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Citation: *J. Chem. Phys.* **2**, 853 (1934); doi: 10.1063/1.1749408

View online: <http://dx.doi.org/10.1063/1.1749408>

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Entropy and the Absolute Rate of Chemical Reactions

I. The Steric Factor of Bimolecular Associations

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(Received September 7, 1934)

The equilibrium constant for a bimolecular association may be expressed in terms of the energy change, ΔE , and standard entropy change, ΔS° , on association. On account of the well-known relation between the equilibrium constant, and the rate constants of the bimolecular association and its reverse, the corresponding unimolecular decomposition, the values of these rate constants could be determined separately, if one could divide each of the terms, ΔE and ΔS° , into two parts, in the proper way. The proper method of dividing ΔE is known; this paper is concerned with the division of ΔS° . Considered from a statistical

point of view, the entropy of a system depends upon the volume in phase space available to the system under fixed thermodynamic conditions. The separate rate constants will depend upon the fraction of the phase space in which it is possible for the reaction under consideration to take place. Application of this principle leads to an interpretation of the collision number and the steric factor of bimolecular association reactions. The known bimolecular associations have been discussed from this point of view.

INTRODUCTION

IN a recent interesting paper Rodebush¹ has shown that it is possible to get considerable information about the kinetics of a reaction from the statistical expression that gives the equilibrium constant in terms of the entropies of the reacting substances. The rôle that the entropy plays in determining the rate of reaction is readily appreciated when we remember that the antilogarithm of the entropy of a system is proportional to the volume of the phase space, or to the number of stationary states, in which the molecules of the system can exist,² and that the rate must depend upon the fraction of the states in which reaction may occur. Essentially this principle has been stated by Rodebush but he has not explicitly made use of it in setting up the rate expression for the simplified reaction that he considered, the association of two atoms to form a diatomic molecule. A more direct application of this fundamental principle turns out to be of interest, not only in connection with the example which Rodebush has treated, but also because it enables one to extend the method and apply it to the bimolecular association of polyatomic molecules, which is of more practical importance, since we may assume that the excess energy may always be taken care of by transfer to the internal vibrations, whereas the

bimolecular association of two atoms is a very improbable process, as the presence of a third body is required to remove the excess energy.³

Only four bimolecular associations have been studied experimentally in sufficient detail for our purposes: the hydrogenation of ethylene,^{4a} and the polymerizations of ethylene,^{4b} butadiene,^{5a} and isoprene.^{5b} One of the characteristic features of these associations is the occurrence of a so-called steric factor which gives the fraction of the total number of collisions (calculated from kinetic theory) that leads to reaction. Except in the case of the hydrogenation of ethylene these steric factors are quite small. A complete theory of bimolecular association would account for these steric factors. Their actual calculation, however, would involve assumptions as to the mechanism of reaction, which in our present state of knowledge would necessarily be highly speculative. In the following, therefore, we have adopted a less ambitious program and have been content to put forth an interpretation of the experimental results, except in the case of the hydrogenation of ethylene for which we have proposed a mechanism and calculated the absolute rate.

³ See Kassel, *Kinetics of Homogeneous Gas Reactions*, pp. 38, ff., Chem. Cat. Co., 1932.

⁴ Pease, J. Am. Chem. Soc. (a) **54**, 1876 (1932), (b) **53**, 613 (1931). Pease's conclusions regarding the ethylene polymerization have been questioned by Storch, J. Am. Chem. Soc. **56**, 374 (1934), who, however, worked in a different pressure range.

⁵ Vaughan, J. Am. Chem. Soc. (a) **54**, 3863 (1932), (b) **55**, 4109 (1933).

¹ Rodebush, J. Chem. Phys. **1**, 440 (1933).

² See Tolman, *Statistical Mechanics*, pp. 302, 306, Chem. Cat. Co., 1927.

GENERAL CONSIDERATIONS

In order to get the expression in the best form for our purposes, and in order that there may be no misunderstanding as to the meaning of the various terms involved, we shall consider the derivation from first principles of the equilibrium constant for a reaction of the type $M_2 + M_3 \rightarrow M_1$ where M_1 , M_2 and M_3 are, in general, polyatomic molecules.

We assume that our system is enclosed in a constant volume V , is kept at a temperature T , that the number of molecules M_1 is N_1 , and that the numbers of *uncombined* M_2 and M_3 are, respectively, N_2 and N_3 . We define the entropies per molecule, S_1 , S_2 and S_3 , by expressions of the type⁶ $S_1 = k \ln (W_1/h^{n_1})$, where k is the Boltzmann constant and h Planck's constant, n_1 is the number of degrees of freedom of the molecule M_1 , and

$$W_1 = \int_0^\infty (d\omega_1/d\epsilon_1) \exp [-(\epsilon_1 - \bar{\epsilon}_1)/kT] d\epsilon_1. \quad (\text{A})$$

