPERATURES

The average energy is taken as the zero in each case

is increased, due to a small value of kT corresponding to a lower temperature. The bounding curve represented by the dotted line remains unchanged.

The zero of energy is always arbitrary. The effect of a change in this arbitrary zero of energy is shown in figure 3. Unit length is always assigned to the level of zero energy. If we wish to take our zero of energy, not as the diagram is drawn but at a point ϵ_0^1 which lies a distance $\dfrac{\epsilon}{kT}$ below ϵ_0 we simply draw a new bounding curve starting with ϵ_0^1. Mathematically this is equivalent to adding the term $\dfrac{\epsilon}{kT}$ to each of the values $\dfrac{\epsilon_1}{kT}$, $\dfrac{\epsilon_2}{kT}$, etc. We now write the partition function,

$$\sum_{i=0}^{\infty} e^{-\frac{\epsilon_i + \epsilon}{kT}} = e^{-\frac{\epsilon}{kT}} \sum e^{-\frac{\epsilon_i}{kT}} \tag{32}$$

It is seen that the change in the zero point of energy is equivalent to multiplying the partition function by the term $e^{-\frac{\epsilon}{kT}}$. The value of the partition function depends upon the arbitrary zero of energy chosen. It must be remembered that the arbitrary zero of energy is not an energy level of the molecule, except as it may coincide with one of the levels.

The partition functions for various kinds of energy

By comparison of equation 25 with equation 31 we see that the partition function for the translational energy of a gas is[6]

$$\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V$$

It has been stated above that the distributions of the rotational and vibrational energies of a diatomic molecule are practically independent of each other. The spacing of the rotational levels

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[6] The complete partition function for the atom of a monatomic gas must include the electronic levels to which the atom is excited in the emission of the line spectrum. The first excited state usually lies so far above the normal state that it need not be considered. However, except for ^1S states the normal levels of the atom are multiple, and a corresponding multiplicity is introduced into the partition function.

depends upon the moment of inertia, and the moment of inertia is not affected by the lower state of vibration. Neither does the rotation affect the vibrational frequency appreciably. On the other hand, electronic excitation usually changes both the moment of inertia and the vibrational frequency.

In the absence of electronic excitation, theoretical expressions can be obtained for the rotational and vibrational partition functions. The rotational partition function is

$$\sum_{n=0}^{\infty} (2n + 1)\, e^{-\frac{n(n+1)h^2}{8\pi^2 IkT}}$$

The sum of this series approaches the limit

$$\frac{8\pi^2 IkT}{h^2}$$

when the term

$$\frac{h^2}{8\pi^2 IkT}$$

is small. For large values of n the moment of inertia I increases due to the stretching effect of the centrifugal force, but this effect is usually negligible. If the term

$$\frac{h^2}{8\pi^2 IkT}$$

is not small the series must be summed term by term. For the vibrational partition function we have

$$\sum_{n=0}^{\infty} e^{-\frac{nh\omega}{kT}} = \frac{1}{1 - e^{-\frac{h\omega}{kT}}} \tag{33}$$

For the higher vibrational states the frequency ω does not remain constant so that an error is introduced. For the more complicated states of molecules, such as the $^3\Sigma$ which characterizes oxygen, or the $^2\Pi$ which characterizes the hydroxyl molecule, various types of multiplicity appear which must be taken into account. In any event the exact value of the partition function may always be calculated by a term by term summation over the energy levels which are given by an analysis of the band spectrum.

THE ENERGY AND HEAT CAPACITY

The total energy of any kind in a system of molecules in any form may be obtained readily if the distribution of that particular kind of energy is independent of other forms of energy. For example, the total rotational energy is given by the expression,

$$E_r = \sum_{i=0}^{\infty} N_i \epsilon_i = \frac{N \Sigma p_i \epsilon_i e^{-\frac{\epsilon_i}{kT}}}{\Sigma p_i e^{-\frac{\epsilon_i}{kT}}} \tag{34}$$

The value obtained for the energy depends naturally upon the particular arbitrary zero that is chosen for the energy. On the other hand the heat capacity is independent of the arbitrary zero of energy. The heat capacity is given by the expression,

$$\frac{\partial E}{\partial T} = \frac{N}{kT^2} \left[\frac{\Sigma p_i \epsilon_i^2 e^{-\frac{\epsilon_i}{kT}}}{\Sigma p_i e^{-\frac{\epsilon_i}{kT}}} - \left(\frac{\Sigma p_i \epsilon_i e^{-\frac{\epsilon_i}{kT}}}{\Sigma p_i e^{-\frac{\epsilon_i}{kT}}} \right)^2 \right] \tag{35}$$

The foregoing formulas are of course exact only under conditions of temperature and pressure where equation 15 is valid, that is, where the Bose-Einstein statistics give the same result as the classical Boltzmann statistics.

