

THE ENERGY DISTRIBUTION OF COMPLEX MOLECULES

BY OSCAR KNEFLER RICE¹

ABSTRACT

It is shown that, for any distribution law in which Boltzmann's law holds for the various quantum states, $d \log W/dT = (\bar{\epsilon}_W - \bar{\epsilon})/kT^2$, where W is the fraction of the molecules in certain specified quantum states, $\bar{\epsilon}_W$ the average energy of the molecules in these states, $\bar{\epsilon}$ the average energy of all the molecules, T the absolute temperature, and k the gas constant. The distribution law will appear to be continuous if not viewed too closely, even though motions of the molecules are quantized. In what follows we consider the continuous outline and neglect the fine structure. If $W_\epsilon d\epsilon$ is the fraction of molecules whose energy lies between ϵ and $\epsilon + d\epsilon$, we have the general rule $\partial^2 \log W_\epsilon / \partial T \partial \epsilon = 1/kT^2$. Proceeding along these lines we can find in a new and simple way the distribution law over a range of energies if the average energy of the molecules (or the energy at which W_ϵ is a maximum) is given over a range of temperatures. At a given temperature we can compare the actual distribution law with a classical one which makes W_ϵ have a maximum at the same energy, and we find a limit beyond which the actual distribution law cannot depart from this particular classical law, provided the molecule is made up of a group of rotators and harmonic oscillators, and is sufficiently complex. An example is considered, which is of interest in the theory of the decomposition of azomethane.

IT IS frequently desirable, especially in connection with the theory of gas reactions,² to be able to make an estimate of the relative numbers of molecules of a complex gas which have various energies. This can be done if we make certain assumptions regarding the nature of the molecules. For example, we may suppose that they are composed of a certain number of classical rotators and oscillators. Or, again, we may suppose that the oscillators are quantized, but if we do this we must make definite assumptions regarding the frequencies involved.³ In the case of actual molecules there must be many frequencies involved, and generally they are not known with any degree of certainty. Furthermore the greater the number of frequencies involved in our problem the more complicated it becomes. This suggests that we should try to throw the distribution law into a form which is independent of the particular frequencies involved, and investigate its general properties. The treatment which is given below is in fact quite independent of the structure of the molecule, though some propositions are considered which hold only of molecules whose energy can be expressed as a sum of squares of coordinates and momenta and which are sufficiently complex.

GENERAL PROPERTIES OF THE DISTRIBUTION LAW

We suppose that the molecule can exist in certain definite quantum states, and assume that the distribution between the various levels follows Boltz-

¹ National Research Fellow.

² See Rice, Proc. Nat. Acad. Sci. **14**, 113 (1928).

³ See Kassel, Proc. Nat. Acad. Sci. **14**, 23 (1928); J. Phys. Chem. (in press).

mann's law. This may not be true at the very lowest temperatures, if we assume that something analogous to Pauli's exclusion principle holds for gas molecules, as has been shown by Fermi,⁴ but will be very accurately true at all ordinary temperatures. We do not need to worry about any similar effect within the molecule, since we are interested in the distribution of all the energy among various molecules, not in the distribution of energy among the different parts of the same molecule, which, in any case, are presumably not affected by such considerations.

We let W be the fraction of the molecules which lie in certain specified quantum states, for example, those states which lie in a certain energy range. We let $\bar{\epsilon}_W$ be the average energy of the molecules in the states W , and $\bar{\epsilon}$ the average energy of all the molecules, k the gas constant and T the absolute temperature. We then have the following general theorem, which is an expression of the fact that the *a priori* probabilities are independent of the temperature:

$$d \log W/dT = (\bar{\epsilon}_W - \bar{\epsilon})/kT^2 \quad (1)$$

The proof of this is as follows⁵:

$$W = \frac{\sum_{i(W)} p_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}}$$

where p_i is the *a priori* probability and ϵ_i the energy of the i th state, and where the summation in the numerator is to be taken over the states W and that in the denominator over all the states. Taking the logarithm of both sides and differentiating we get

$$\frac{d \log W}{dT} = \frac{\sum_{i(W)} p_i \epsilon_i e^{-\epsilon_i/kT} / kT^2}{\sum_{i(W)} p_i e^{-\epsilon_i/kT}} - \frac{\sum_i p_i \epsilon_i e^{-\epsilon_i/kT} / kT^2}{\sum_i p_i e^{-\epsilon_i/kT}}$$

But the fractions on the right hand side are simply $\bar{\epsilon}_W$ and $\bar{\epsilon}$ by definition of average.