Here $(d\omega_1/d\epsilon_1)d\epsilon_1$ is the volume in the phase space of a single molecule which lies between energies ϵ_1 and $\epsilon_1 + d\epsilon_1$ and $\bar{\epsilon}_1$ is the average energy per molecule. $h^{-n_1} \int_0^\infty (d\omega_1/d\epsilon_1) \exp (-\epsilon_1/kT) d\epsilon_1$ is the *Zustandsumme* or partition function of the molecule; we assume that we are at such a high temperature that the summation can be replaced by an integral. $(d\omega_1/d\epsilon_1)d\epsilon_1$, the total volume of its phase space which the molecule can visit if its energy be between ϵ_1 and $\epsilon_1 + d\epsilon_1$, is multiplied by the relative probability that it be in this energy range as compared to the probability that it be in an equal range near $\bar{\epsilon}_1$. W_1 may therefore be said in a certain sense to be the total effective volume in the phase space of the molecule M_1 which conforms to the condition that its temperature be T (corresponding to $\bar{\epsilon}_1$).

The total entropies for each of the various types of gas which exist in the system are, then,

⁶ Our definition of the entropy per molecule is just the usual one; it may be shown to be entirely equivalent to the upper limit of Eq. (208), p. 109 of Tolman.³ (Including the lower limit of Tolman's equation is equivalent to subtracting off the part of the entropy due to any multiplicity of the lowest state, which we, of course, do not wish to do. Tolman's equation is given for rotational entropy only, but may be readily generalized.) On the other hand, our definition of the total entropy differs from that ordinarily used in thermodynamics. The relation between them is given by S_1 (thermo) = S_1 (ours) - $\ln N_1!$

$N_1 S_1$, $N_2 S_2$ and $N_3 S_3$. But these expressions assume that specified individuals of the type M_2 and M_3 are uncombined and other specified individuals are combined. In setting up an expression for the whole system we must allow for the interchange of molecules, in particular for the interchange of *combined* M_2 and M_3 with each other and with uncombined ones.⁷ In this way we get an expression for the entropy of the whole system

$$S = N_1 S_1 + N_2 S_2 + N_3 S_3 + k \ln [(N_1 + N_2)! (N_1 + N_3)! / N_1! N_2! N_3!].$$

If we allow N_1 , N_2 and N_3 to vary

$$\begin{aligned} \delta S = & S_1 \delta N_1 + S_2 \delta N_2 + S_3 \delta N_3 + (\delta N_1 + \delta N_2) k \\ & \times \ln (N_1 + N_2) + (\delta N_1 + \delta N_3) k \ln (N_1 + N_3) \\ & - \delta N_1 k \ln N_1 - \delta N_2 k \ln N_2 - \delta N_3 k \ln N_3. \end{aligned}$$

However, on account of the conservation of particles, we have $\delta N_1 = -\delta N_2 = -\delta N_3$. So

$$\begin{aligned} \delta S = & \delta N_1 (S_1 - S_2 - S_3) - \delta N_1 k \ln (N_1 / N_2 N_3) \\ = & \delta N_1 [\Delta S - k \ln (N_1 / N_2 N_3)]. \end{aligned}$$

Now if ΔE is the change of energy on association then the entropy change of the thermostat is $-\delta N_1 \Delta E / T$. At equilibrium we must have $\delta S - \delta N_1 \Delta E / T = 0$, which gives

$$k \ln (N_1 / N_2 N_3) = \Delta S - \Delta E / T.$$

Now the equilibrium constant is equal to $V N_1 / N_2 N_3$. It is also equal to k_2 / k_1 , where k_1 and k_2 are the rate constants of the unimolecular decomposition and bimolecular association, respectively. Hence

⁷ In thus assuming that we can distinguish between individual molecules of the same kind, we are of course using the Boltzmann statistics rather than the Fermi or Bose statistics. It is, however, well known that the latter types of statistics will give the same results at high temperatures as the Boltzmann. The fact that molecules of the same kind are really indistinguishable simply reduces the entropy, S , of the whole system by $k \ln [(N_1 + N_2)! (N_1 + N_3)! / (N_1 + N_2)! (N_1 + N_3)!]$, $(N_1 + N_2)!$ and $(N_1 + N_3)!$ being the number of permutations of all (combined and uncombined) M_2 and M_3 , respectively. At high temperatures, where the energy levels are very close together compared with the total energy, this amounts simply to a thinning out of the number of possible energy levels, which can make no difference in the distribution function, nor in any of the observable properties of the system. Our calculations come to rest ultimately upon the entropy expression for the case, $N_1 + N_2 = N_1 + N_3 = 1$. At high temperatures the value of this expression will obviously be independent of whether Boltzmann, Fermi, or Bose statistics are used.

$$k \ln (k_2/k_1) = \Delta S + k \ln V - \Delta E/T.$$

If now we let our volume be unity, and define our standard entropy as that for unit volume, we may write

$$\ln (k_2/k_1) = \Delta S^\circ/k - \Delta E/kT. \quad (1)$$

This has nearly the same form as the ordinary thermodynamic equation, but it must be noted that entropy, as we have defined it, has slightly different properties than the thermodynamic entropy.⁶ Our entropy doubles when the amount of gas doubles, the volume remaining the same. The thermodynamic entropy doubles when the amount of gas is doubled if the *pressure* remains the same. Also our ΔS refers to a process taking place at constant volume while the ordinary thermodynamic ΔS assumes that all the partial pressures remain fixed, which accounts for the slight difference in form between our equation and the usual thermodynamic one used by Rodebush.