THE ENTROPY

The customary *a priori* definition of entropy is by the relation

$$S = K \ln P \tag{36}$$

Where P is the total number of possible arrangements of a system of molecules. For a system of molecules obeying the Bose-Einstein statistics we evaluate P as in equation 3 since, as has already been pointed out, the most probable distribution includes all but a negligible fraction of the total possible arrangements. From equation 3 therefore,

$$S = K \ln \prod_{i=0}^{\infty} \left(\frac{(N_i + p_i)!}{N_i! \, p_i!} \right) \tag{37}$$

Expanding the factorials as before we have

$$S = K \sum_{i=0}^{\infty} \ln \left(1 + \frac{p_i}{N_i}\right)^{N_i} + K \sum_{i=0}^{\infty} \ln \left(1 + \frac{N_i}{p_i}\right)^{p_i} \tag{38}$$

From equation 11 the first term of this expansion becomes, for one mole,

$$k \sum_{i=0}^{\infty} N_i \left(\alpha + \frac{\epsilon_i}{kT}\right) = R \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N}\right] + \frac{E}{T}$$

$$= R \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} e^{\frac{3}{2}}\right] \tag{39}$$

where E is the total energy per mole $\left(= \frac{3}{2}RT\right)$. In order to evaluate the second term in this equation we may rewrite it,

$$k \sum_{i=0}^{\infty} N_i \ln \left(1 + \frac{N_i}{p_i}\right)^{\frac{p_i}{N_i}}$$

If $\frac{p_i}{n_i}$ is small, the value of the expression approaches unity and the logarithm is zero; if $\frac{p_i}{n_i}$ is large, the expression approaches the number e as a limit and the expression becomes

$$K \Sigma N_i = R \tag{40}$$

The value of the second term therefore increases from a limiting value of zero at 0°K. to R, at temperatures where equation 25 holds for a gas. The entropy of a monatomic gas is given exactly under ordinary conditions by the equation,

$$S = R \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} e^{\frac{5}{2}}\right] \tag{41}$$

ROTATIONAL AND VIBRATIONAL ENTROPIES

We have seen that where the distribution of one form of energy is independent of other forms, a separate distribution equation can be written for this form of energy as equation 34. By the

same process of reasoning we can separate the terms involving the rotational or vibrational entropy. By substituting from equation 27 in equation 41 we obtain as the general expression for the entropy of a diatomic gas

$$S = R \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} e^{\frac{5}{2}} \right] + \frac{E_r}{T} + R \ln \sum_{i=0}^{\infty} p_i e^{-\frac{\epsilon_{i(r)}}{kT}} + \frac{E_v}{T} + R \ln \sum_{i=0}^{\infty} e^{-\frac{\epsilon_{i(v)}}{kT}}$$

This equation may be written as a sum of entropy terms of which, for example, the rotational entropy is

$$S = R \ln \sum_{i=0}^{\infty} p_i e^{-\frac{\epsilon_{i(r)}}{kT}} + \frac{E_r}{T} \tag{43}$$

If we write

$$E = N_0 \bar{\epsilon} \tag{44}$$

where $\bar{\epsilon}$ is the average rotational energy per molecule, equation 42 may be written

$$S = R \ln \sum_{i=0}^{\infty} p_i e^{-\frac{\epsilon_i}{kT}} + R \ln e^{-\frac{\bar{\epsilon}}{kT}} = R \ln \sum_{i=0}^{\infty} p_i e^{-\frac{\epsilon_i - \bar{\epsilon}}{kT}} \tag{45}$$

The same transformation may be made for any form of energy which is independently distributed.