Having proved this very general proposition let us now consider in some detail the general characteristics of the distribution law of a molecule of complex structure. If not viewed too closely it will appear to be continuous, on account of the various modes of quantization of the various parts of the molecule. Looked at more closely it will be seen to be in reality discontinuous. We shall, however, not concern ourselves with the fine structure, but only with the continuous outline, which is what we shall mean when we speak of the distribution law. We shall examine it with the aid of the theorem just proved.

If $W_\epsilon d\epsilon$ is the fraction of molecules having their energy in a certain small range ϵ to $\epsilon + d\epsilon$ the average energy in this range is practically ϵ , so

$$d \log (W_\epsilon d\epsilon)/dT = (\epsilon - \bar{\epsilon})/kT^2$$

⁴ Fermi, Zeits. f. Physik **36**, 902 (1926).

⁵ A similar proposition has been considered by Tolman, "Statistical Mechanics," p. 260 (Chemical Catalog Co., 1927).

Similarly for a range ϵ' to $\epsilon' + d\epsilon$

$$d \log (W_{\epsilon'} d\epsilon) / dT = (\epsilon' - \bar{\epsilon}) / kT^2$$

Since $d\epsilon$ is independent of T it could be omitted from these equations. Subtracting one of these equations from the other

$$\frac{d \log W_{\epsilon'}}{dT} - \frac{d \log W_{\epsilon}}{dT} = \frac{d \log (W_{\epsilon'} / W_{\epsilon})}{dT} = \frac{\epsilon' - \epsilon}{kT^2} \quad (2)$$

This resembles the equation for the effect of temperature on an equilibrium constant.

If we divide Eq. (2) through by $\epsilon' - \epsilon$, and allow $\epsilon' - \epsilon$ to approach zero, Eq. (2) takes the form

$$\left[\frac{\partial}{\partial \epsilon} \left(\frac{\partial \log W_{\epsilon}}{\partial T} \right) \right]_{\epsilon} = \frac{\partial^2 \log W_{\epsilon}}{\partial T \partial \epsilon} = \frac{1}{kT^2} \quad (3)$$

This is true of any distribution law.

FINDING THE DISTRIBUTION LAW OVER A RANGE OF ENERGIES FROM THE AVERAGE ENERGY OVER A RANGE OF TEMPERATURES

We shall use the above notions in the solution of a problem which is the converse of the one usually attempted, namely, we shall show how to find the distribution law for a range of energies if we are given the average energy of the molecules for a range of temperatures. This is a useful result, since we are often able to make some estimate as to the average energy.

Actually, however, we shall take as given, not the average energy, but the energy at which W_{ϵ} has a maximum, over a range of temperatures. These two quantities will not differ greatly in a complex molecule, and once a distribution law is constructed a relation between them can be found, and a second and further approximations made if necessary.

Now for a sufficiently small range of energies we may always set

$$W_{\epsilon} = B\epsilon^{(m-2)/2} e^{-\epsilon/kT} / (kT)^{m/2} \quad (4)$$

where m and B are independent of ϵ . By Eq. (2) or Eq. (3) m will be independent of T , but B may be a function of T since it does not affect the relative numbers of molecules which have different energies in the small range considered, but only the whole number which lies in the range. If the classical laws held, and if the energy of the molecule were expressible as a sum of squares, n in number, Eq. (4) with m set equal to n and B to $1/\Gamma(n/2)$ would hold over the whole range of energies, but with fixed values of B and m it can in general hold only over a small range in an actual case. For some other small range of energies different values of B and m must be used. Thus these quantities can in a sense be considered to be functions of ϵ , though in using

the distribution law (4) in the small range of energies in which it is approximately correct we regard them as constants. For our purposes it is going to be unnecessary to find the value of B ; m can be approximately evaluated as follows. We take logarithms of both sides of Eq. (4) and differentiate, obtaining

$$\frac{\partial \log W_\epsilon}{\partial \epsilon} = \frac{m-2}{2\epsilon} - \frac{1}{kT} \quad (5)$$