In order to determine the absolute values of k_1 and k_2 we must be able to separate the right-hand side of Eq. (1) into two parts. The first term can be so divided by the relation⁸

$$-\Delta E = \epsilon_a - \epsilon_a', \quad (2)$$

where ϵ_a and ϵ_a' are, respectively, the activation energies of the unimolecular decomposition and the bimolecular association. We may then write

$$k_1 = A_1 \exp(-\epsilon_a/kT); k_2 = A_2 \exp(-\epsilon_a'/kT), \quad (3)$$

where the A 's could be determined if we could divide the ΔS° term in a similar unique fashion.

Before considering how to do this, however, it will be well to examine the general formula for the entropy of a polyatomic molecule.⁹ The standard entropy S_i° (where $i=1, 2$, or 3) may be conveniently expressed in the following form

$$S_i^\circ = k \ln B_i + k \ln C_i + k \ln D_i + k \ln E_i, \quad (4)$$

where $\ln B_i$ is the part due to the translational motion of the molecule (that is to say, $B_i = W_{it}/h^{n_{it}}$, where $n_{it}=3$ is the number of translational degrees of freedom and W_{it} is the

total volume in the translational part of the phase space of the molecule, which conforms to the condition that the gas is at temperature T), $\ln C_i$ is the part due to rotation, $\ln E_i$ the part due to vibration, and $D_i = \rho_{ie}\rho_{in}$, where ρ_{ie} is the degeneracy due to electronic spin and ρ_{in} that due to nuclear spin.

We may calculate B_i , C_i , and E_i by means of relations which (neglecting a power of h) are of exactly the same form as Eq. (A), except that each one deals with its specific part, the translational, the rotational, or the vibrational part, of the energy and phase space, this being, in fact, the usual method for calculating these entropies.¹⁰ General formulas may be given¹¹ for B_i and E_i .

$$B_i = (2\pi e m_i kT/h^2)^{3/2} \quad (5)$$

where e is the base of the natural logarithms, and m_i is the mass of the molecule.

$$\ln E_i = \sum_j \{ (h\nu_{ij}/kT) [\exp(h\nu_{ij}/kT) - 1]^{-1} - \ln [1 - \exp(-h\nu_{ij}/kT)] \}, \quad (6)$$

where the ν_{ij} are the frequencies of the molecule, the summation being taken over all frequencies. In each specific instance it will be necessary to consider the rotational terms separately. However, we shall often find it convenient to divide the term C into parts, writing

$$C = C_i' C_i'' C_i''' \cdots, \quad (7a)$$

where

$$C_i' = \pi^{-1} (8\pi^3 e I_i' kT/h^2 \sigma_i'^2)^{l_i'/2}, \quad (7b)$$

$$C_i'' = (8\pi^3 e I_i'' kT/h^2 \sigma_i''^2)^{l_i''/2},$$

$$C_i''' = (8\pi^3 e I_i''' kT/h^2 \sigma_i'''^2)^{l_i'''/2}.$$

In these equations I_i' or I_i'' or I_i''' or \cdots represents the moment of inertia connected with a given degree or group of degrees of freedom of rotation and $I_i' > I_i'' > I_i''' > \cdots$; $l_i' + l_i'' + l_i''' + \cdots$ gives the total number of degrees of freedom of rotation; and σ_i' , σ_i'' , σ_i''' , \cdots are the symmetry numbers related to the respective rotations.

⁸ See Tolman, reference 2, p. 109.

¹¹ If V were not unity we would have, instead, $B_i = (2\pi e m_i kT/h^2)^{3/2} V$. Thus for the entropy of the N_i molecules we would have $kN_i \ln [(2\pi e m_i kT/h^2)^{3/2} V]$. If now to this expression we should add the term $-k \ln N_i! \cong -kN_i \ln N_i + kN_i \ln e = -kN_i (\ln N_i - 1)$, in order to get the thermodynamic entropy (see reference 6) we would arrive at the familiar Sackur-Tetrode expression. (See Tolman, reference 2, p. 138.)

⁸ Gershinowitz and O. K. Rice, J. Chem. Phys. 2, 275 (1934).

⁹ This has been discussed by Mayer, Brunauer and Mayer, J. Am. Chem. Soc. 55, 37 (1933).