The entropy is seen to be equal to R times the logarithm of the partition function when the average energy per molecule is arbitrarily taken as the zero of energy. Reference to figure 4 will make this clear. In accordance with our graphical scheme of representation the zero of energy is a line of unit length. As the temperature approaches zero, the average energy per molecule approaches and coincides with the lowest level and the partition function takes on the value unity and the entropy becomes zero. It would be a case of *petitio principii* to assume that this was a demonstration of the absolute character of entropy, because we must remember that we assumed in our derivation of the equation for entropy that the additive constant was zero. However, this seems to be a very illuminating illustration of the significance of entropy. The entropy of a system of molecules is a measure

of the extent to which the molecules are distributed over different levels.

It is important to notice the effect of the weight factor p_n in cases where it is different from unity. This factor gives the multiplicity of the level and is taken care of in our graphical representation by actually representing the levels as multiplets. In the absence of a perturbing field these multiplets would coincide, but we may always assume that some perturbing field is present due to adjacent molecules. Under these conditions we may be sure that the multiple levels will be separate, and this has an important bearing on the entropy at $0°K.$ of substances such as molecular oxygen or ortho-hydrogen. Each of these molecules has a resultant spin of one unit. The spin in the oxygen molecule is due to the electrons and in the ortho-hydrogen molecule it is due to the protons. In addition, the ortho-hydrogen molecule has an angular momentum of one unit in its lowest state. On account of the different orientations of the spin and angular momentum in the external field, which may always be assumed to be present with corresponding slight differences in energy, the lowest level for the oxygen molecule is threefold, and for the ortho-hydrogen molecule ninefold. As the temperature is lowered to near absolute zero, however, the molecules will be found to lie on the lowest level of the multiplet, which of coures gives a zero entropy.[7]

In table 1 are given the values of the entropy and heat capacity at constant volume as calculated from the data of the band spectra for a number of molecules. The calculations for a number of these molecules have been published elsewhere by various authors. The data calculated in this way, while in general agreement with the data obtained by direct thermal measurements, are more accurate. The entropy of the hydrogen compounds includes a term $R \ln 2$ for each atom of hydrogen in the molecule. This is to take account of the multiplicity produced by the proton spin which has been discussed above. No term is added for the nuclear spin of other elements such as chlorine.

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[7] Contrast Stern, T. E.: Proc. Roy. Soc. London **130A,** 367 (1931).

because the spin is not known with certainty. In the case of hydrogen, the spin effect may be obtained by direct thermal measurements on the equilibrium mixture of ortho- and para-hydrogen.[8] In figure 5 is given the heat capacity curve, as calculated by Bonhoeffer and Harteck (9) for hydrogen gas, in the presence of a catalyst for the interconversion of ortho- and para-molecules. This curve rises to a very high peak at low temperatures, which gives a large contribution to the entropy and goes to make up the additional value of $R \ln 4$ which is to be included in the entropy of the hydrogen molecule. Giauque and

TABLE 1

Entropies and heat capacities calculated from spectroscopic data[9]

SUBSTANCE	REFERENCES TO LITERATURE	ENTROPY 298°K. 1 ATMOSPHERE PER MOLE	HEAT CAPACITY AT CONSTANT VOLUME AT 298°K. PER MOLE
H_2.............................	(1)	34.0	4.91
O_2.............................	(2)	49.0	5.03
Cl_2............................	—	54.0	6.09
I_2.............................	(3)	62.3	6.81
HCl............................	(4)	46.3	4.97
HBr............................	(5)	49.2	4.97
HI.............................	(6)	51.1	4.97
CO.............................	—	47.3	4.97
NO.............................	(7)	50.4	5.13
OH.............................	(8)	45.3	

Johnston (10) and R. H. Fowler (11) have calculated the entropy of the metastable 3 to 1 mixture of ortho- and para-hydrogen at low temperatures. It is possible to do this, and the entropy will

[8] The nuclear spin of an atom makes the same contribution to the entropy per gram-atom in the elementary state and in compounds. So far as practical calculations are concerned, therefore, this entropy may be included or omitted, provided only that the practice be consistent.

[9] The particular values given herewith were calculated by the members of the author's seminar in physical chemistry in 1929–30.