Now we shall in general let T_ϵ be the temperature at which W_ϵ has a maximum at the energy ϵ . Then if ϵ is an energy lying in the range in which Eq. (4) is to be approximately true we get from Eq. (5), by setting it to zero for the proper energy and temperature,

$$(m-2)/2 = \epsilon/kT_\epsilon \quad (6)$$

T_ϵ is, by hypothesis, known as a function of ϵ . Eq. (6) may therefore be said to define m as a function of ϵ , since this will give the best value of m to use in the neighborhood of any given value of ϵ .

We may remark, in passing, since it is a conception that we are going to wish to use frequently, that m may also be considered to be, in a certain sense, a function of T . For we associate with every value of ϵ a temperature T_ϵ such that at T_ϵ the maximum of W_ϵ comes at ϵ , and there will be a one-to-one correspondence between values of ϵ and T_ϵ . If, however, we wish to think of T as the independent variable it will be convenient to write ϵ_T and T rather than ϵ and T_ϵ . Thus we would write Eq. (6) in the form

$$(m-2)/2 = \epsilon_T/kT \quad (7)$$

In general in an equation which contains m or ϵ_T (or both) and T we consider m and ϵ_T as functions of T , while if it contains m or T_ϵ (or both) and ϵ , we consider them as functions of ϵ ; if no subscript is written T and ϵ are to be taken as independent variables.

If now we wish to find the relative number of molecules which have two different energies, ϵ_1 and ϵ_2 , so far removed from each other that Eq. (4) cannot hold over that range, we may do it by integration of Eq. (5) replacing m by the function of ϵ we have found by use of Eq. (6). It is to be noted that in Eq. (5) T and ϵ appear as independent variables. In the integration T is held constant at some definite value, say T_0 . The result is

$$\log (W_{\epsilon_2}/W_{\epsilon_1}) = \int_{\epsilon_1}^{\epsilon_2} \frac{m-2}{2\epsilon} d\epsilon - \frac{\epsilon_2 - \epsilon_1}{kT_0} = \frac{\bar{m}-2}{2} \log (\epsilon_2/\epsilon_1) - \frac{\epsilon_2 - \epsilon_1}{kT_0} \quad (8)$$

where \bar{m} is a sort of average value of m . It is to be noted that we cannot replace m by the proper function of ϵ directly in Eq. (4) since we have evaluated m only after differentiating.

The problem which we set ourselves in this section is solved by means of this equation, or at least it can be solved by successive approximations, as suggested at the beginning of this section.⁶

MOLECULES WHOSE ENERGY FUNCTION IS A SUM OF SQUARES

The preceding considerations have been independent of any considerations regarding the structure of the molecule. It is often true, however, that we may consider, for a first approximation, that the molecules consist of groups of rotators and harmonic oscillators. Then the energy of a molecule is expressible as a sum of squares (n in number) of coordinates and momenta with constant coefficients, whether the motions of the molecule are quantized or not. In an actual case the oscillators will be quantized, while the rotators may be considered to act classically at all ordinary temperatures. The translational energy may also be assumed to be completely excited. If the molecules are sufficiently complex the individual molecules will all have energies fairly well bunched around the average energy, and the energy which makes W_ϵ a maximum will be fairly close to the average energy. The average energy will always be less than the classical energy, and will approach its classical value $nkT/2$ at high temperatures. In such a molecule it seems safe to assume that the energy, ϵ_T , which makes W_ϵ a maximum at a given temperature T is also less than the corresponding classical value, $(n-2)kT/2$, and approaches it as the temperature increases. If this is true $m < n$ and m gradually approaches n as T increases. Also, in the case we are considering $d\bar{\epsilon}/dT$ gradually approaches its classical value, and we shall assume that $d\epsilon_T/dT$ approaches its classical value $(n-2)k/2$. We may draw certain conclusions concerning the distribution law for a molecule such as is described above.