Let us now return to the question of determining A_1 and A_2 separately. If we assume as a zero approximation that A_1 does not depend upon the properties of M_2 and M_3 and A_2 does not depend upon the properties of M_1 , and write, provisionally,¹²

$$A_1 \doteq (B_1 C_1 D_1 E_1)^{-1} kT/h \quad (8a)$$

and

$$A_2 \doteq (B_2 C_2 D_2 E_2 B_3 C_3 D_3 E_3)^{-1} kT/h \quad (8b)$$

we see from Eqs. (3) and (4) that these expressions are consistent with Eq. (1). The significance of (8a) and (8b) becomes evident if we note that $B_1 C_1 D_1 E_1$ is just equal to the phase-space, divided by h^3 , of a single molecule M_1 confined in unit volume, while $B_2 C_2 D_2 E_2 B_3 C_3 D_3 E_3$ is that of a single pair of molecules M_2 and M_3 confined in unit volume. They give the probability that the system be in a region of the phase space equivalent to one *single* quantum state, divided by the characteristic time, h/kT . To say that the rates are given by the above expressions is essentially equivalent to stating that there is only *one* energy distribution which will lead to reaction, and that the average time necessary for reaction to occur from this distribution is h/kT . These provisional values of A_1 and A_2 will be very small; but if these expressions could be modified in the proper manner, one could determine the rate of reaction. The first correction will have to do with the time factor; this is included in the discussion of the collision factor, in the next section. The other necessary modifications could be made, if one could determine in what states the molecules actually exist when reaction occurs.

One such modification is easily made, and serves to illustrate a principle of which we shall make much use. In general we do not expect the probability of reaction to be affected by the spin degeneracy of the nuclear and electronic states, provided, as we shall assume for the cases of interest to us here, the spin degeneracy does not change when the reaction takes place.¹³ In other words the number of such states available

for the reaction is the same as the total number of such states. Therefore we multiply A_2 by the corresponding entropy expression $D_2 D_3$. A_1 must, of course, be multiplied by the same thing in order that Eq. (1) may continue to be valid. But by the assumptions we have made $D_1 = D_2 D_3$ and these three quantities are simply eliminated from the rate expressions leaving,

$$A_1 \doteq (B_1 C_1 E_1)^{-1} kT/h, \quad (9a)$$

$$A_2 \doteq (B_2 C_2 E_2 B_3 C_3 E_3)^{-1} kT/h. \quad (9b)$$

We would, of course, have arrived at the same result if we had considered A_1 first and noted that both expressions have to be multiplied by D_1 .

THE COLLISION FACTOR

We shall next obtain the collision factor, which we define as the number of collisions per cc per second at unit concentration (one molecule per cc). This quantity, which must be an important part of A_2 , we shall get by a method which we believe brings out the physical principle involved more clearly than that of Rodebush.

When a diatomic molecule splits into two atoms it is easy to trace the fate of each degree of freedom. The two rotational and one vibrational degrees of freedom simply pass over into three of translation. To establish a similar correspondence for the dissociation of a polyatomic molecule is more difficult. In general a polyatomic molecule has three rotational degrees of freedom (neglecting internal rotation), and after dissociation *each* fragment has three degrees of freedom of rotation and three degrees of freedom of translation. Since the total number of degrees of freedom in the system must be conserved these six new degrees of freedom must have been vibrations in the associated molecule. The chief difficulty is encountered in determining which of the original degrees of freedom corresponds to a particular new one, and of course no exact answer is possible on account of the change in character of the normal vibrations. However, it will usually be reasonable to assume that the two rotational degrees of freedom connected with the largest moments of inertia of M_1 (which moments we assume, for the sake of simplicity,

¹² We use the symbol \doteq to mean "equals provisionally."

¹³ The reaction $H_2 \rightarrow 2H$ is a reaction in which the net spin degeneracy *does* change, and in which our considerations will not hold. The effect of spin on the steric factor has been considered generally by Bates and Rosen (unpublished work).

to be equal, as in the symmetrical top), together with one degree of freedom which is concerned with the relative vibration of the parts¹⁴ which are to form M_1 , are connected with the relative translational motion of M_2 and M_3 . We may thus break (9a) and (9b) each into two factors,

$$A_1' \doteq (B_1 C_1' E_1')^{-1} kT/h, \quad (10a)$$

$$A_2' \doteq (B_2 B_3)^{-1} kT/h, \quad (10b)$$

in which the degrees of freedom just mentioned and those concerned with the translation of the center of gravity of the system are included; and

$$A_1'' \doteq (C_1'' E_1'')^{-1}, \quad (11a)$$

$$A_2'' \doteq (C_2 E_2 C_3 E_3)^{-1}, \quad (11b)$$

which include all the rest of the degrees of freedom. We now make the assumption that A_1' and A_1'' , A_2' and A_2'' are independent and can be treated separately.