In stating values of the heat capacity for gases at temperatures and pressures where appreciable dissociation occurs, it is necessary to state whether the heat capacity is calculated for the *pure* diatomic gas or for an equilibrium mixture. The values given in this table are for the pure diatomic gas.

have significance for any equilibrium in which the relative proportions of the two kinds of molecules are not disturbed. The equilibrium between vapor and solid or liquid hydrogen is presumably such an equilibrium, although here it is possible that the vapor is not in equilibrium with a condensed phase of the same composition.
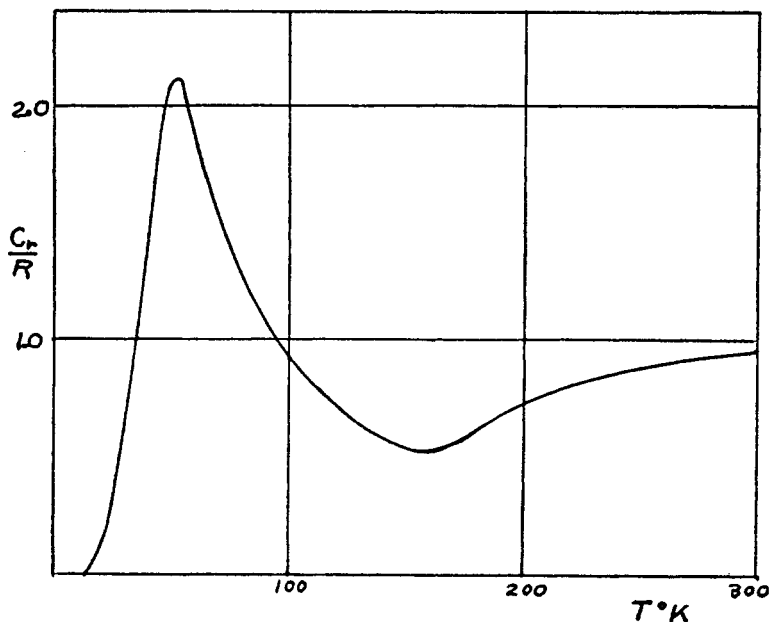

FIG. 5. THE ROTATIONAL HEAT CAPACITY CURVE FOR HYDROGEN ASSUMING INTERCOMBINATION OF ODD AND EVEN STATES

The entropy of the electron

According to the new quantum mechanics the electron should have a weight factor of two in the vapor state because of its spin. This leads to an equation for the emission of electrons from hot filaments of the form

$$I = AT^2 e^{-\frac{b_0}{T}} \tag{68}$$

in which theoretical value of the constant A should be 120.4. Dushman (12) has shown that the best experimental value for this

constant A is 60.2, or one-half the required value. This might be taken to indicate that the electron does not have a statistical weight of two in the vapor state. Another possibility is that the reflection coefficient of electrons from filaments is about 0.5. It seems more probable, however, that some error exists in the emission data themselves. The problem requires further investigation and is an interesting one because it is the only way that has so far been proposed for a direct experimental proof of the existence of spin in the free electron.

The isotope effect in the entropy of chlorine

An interesting effect is to be predicted in the entropy of chlorine. Since there are present atoms of Cl_{35} and Cl_{37} we may expect an equilibrium of the following sort.

$$Cl_{35}Cl_{35} + Cl_{37}Cl_{37} = 2Cl_{35}Cl_{37} \tag{46}$$

If we assume the heat of dissociation of the three kinds of molecules to be exactly the same, then it follows from simple kinetic considerations that the chances of forming a heteronuclear molecule are twice as great as for a homonuclear molecule. As a result we should have at equilibrium

$$\frac{P^2_{Cl_{35}Cl_{37}}}{P_{Cl_{35}Cl_{35}} P_{Cl_{37}Cl_{37}}} = 4 \tag{47}$$

Since

$$\Delta F^\circ = -RT \ln K$$

and

$$\Delta H = 0$$

it follows that

$$\Delta S = R \ln 4 \tag{48}$$

or that the entropy of the heteronuclear molecule is greater by $R \ln 2$ than that of the homonuclear molecule. This result is confirmed by the quantum mechanics, which predicts that alternate rotational levels will be missing for homonuclear molecules. This effect has nothing to do with the entropy of mixing or with

nuclear spin effects. At low temperatures the equilibrium will be shifted in an irregular manner until finally at very low temperatures, where all rotational energy has been lost, it may be predicted that the entropy of homonuclear and heteronuclear molecules would be the same and the equilibrium constant of equation 47 will be unity. In this discussion the slight variation of the entropy with the masses of the different isotopes has been neglected.