We shall be interested in comparing W_ϵ for any given energy at a fixed temperature T_0 with its value $W_{\epsilon_{T_0}}$ at the energy, ϵ_{T_0} , at which it has its maximum. We shall assume that we know the value of ϵ for which W_ϵ is a maximum at this particular temperature only, and shall then find two distribution laws, such that, if we plot $W_\epsilon/W_{\epsilon_{T_0}}$ against ϵ , the actual value of $W_\epsilon/W_{\epsilon_{T_0}}$ will lie between those given by the two laws. (Absolute values can always be found by means of the relation $\int_0^\infty W_\epsilon d\epsilon = 1$.)

One of these limiting curves will be the corresponding classical curve for the given temperature, which we shall define as the classical curve, in which W_ϵ has its maximum at the same value of ϵ as the actual curve. It is

⁶ Another method of solving this problem has been worked out by Darwin and Fowler, *Phil. Mag.* **44**, 840 (1922). Their solution of the problem gives the distribution law with all its discontinuities, but the average energy must be known as a function of temperature over the whole range of temperatures. Its chief disadvantage, however, is that it requires a large number of mechanical integrations in the complex plane, and these would be practically impossible to carry out. It seems that in some cases it will be necessary to replace the "Zustandsumme" or partition function by a related function to insure the convergence of the integral in their definition of $J(q)$.

See also Fowler, *Proc. Roy. Soc.*, **99A**, 462 (1921) and Ehrenfest, *Ann. d. Physik.* **36**, 111 (1911).

found from Eq. (4) by setting m constant and equal to the value given by Eq. (7) for the temperature T_0 and energy ϵ_{T_0} . Since the real m is an increasing function of ϵ , it will be found, if we put $\epsilon_1 = \epsilon_{T_0}$ in Eq. (8) that the actual distribution ($W_\epsilon/W_{\epsilon_{T_0}}$) spreads more on either side of the maximum than the corresponding classical distribution; or, in other words, its maximum is not as sharp as the classical one.

We now find another limiting curve, such that the actual curve must lie between it and the corresponding classical curve, in the following manner. From Eq. (7) we have (regarding m now as a function of T , as explained in the previous section)

$$\frac{1}{2} \frac{dm}{dT} = \frac{d\epsilon_T/dT}{kT} - \frac{\epsilon_T}{kT^2} = \frac{d\epsilon_T/dT}{kT} - \frac{m-2}{2T} \quad (9)$$

Now the greater dm/dT the greater will be the deviation from the result of setting m constant in Eq. (8). In the case we are considering $d\epsilon_T/dT$ will gradually approach its classical value $k(n-2)/2$, and is actually less than this value. If we substitute this classical value in Eq. (9) we get

$$dm/dT = (n-m)/T \quad (10)$$

which gives a greater value than dm/dT can actually have. n being constant, this is easily integrated to give

$$(m-n)/2 = c/T \quad (11)$$

c is a constant of integration which we determine from the value of m , at the temperature T_0 , given by Eq. (7). The value of m then obtained from Eq. (11) must be greater or less than the true value of m depending upon whether T is greater or less than T_0 . If we wish to consider ϵ as independent variable rather than T , we can indicate this by writing Eq. (11)

$$(m-n)/2 = c/T_\epsilon \quad (12)$$

Consider now the equation⁷ $d\epsilon_T/dT = k(n-2)/2$, which we used in getting Eq. (12). If we want to make ϵ the independent variable in this equation we write it

$$d\epsilon/dT_\epsilon = k(n-2)/2 \quad (13)$$

Inverting and integrating from ϵ_{T_0} to ϵ we get

$$T_\epsilon = T_0 + 2(\epsilon - \epsilon_{T_0})/k(n-2) \quad (14)$$

This is of the same form as a classical equation in which the number of energy terms is equal to n , but is not such an equation at all, since the quantities ϵ_0 and T_0 which we started with were not classically related. It represents the variation of T_ϵ with ϵ which we used to obtain Eq. (12), and it may con-

⁷ Not really a true equation but a limiting form.