We shall now apply to these equations the method that was used in the preceding section to eliminate D_1 , D_2 and D_3 from Eqs. (8a) and (8b). Let us first consider the unimolecular reaction. In theories of unimolecular reactions it is usually assumed that the probability of dissociation is independent of the rotational and translational energy of the molecule. This means that all rotational and translational states are available for reaction. Therefore A_1' should be multiplied by $B_1 C_1'$. A_2' must be multiplied by the same factors as A_1' . We thus get

$$A_1' \doteq (E_1')^{-1} kT/h,$$

$$A_2' \doteq (B_1 C_1' / B_2 B_3) kT/h.$$

It can easily be seen that if the expression for A_2' be multiplied by $e \exp (-Q - kT/2)/kT$ it gives the number of collisions per unit time with energy along the line of centers greater than Q , provided that the effective radius of the collision is given by r_1' , the distance which come into¹⁵ I_1' . $Q + kT/2$ is the part of the activation energy connected with the translational motion, since the average energy of all pairs of mole-

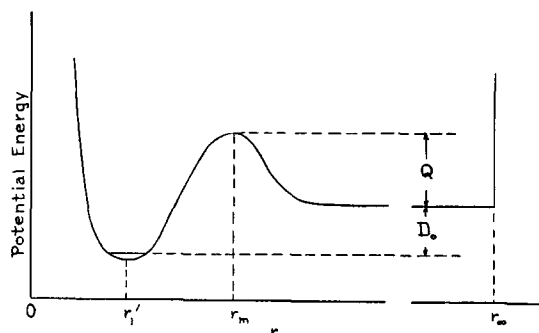


FIG. 1.

cules in collision exceeds the average energy of all pairs by¹⁶ $kT/2$. The factor, e , that it has been necessary to introduce is not included in the activation energy and hence it must also be multiplied into A_1' , giving the final expressions

$$A_1' = e(E_1')^{-1} kT/h, \quad (12a)$$

$$A_2' = e(B_1 C_1' / B_2 B_3) kT/h. \quad (12b)$$

Effectively, this imposes a condition on the vibration involved in E_1' , which also includes any correction which may be necessary in the time factor h/kT . The nature of the condition thus imposed we shall now proceed to investigate.

Suppose the potential between M_2 and M_3 (assuming for simplicity that it is a function of r alone) is of the form¹⁷ shown in Fig. 1. The potential is supposed to go to infinity at r_∞ , which ties the two molecules together, and which converts the continuous part of the spectrum into a close spaced set of discrete levels. We assume throughout that $r_\infty \gg r_m$. We can now consider the distribution of energy in this system of two molecules. We let K be the asymptotic value of the relative kinetic energy of a pair of molecules in the continuum.¹⁸ The number of energy levels lying between K and $K + dK$ will be given by¹⁹ $r_\infty (2\mu/Kh^2)^{1/2} dK$, where μ is the reduced mass of M_2 and M_3 . The probability of finding a pair of molecules in an energy level

¹⁶ See Gershinowitz and Rice, reference 8, p. 275 (footnote 11).

¹⁷ As far as the considerations of this paragraph go, the hump at r_m may be vanishingly small.

¹⁸ We neglect the possibility of leakage through the hump, and assume always that K is greater than Q .

¹⁹ This is the usual expression, obtained from the boundary conditions which are imposed on the wave functions.

¹⁴ This vibration actually will not be a normal vibration, but we make the approximation of treating it as such. The considerations of this section can at best have only an approximate significance.

¹⁵ Tolman, reference 2, p. 70.

of kinetic energy K is given by the usual expression,

$$\exp [-(D_0+K)/kT] / \sum_i \exp (-\epsilon_i/kT),$$

where D_0 is the dissociation energy from the lowest vibrational level, and the summation is taken over all possible energy levels²⁰ ϵ_i . Now if a pair of molecules has a relative kinetic energy K the relative velocity is $(2K/\mu)^{1/2}$, and a time equal to $2r_\infty(2K/\mu)^{-1/2}$ will be required for r to go from its smallest possible value to r_∞ , and back again. Thus, on the average, the number η of times per unit time that a given pair of particles having relative kinetic energy greater than Q will pass a given value of the coordinate, r , while moving so that r is increasing, will be

$$\eta = \int_Q^\infty 2^{-1} r_\infty^{-1} (2K/\mu)^{1/2} r_\infty (2\mu/Kh^2)^{1/2} \\ \times \exp [-(D_0+K)/kT] dK / \sum_i \exp (-\epsilon_i/kT) = \\ (kT/h) \exp [-(D_0+Q)/kT] / \sum_i \exp (-\epsilon_i/kT).$$

Now we can evaluate approximately the sum in the denominator (which is the *Zustandsumme*) on the assumption that when the molecules M_2 and M_3 are bound together they behave as a simple harmonic oscillator with frequency ν_1' . We have

$$\sum_i \exp (-\epsilon_i/kT) = [1 - \exp (-h\nu_1'/kT)]^{-1} \\ = E_1' \exp (-\epsilon_{av}/kT),$$

where ϵ_{av} is the average energy of oscillation. This last relation will be understood by reference to Eq. (6) if we remember that the average energy of the oscillator is given by $h\nu_1'[\exp (h\nu_1'/kT) - 1]^{-1}$. Therefore

$$\eta = (kT/h) e(E_1')^{-1} \exp [-(D_0+Q-\epsilon_{av}+kT)/kT].$$

Since, as may be readily verified, D_0+Q+kT is the average energy of the pairs of molecules whose coordinates, r , pass a given value, $D_0+Q-\epsilon_{av}+kT$ is the activation energy, provided η may be assumed to give the rate of dissociation of the complex M_1 . The part of the expression in front of the exponential is just equal to the right-hand side of (12a). It is thus seen that the condition, which we have above imposed on

the vibration, is just that it be allowable to assume that η gives the rate of decomposition of M_1 , or, in other words, that it is possible to calculate the rate of decomposition from the flux at equilibrium.