CHEMICAL EQUILIBRIUM

In a general discussion of chemical equilibrium the liquid and solid phases must be considered. While it is beyond the scope of this article to discuss them, partition functions exist for the liquid and solid states as well as for the gas, and these partition functions are related in the same way to the thermodynamic functions as the partition functions for gases are.

In the following discussion we shall limit ourselves to equilibria in which the gaseous phase is present.

Let us consider first an equilibrium wholly within the gaseous phases. Let the equilibrium be of the form.

$$A = nA' \qquad (49)$$

For each species of molecule present there exists a partition function. Let us suppose a volume V to contain N molecules of A and N_1 molecules of A'. The condition for equilibrium is that the proportions of N and N_1 in the vessel must be such that the maximum number of possible arrangements of the two species is possible. If P_A is the total possible number of arrangements of A, and $P_{A'}$ the total number of arrangements of A', then the total number of arrangements of both species is the product $P_A P_{A'}$. The condition for equilibrium is that this product shall be a maximum, and this condition may be conveniently expressed by taking logarithms and differentiating

$$\delta \ln P_A + \delta \ln P_{A'} = 0 \qquad (50)$$

It turns out that P_A likewise $P_{A'}$ are represented by equations,

$$P_A = Q_A^N \qquad (51)$$

$$P_{A'} = Q_{A'}^{N_1} \qquad (52)$$

where Q_A and $Q_{A'}$ do not depend upon the total number of molecules present but only upon the number of molecules of each species per unit volume respectively.

We may now write

$$\ln P_A P_{A'} = N_1 \ln Q_A + N_2 \ln Q_{A'} \tag{53}$$

If we now imagine the number of molecules to be varied by transforming a small number δN_1 molecules of A into δN_1 molecules of A', the concentration of N and N_1 will not be affected appreciably and $Q_{A_1} Q_{A'}$ will remain constant. Equation 50 becomes therefore,

$$\delta N \ln Q_A + \delta N_1 \ln Q_{A'} = 0 \tag{51}$$

Remembering that

$$\delta N = n \delta N_1 \tag{52}$$

we have

$$\ln Q_A = n \ln Q_{A'} \tag{53}$$

or

$$Q_A = Q_{A'}^n \tag{54}$$

Now the number of possible arrangements per molecule is measured by the partition function. We can see intuitively that this must be so since the number of possible arrangements of a molecule must depend upon the number of energy levels and also, of course, on the values of the energy for each level in precisely the way that the partition function does.

The statement can be demonstrated rigorously however, by considering the expansion of equation 37 for the total number of arrangements of a gas. This expansion leads to two varieties of terms. One of these terms is made up of the product of the partition functions for the various forms of energy divided by the total number of molecules N. The second term arising from the expansion is the total energy of N molecules, divided by the absolute temperature. The term R for example in equation 40 is equal to $\dfrac{PV}{T}$, and represents the potential energy of the gas, due

to the volume occupied under an external pressure, divided by the absolute temperature. This energy term appears in the expression for the total number of arrangements as an exponential multiplier $\left(e^{\frac{\bar{\epsilon}}{kT}}\right)$. The whole expression is the partition function as expressed in equation 45. If we multiply by $\left(e^{-\frac{\bar{\epsilon}}{kT}}\right)$ we refer the partition function to its lowest energy level as zero. This is permissible, since the zero of energy is arbitrary. Only in comparing two partition functions we must refer both functions to the same zero of energy and this may be done by multiplying one partition function by $e^{-\frac{\epsilon_0}{kT}}$, as is demonstrated in equation 32 and figure 3.

The condition for the equilibrium (equation 49) may be written down by substituting in equation 54 the partition functions for A and A' divided by N and N_1 respectively.

$$\left(\frac{2\pi m_{\mathrm{A}}kT}{h^2}\right)^{\frac{3}{2}}\frac{V}{N}\Sigma p_i e^{-\frac{\epsilon_i}{kT}} = \left[\left(\frac{2\pi m_{\mathrm{A}'}kT}{h^2}\right)^{\frac{3}{2}}\frac{V}{N}\Sigma p_i e^{-\frac{\epsilon_i'}{kT}}\left(e^{-\frac{\epsilon_0}{kT}}\right)\right]^n \quad (55)$$