sequently be substituted in Eq. (12) without inconsistency. c has the value determined as above. This enables us to get a value of m as a function of ϵ , the value of m thus obtained being greater or less than the true value of m if ϵ is greater or less, respectively, than ϵ_{T_0} . If the result is put into Eq. (8) and the integration with respect to ϵ performed, letting $\epsilon_1 = \epsilon_{T_0}$ and $T_{\epsilon_1} = T_{\epsilon_{T_0}} = T_0$ and writing ϵ instead of ϵ_2 in the final result we get

$$\log (W_{\epsilon}/W_{\epsilon_{T_0}}) = \frac{n-2}{2} \log \left(1 + \frac{2(\epsilon - \epsilon_{T_0})}{kT_0(n-2)} \right) - \frac{\epsilon - \epsilon_{T_0}}{kT_0} \quad (15)$$

This is the limiting curve we have been striving for, the value of $W_{\epsilon}/W_{\epsilon_{T_0}}$ calculated from it being always greater than the actual value of this quantity. Indeed, we can probably count on the value of $W_{\epsilon}/W_{\epsilon_{T_0}}$ thus calculated considerably exceeding the actual value of the quantity.

APPLICATION TO A SPECIAL PROBLEM

We shall illustrate these considerations by an application to a problem which concerned us in the quantum theory treatment of the decomposition of azomethane.⁸ We wished to find whether there was a large chance that, if a molecule of 54,000 calories per mole energy should collide with an average molecule which we estimated to have 6,000 calories per mole at the temperature of interest, either molecule should emerge from collision with more than 50,000 calories per mole. (These are internal energies, as in these considerations we were not interested in translational energies.) This is the same as finding the chance that one of the molecules should have more than 50,000 or less than 10,000 calories per mole. The chance would be 1/3 if a molecule were as likely to have one energy as another after collision. In order to find the chance that the molecules should have widely different rather than nearly equal energies we attempted to compare the probability that both molecules should have 30,000 calories per mole with the chance that one of them should have 50,000 and the other 10,000.

We assume that statistical equilibrium is established between the various degrees of freedom at a collision. Then the ratio of the probability that one will have 10,000 and the other 50,000 calories per mole to the probability that both will have 30,000 calories per mole is given by $W_{10}W_{50}/W_{30}^2$ where W_{10} is the probability (per unit energy range) calculated from the distribution law that a molecule should have 10,000 calories per mole, etc.⁹

This ratio is independent of temperature as is readily seen from Eq. (8), since \bar{m} is independent of T_0 , or from the fact that the result of a collision of definite energy cannot depend upon the temperature. We may accordingly assume the temperature to be such that W_{30} is the maximum value of W_{ϵ} at that temperature. This temperature will be approximately that at which 30,000 is the average energy, and we have previously estimated it to be about 1250°C, abs.⁸ Then by using Eq. (15) we find (n is 51 in the case

⁸ Rice, Proc. Nat. Acad. Sci. **14**, 122 (1928).

⁹ See Rice and Ramsperger, J. Am. Chem. Soc. **49**, 1622, 1625 (1927).

of azomethane, excluding the translational terms) $W_{10}W_{50}/W_{30}^2 = 0.064 \cdot 1250^\circ$ may be a little low, since the average energy is probably higher than the energy of the maximum, but had we used 1500 for T_0 , a value which seems certainly too high, we should have obtained 0.15. Since using Eq. (15) gives us a result which is too large, these figures give us some confidence that for the purposes of our previous considerations we may neglect the chance that a molecule should emerge from collision with more than 50,000 calories per mole.

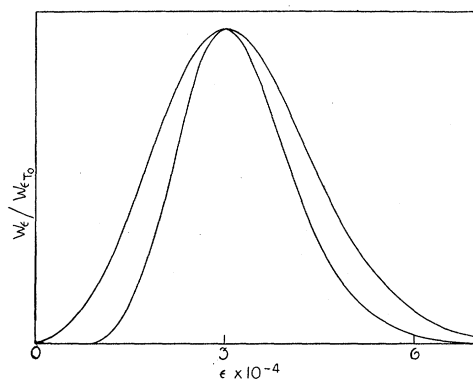


FIG. 1

In order to illustrate the sort of range in which the distribution law may lie we have plotted in Fig. 1 the two extreme distribution curves in the case just considered. Assuming that at 1250°C , abs., $\epsilon_T = 30,000$ calories per mole, we calculate from Eq. (7) that m is 26. Assuming that it is constant at this value we get the lower curve in Fig. 1. Using Eq. (15) we get the upper curve.

GATES CHEMICAL LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
January 19, 1928.