That the effective collision radius is equal to r_1' depends, as we have noted, on the assumption that the probability of decomposition is independent of the rotational state. Actually, of course, this is not strictly true, and the calculated value of the collision radius will be correspondingly altered. A simple calculation, in which we make the simplifying assumption that the combined pair of molecules M_2 and M_3 acts like a simple diatomic molecule, will illustrate how this comes about. If the molecule, M_1 , is in a rotational state defined by the quantum number j , it is well known that this results in what is effectively an added term to the potential energy, equal to $\kappa^2 j(j+1)/r^2$, where $\kappa^2 = 8\pi^2\mu/h^2$. Thus the minimum at r_1' is reduced by approximately $\kappa^2 j(j+1)/(r_1')^2$, so that the dissociation energy becomes $D_0 - \kappa^2 j(j+1)/(r_1')^2$. Similarly Q becomes $Q + \kappa^2 j(j+1)/r_m^2$. Thus, replacing Q and D_0 in the expression for η by these new quantities, we get the following relation between η_j and η_0 (where the subscript indicates the rotational state):

$$\eta_j = \eta_0 \exp [\kappa^2 j(j+1) \{ (r_1')^{-2} - r_m^{-2} \} / kT].$$

Now the probability that the rotational state should be the j th is given approximately by

$$P_j(r_1') / \sum_{j=0}^{\infty} P_j(r_1'),$$

where

$$P_j(r_1') = (2j+1) \exp [-\kappa^2 j(j+1)(r_1')^{-2} / kT].$$

The average probability of decomposition from any state will be given by

$$\sum_{j=0}^{\infty} \eta_j P_j(r_1') / \sum_{j=0}^{\infty} P_j(r_1') = \eta_0 \sum_{j=0}^{\infty} P_j(r_m) / \sum_{j=0}^{\infty} P_j(r_1').$$

As may readily be seen by evaluating the sums in the usual manner, this becomes equal to $\eta_0 r_m^2 (r_1')^{-2}$ at high temperatures. To get a more exact expression for A_1' than is given by Eq. (12a) it is thus necessary to multiply the right-hand side of (12a) by $r_m^2 (r_1')^{-2}$. Naturally the

²⁰ This includes the continuous energy levels, but we can assume that they make but a negligible contribution to the sum.

right-hand side of (12b) must be multiplied through by the same quantity, and it is obvious that the collision radius r_1' is thus replaced by r_m , which is certainly a very reasonable result. Since, however, r_m will not ordinarily be expected to differ greatly from r_1' , it will generally be safe to use the latter as an approximation.

THE STERIC FACTOR

The steric factor is to be obtained by a consideration of (11b). To take care of the factors E_2 and E_3 , we shall assume either (1) that the probability that M_2 and M_3 will recombine does not depend on their vibrational state, that is, that the activation energy is entirely translational energy or (2) that a certain localization of energy in some particular bond or bonds of either M_2 or M_3 or both is necessary, but that the entropy of those states which can react is the same as the entropy of all states.²¹ This is essentially similar to the assumptions of Kassel's theory of unimolecular decompositions,²² and our recent work⁸ makes it appear very probable that this assumption is approximately correct, especially if the localization of energy does not affect the frequencies of the molecule. Thus we multiply A_2'' through by E_2E_3 .

There seem, however, to be grounds for the belief that not all rotational states²³ of M_2 and M_3 are equally available for association. (Do not confuse with the statement of the last section that all rotational states of M_1 are equally available for dissociation.) A comparison of the experimental data with the numerical values of the entropy shows that the steric factors are of the order of magnitude that would be expected

if some of the rotational degrees of freedom are more or less "frozen out" when reaction occurs. That is, in order that reaction may take place there must be a certain orientation of the molecules with respect to each other. Therefore, instead of multiplying (11b) by C_2C_3 we can multiply through only by some of the primed factors of these quantities, i.e., those representing rotations that have no effect on the probability of association. The factors that remain in the denominator then give us the steric factor.²⁴ If there were some way of determining which rotational degrees of freedom are relevant to each reaction we could calculate an absolute rate for the reaction that could be compared with experiment. There are, however, so little data on the mechanism and kinetics of these reactions, that rather than adopt particular mechanisms we have preferred to develop, on the basis of the above considerations regarding the degrees of freedom involved in the reaction, a new method of handling the experimental data.