The requirement that both partition functions be referred to the same zero is met by multiplying the second term of the equation by $e^{-\frac{\epsilon_0}{kT}}$ where ϵ_0 is the difference between the lowest energy level of A and the lowest energy level of A' (figure 6). By taking logarithms and multiplying by R we obtain

$$R\ln\left[\left(\frac{2\pi m_{\mathrm{A}}kT}{h^2}\right)^{\frac{3}{2}}\frac{V}{N}\Sigma p_i e^{-\frac{\epsilon_i}{kT}}\right] = nR\ln\left[\left(\frac{2\pi m_{\mathrm{A}'}kT}{h^2}\right)^{\frac{3}{2}}\frac{V}{N}\Sigma p_i e^{-\frac{\epsilon_i}{kT}}\right] - \frac{nN_0\epsilon_0}{T} \quad (56)$$

The first two terms of this equation are respectively $S_1 - \dfrac{H_1}{T}$ and $n\left(S_2 - \dfrac{H_2}{T}\right)$, where S_1 and S_2 are the molal entropies and H_1 and H_2 the molal heat contents, referred to 0°K., for A and A', respectively. The last term is $\dfrac{\Delta H_0}{T}$. Since
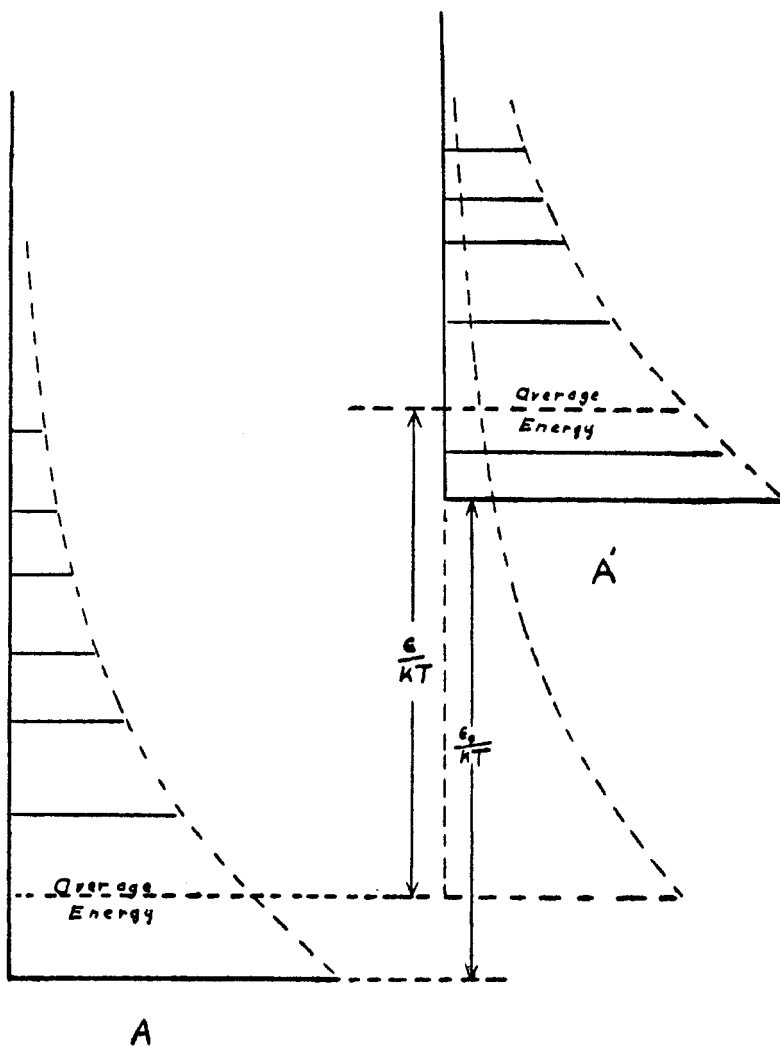
$$\Delta H = \Delta H_0 - H_1 + nH_2$$

FIG. 6. PARTITION FUNCTIONS FOR TWO STATES A AND A' IN EQUILIBRIUM

we have

$$\Delta S = \frac{\Delta H}{T} \tag{57}$$

which is the fundamental thermodynamics condition for equilibrium.