First we set up a collision factor as in Eq. (12). We then divide the experimental absolute rate by this collision factor to get what we may call an experimental A_2'' . Next we set up an expression of the form $[\pi^{-1}(8\pi^3eIkT/h^2)]^{-n/2}$, in which we have neglected the symmetry factors. For I we use the geometric mean of the estimated moments of inertia of the associating molecules. The factor of π^{-1} is introduced as a compromise, since we do not know which degrees of freedom are frozen out and cannot tell whether they should have the factor of π^{-1} such as appears in C_i' of Eq. (7b). We can then determine n so the expression will best reproduce the experimental value of A_2'' . This value of n will tell us approximately how many degrees of freedom of rotation must be fixed, or, in other words, how stringent are the conditions that must be satisfied in order that reaction may take place when the

²¹ The reasonableness of this assumption is evident from the following considerations. If we consider a simple harmonic oscillator molecule and arbitrarily say that every molecule whose vibrational energy is greater than a certain amount shall be considered one of a new species, then the vibrational entropy calculated for this new species is the same as that for all the molecules. Localization of the vibrational energy of the molecule is very much like the excitation of a single mode of vibrations, provided the frequencies of the molecule are not changed in the process.

²² Kassel, J. Phys. Chem. 32, 1065 (1928).

²³ It is understood when we speak of a "rotational state" in this manner that it should not be thought of as too closely associated with the ordinary rotational levels of the molecule. We really use the term "rotational state" as a shorthand expression for a region in the phase space which has a certain definite size, namely h or some power thereof, according to the number of dimensions involved.

²⁴ It is possible that, for reaction to occur, the molecule must be more or less twisted out of shape and that something equivalent to the fixing of one or more vibrational degrees of freedom is also necessary. As already noted, we have neglected this entirely. In general the restriction of a vibrational degree of freedom would have much less effect on the magnitude of the steric factor than the fixing of a rotation since the terms in the summation of Eq. (6) are relatively small for the frequencies that ordinarily occur.

TABLE I.

Reaction	A_2 (expt)	I_1' (est) ^(a)	I (est) ^(a)	A_2' ^(b)	A_2''	n
Ethylene and Ethylene ^{4b}	6.6×10^{-13}	1.5×10^{-38}	$0.3 \times 10^{-38(c)}$	1.72×10^{-10}	3.8×10^{-3}	1.7
Isoprene and Isoprene ^{5b}	1.4×10^{-12}	4×10^{-38}	1.1×10^{-38}	2.25×10^{-10}	6.2×10^{-3}	1.1
Butadiene and Butadiene ^{5a}	6.8×10^{-14}	2.7×10^{-38}	0.6×10^{-38}	2.18×10^{-10}	3.1×10^{-4}	1.9

(a) These are for the most part rough estimates made with the aid of the structural formulas of the compounds involved, insofar as these are known, and the figures of Badger, Phys. Rev. **45**, 648 (1934).

(b) Except in the case of ethylene the expression for A_2' in Eq. (12b) has been used as it stands and has not been divided by 2, for although the two molecules colliding are the same it is unlikely that they form a symmetrical configuration on combining. See Rodebush, reference 1, pp. 441, 443.

(c) Average includes large moments only. In this case, allowance has been made for the symmetry factor and π^{-1} has been put in place of $\pi^{-\frac{1}{2}}$ in the expression for calculating n .

molecules collide. n should, of course, always be a small number.

We have applied this procedure to the various association reactions that are known (excepting the hydrogenation of ethylene which will be further considered below), and the results are presented in Table I.

The value of n for isoprene is surprisingly low, since it is the most complicated molecule and we might expect that it would have the most stringent conditions with respect to orientation. The relative values of the n 's in the table, however, agree with the relative magnitudes of the steric factors calculated by Vaughan,⁵ using kinetic theory collision numbers. We would expect that both molecules would have to be oriented thus fixing at least one degree of freedom for each. If we arbitrarily set $n=2$ for isoprene, we miss the observed rate by a factor of about 50, which could be interpreted to mean that each degree of freedom would be only partly frozen out, so that there would be 7 ($\cong \sqrt{50}$) quantum states in which reaction could occur. If the polymerization of isoprene results in the creation in the polymer of two very low vibrational frequencies, corresponding to the two degrees of freedom which are fixed, then this would not be unexpected, for in the reverse reaction decomposition could occur from a number of levels, corresponding to the number of low energy states excited. The other rotations of the isoprene, which do not have to be fixed, become internal rotations in the molecule, which are completely excited, at least in the excited state of the polymer which is first formed and which conversely, is the state from which decomposition takes place.

In the case of butadiene, where n is about 2,

the evidence seems to indicate that a dicyclic, and, hence, rather stiff structure is formed, and the structure of the polymer seems to be not too closely related to the structure of the butadiene. Thus one might expect that more rotations would have to be fixed, and so it may very well be that actually a greater number, perhaps 3 or 4 degrees of freedom are *partially* frozen out.

The cases discussed illustrate what can be done with the approach to the experimental data developed above. We believe that this method gives a greater insight into the actual mechanism of the reaction than a mere calculation of collision frequency and steric factor by means of kinetic theory collision diameters.

THE COMBINATION OF ETHYLENE AND HYDROGEN²⁵

This reaction needs special treatment, since the relation between the degrees of freedom before and after combination is more complicated than assumed above. Ethane has 3 translational degrees of freedom, 4 rotational (one due to the free rotation of the methyl group), and 17 vibrational. The hydrogen and ethylene between them have 6 translational degrees of freedom, 5 rotational, and 13 vibrational. It is obvious that 3 of the rotational degrees of freedom of the ethane correspond directly to the 3 rotational degrees of freedom of ethylene, while the degree of freedom corresponding to

²⁵ We assume in this discussion that the hydrogen molecule comes off in one step from the ethane, and that no chain, such as suggested by F. O. Rice and Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934) is involved. If there is such a chain, then, of course, all the separate steps in the chain will need separate treatment.

the free rotation of the methyl groups presumably goes over into a transverse vibration of the ethylene. Thus, in the unimolecular reaction we must have 6 vibrational degrees of freedom of the ethane going over into 3 of relative translation, 2 of rotation of the hydrogen, and 1 of vibration of the hydrogen. We thus separate off these degrees of freedom, together with the rest of the translation and write:

$$A_1' \doteq (B_1 E_1')^{-1} kT/h, \quad (13a)$$

$$A_2' \doteq (B_2 B_3 C_3 E_3)^{-1} kT/h, \quad (13b)$$

where subscripts 1, 2 and 3 refer to ethane, ethylene, and hydrogen respectively, E_1' being the term for the 6 vibrations of the ethane which are concerned.

Now if we can assume that the vibration and rotations of the ethylene have no effect on the reaction, then the proper evaluation of A_2' will actually give us A_2 and so the rate of recombination of ethylene and hydrogen.

The vibrations of ethane included in E_1' may be thought of as belonging to the two hydrogens which are going to leave the ethane, though this can only be approximate, as such vibrations would not be normal vibrations. It is obvious that before the reaction occurs the forces holding these hydrogen to the rest of the structure will have become very much weakened. Thus we will not be able to take care of them simply by multiplying A_1' through by E_1' . Rather we should think of some intermediate complex, in which these two hydrogens have to all intents and purposes already formed a hydrogen molecule, with its characteristic rotations and vibrations; this hydrogen molecule is, however, still held to the ethylene by weak forces. The hydrogen molecule would vibrate with respect to the ethylene, and could rotate freely around the ethylene, at least about the line of centers of the carbon atoms. The hydrogen molecule would be expected to be about 1A from the line of centers of the carbon atoms and the effective moment of inertia will be obtained approximately by multiplying the mass of a hydrogen molecule by the square of this distance, and is thus 3.3×10^{-40} c.g.s. units. Motion along the line of centers will probably be more of a vibration than a rotation, but it seems reasonable to

assume in calculating the entropy that it is actually more like a rotation with about the same moment of inertia as that given above. Assuming now that all of these "rotational states" are equally available for reaction, that to take care of the vibration of the hydrogen molecule with respect to the ethylene we multiply by e , as above, and that the various vibrational and rotational states of the hydrogen molecule are all equally good for reaction, it is seen that we should multiply A_1' and hence A_2' by $e B_1 C_0 C_3 E_3$, where

$$C_0 = 8\pi^2 e I_0 kT/h^2, \quad (14)$$

I_0 being 3.3×10^{-40} c.g.s. units. This gives us, at 800°K,

$$k_2 = (e B_1 C_0 / B_2 B_3) (kT/h) \exp(-\epsilon_a'/kT) \\ = 1.66 \times 10^{-10} \exp(-\epsilon_a'/kT). \quad (15)$$

The experimental value²⁶ is $0.91 \times 10^{-10} \exp(-\epsilon_a'/kT)$. (ϵ_a' has the value 44,750 calories per mole.)²⁷ There is, therefore, very close agreement between experiment and theory, on the basis of the assumptions we have made. Had the experimental value come out much smaller than the theoretical, we would have presumed that our assumption that the vibration of the hydrogen molecule in the intermediate complex along the line of centers of the carbon atoms was more restricted than we supposed, and this would have corresponded to a restriction in the direction in which the hydrogen molecule could leave the ethylene. Any such restriction is certainly far less than would correspond to the freezing out of one rotational degree of freedom. This last observation affords us an insight into the relative importance of the various degrees of freedom with respect to probability of reaction.

While in the above we have restricted ourselves to a discussion of bimolecular associations, we have incidentally obtained an equal amount of information about the reverse reactions. In future work we shall attempt to discuss some of the experimentally known unimolecular reactions from this point of view.

²⁶ We have recalculated this value from the original data of Pease,^{4a} since he has made several minor errors in the calculation of his results. Our effective collision diameter is appreciably different from what he assumes.

²⁷ Gershinowitz and Rice, reference 8, p. 276.