One of the simplest types of gaseous equilibria is the equilibrium between the $^2\Pi_{\frac{3}{2}}$ and the $^2\Pi_{\frac{1}{2}}$ states of a molecule such as hydroxyl. For this equilibrium $n = 1$ and we have from equation 55

$$\frac{N_1}{N} = \frac{\left(\Sigma p_i e^{-\frac{\epsilon_i}{kT}}\right)_{\pi_{\frac{1}{2}}} e^{-\frac{\epsilon_0}{kT}}}{\left(\Sigma p_i e^{-\frac{\epsilon_i}{kT}}\right)_{\pi_{\frac{3}{2}}}} \tag{58}$$

A specific example of the equilibrium (equation 49) is a dissociation, for example

$$I_2 = 2 I \tag{59}$$

Here the condition (equation 55) becomes

$$\left(\frac{2\pi m_2 kT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} \Sigma_{I_2} p_i e^{-\frac{\epsilon_i}{kT}} = \left[\left(\frac{2\pi m kT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N_1} \Sigma_I p_i e^{-\frac{\epsilon_i}{kT}} \left(e^{-\frac{\epsilon_0}{kT}}\right)\right]^2 \tag{60}$$

where $m_2 = 2m$. Making the substitution

$$\frac{V}{N} = \frac{kT}{P} \tag{61}$$

equation 60 becomes,

$$\ln \frac{P_1^2}{P} = \ln K - \frac{\Delta H_0}{RT} + \frac{5}{2} \ln (kT) + \ln \left(\frac{\pi m}{h^2}\right)^{\frac{3}{2}} - \ln \Sigma (2n+1) e^{-\frac{n(n+1)h^2}{8\pi^2 I kT}} -$$

$$\ln \Sigma e^{-\frac{n h \omega}{kT}} + \ln \Sigma_I p_i e^{-\frac{\epsilon_i}{kT}} \tag{62}$$

Here P is the partial pressure of the iodine molecules, P_1 the partial pressure of the iodine atoms, I the moment of inertia of the molecule, ω the vibrational frequency and

$$\Sigma_i p_i e^{-\frac{\epsilon_i}{kT}}$$

the partition function for the electronic levels of iodine atom. ΔH_0 is equal to the spectroscopic heat of dissociation. Since half the rotational levels are missing for the iodine molecule we have for the rotational partition function,

$$\frac{1}{2}\left(\frac{8\pi^2 I kT}{h^2}\right)$$

The lowest level of the iodine atom has a multiplicity of 4 and the next levels are so high that they may be neglected. Hence we have (13)

$$\ln K = -\frac{\Delta H_0}{RT} + \frac{3}{2}\ln\left(\frac{\pi mkT}{h^2}\right) - \ln\left(\frac{8\pi^2 I}{h^2}\right) + \ln\left(1 - e^{-\frac{h\omega}{kT}}\right) + 5\ln 2 \qquad (63)$$

Another simple illustration of equilibrium is the vapor pressure of a crystal whose vapor is monatomic. For this equilibrium

$$\Sigma_{\text{crystal}} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} e^{-\frac{\epsilon_0}{kT}} \qquad (64)$$

This gives the equation

$$\ln P = -\frac{\Delta H}{RT} + \frac{5}{2}\ln T - \frac{S_{\text{crystal}}}{R} + \ln\left[\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}} k^{\frac{5}{2}}\right] + \frac{5}{2} \qquad (65)$$

The term

$$\ln\left[\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}} k^{\frac{5}{2}}\right]$$

is the "true" chemical constant of Nernst.

The hydroxyl equilibrium

The reaction

$$H_2O_g + \tfrac{1}{2}O_2 = 2\,OH \qquad (66)$$

is an example of one for which it is possible to calculate the thermal equilibrium from data obtained chiefly from spectroscopy. For this reaction ΔH is estimated to be 18,000 calories. The entropy for water vapor at 298°K. is estimated to be 46.9 E.U. Hence $\Delta S = 19.6$. We have therefore

$$\Delta F^\circ = 18,000 - 19.6\,T \qquad (67)$$

At ordinary temperatures there will be very little hydroxyl at equilibrium. At higher temperatures there will probably be only small changes in ΔH and ΔS, so that the equilibrium will be shifted toward the hydroxyl. It is possible that ΔF° may be negative at 1000°K.

346 WORTH H. RODEBUSH

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