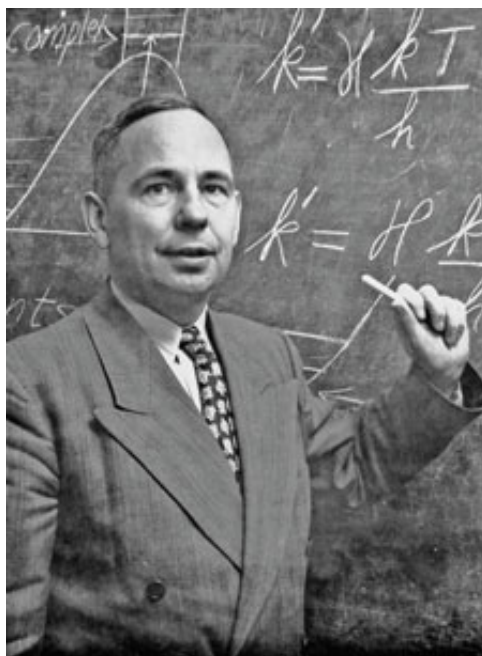


The Activated Complex in Chemical Reactions

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The calculation of absolute reaction rates is formulated in terms of quantities which are available from the potential surfaces which can be constructed at the present time. The probability of the activated state is calculated using ordinary statistical mechanics. This probability multiplied by the rate of decomposition gives the specific rate of reaction. The occurrence of quantized vibrations in the activated complex, in degrees of freedom which are unquantized in the original molecules, leads to relative reaction rates for isotopes quite different from the rates predicted using simple kinetic theory. The necessary conditions for the general statistical treatment to reduce to the usual kinetic treatment are given.

INTRODUCTION

The customary procedure for calculating bimolecular reaction rates has been to estimate the number of collisions between reacting molecules by using a cross-sectional area taken from measurements on momentum transfer. Such a cross section bears no very clear relationship to the area within which two molecules must fall in order to permit exchange of partners, i.e., to transfer mass. The violence of the collisions is of different orders of magnitude for one thing, and it is quite clear that many collisions which might result in momentum transfer are not oriented properly to permit exchange of atoms. This last difficulty is ordinarily met by introducing an empirical steric or orientation factor to take care of whatever discrepancy may arise between the observed and assumed collision area. This factor is often between 1 and 10^{-1} but may be as small as 10^{-8} .¹ We propose here to obtain explicit expressions for the reaction rates.

The ideas underlying the present calculations are the following ones. The forces between atoms are due to the motion and distribution of electrons and must be calculated, therefore, using quantum mechanics. However, after this is done, the nuclei themselves can be assumed to move under the influence of these forces according to classical mechanics. It must be possible, therefore, to calculate the reaction rates by the methods of statistical mechanics (or kinetic theory), if one assumes the aforementioned forces to be known. This is what is done in the present paper using a modification of the schemes developed by Herzfeld,² Tolman³ and Fowler⁴ among others and more recently applied in a very interesting way to the ortho-para hydrogen conversion by Pelzer and Wigner.⁵

Cases occur when classical mechanics does not apply to the motion of the nuclei. Zero point energy may be present for some vibrations, and it will be necessary to deal with quantized vibrations in a semi-classical way. Tunneling may occasionally play some role in the motion. In other cases, probably also of very rare occurrence, there may be jumps from one energy level to another. The latter factors may also change the results calculated by neglecting them by orders of magnitude as, e.g., in the case of N_2O .⁶ We are not concerned here with reactions in which the last two effects are important.

¹ Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford Press (1933). W. E. Vaughan, *J. Am. Chem. Soc.* 55, 4115 (1933).

² K. F. Herzfeld, *Kinetische Theorie der Wärme*; (Müller Pouillet's Lehrbuch der Physik), 1925.

³ R. C. Tolman, *Statistical Mechanics*, Chemical Catalog Co., 1927.

⁴ R. H. Fowler, *Statistical Mechanics*, Cambridge Univ. Press, 1929.

⁵ H. Pelzer and E. Wigner, *Z. Phys. Chem.*, B15, 445 (1932).

⁶ Volmer and Kummerow, *Z. Phys. Chem.*, B9, 141 (1930).

We now consider in more detail the nature of the surfaces and the motion which corresponds to a reaction. A group of atoms may of course arrange themselves in an infinitely large number of ways. If the energy of such a system of atoms for the lowest quantum state of the electrons is plotted against the various distances between the nuclei, we obtain the potential surface which governs (except in the aforementioned cases) the motion of the nuclei.

Now a system moving on this surface will have kinetic energy which may be quantized for the different degrees of freedom in a variety of ways, consistent with the particular energy and the particular position on the surface. Low places in the potential surfaces correspond to compounds. If a particular low lying region is separated from all other low places by regions higher than about 23 kilocalories, the compound will be stable at and below room temperature. The higher the lowest pass the higher is the temperature at which the compound is still stable. A reaction corresponds to a system passing from one low region to another. In thermal reactions the Boltzmann factor makes it certain that the reaction will proceed by way of the lowest pass. The activated state is the highest point along this lowest pass. Before considering the activated state further we discuss the general problem of constructing our partition functions for a given surface.

FORMULATION OF PARTITION FUNCTIONS

We here simply sketch the procedure for the gas phase and indicate where the modifications for reactions in solution will come. If a system of atoms is represented by a point on a potential surface such that for the motion in every direction the potential increases or remains constant, we may apply the well-known method of small vibrations to obtain the normal coordinates.⁷ Now our system will show translational, vibrational and rotational degrees of freedom. The weighted number of states associated with a degree of translation are

$$\frac{1}{h} \cdot \int_0^{l_i} dq_i \int_{-\infty}^{\infty} \exp\left(\frac{-p_i^2}{2m_i kT}\right) dp_i = \frac{(2\pi m_i kT)^{\frac{1}{2}} l_i}{h}$$

where q_i , p_i , and m_i , are the generalized length, momentum and mass for this degree of freedom, respectively.⁸ For a solution or highly compressed gas the integration over the length l_i would involve a potential function in an important way. Also the reacting system would now include in an essential way the degrees of freedom of a certain number of the solvent molecules. If we set the length $l_i = 1$ we have the number of unit cells per cm of length, a quantity frequently used in what follows. The other universal constants require no definition. Similarly for a vibrational degree of freedom we obtain for the weighted number of states using classical theory

$$\frac{1}{h} \cdot \int_{-\infty}^{\infty} \exp\left(\frac{-p_i^2}{2m_i kT}\right) dp_i \cdot \int_{-\infty}^{\infty} \exp\left(\frac{-f_i q_i^2}{2kT}\right) dq_i = \frac{kT}{hv_i}$$

⁷ See, for example, Whittaker, *Analytic Dynamics*, Cambridge Univ. Press, 1927. J. H. Van Vleck and P. C. Cross, *J. Chem. Phys.* 1, 357 (1933).

⁸ k is the Boltzmann constant ($1.38064852(79) \cdot 10^{-23}$ JK⁻¹), h is the Planck constant ($6.626070040(81) \cdot 10^{-34}$ Js), T is the thermodynamic temperature.

where

$$v_i = (1/2\pi) \cdot (f_i/m_i)^{\frac{1}{2}}.$$

Here f_i and v_i , are the force constant and frequency, respectively. However, summing over the quantized states, we obtain the familiar quantum theoretical expression $(1 - \exp(-hv_i/kT))^{-1}$ for the weighted number of states for the harmonic oscillator. For $hv_i \ll kT$ of course $(1 - \exp(-hv_i/kT))^{-1} = kT/hv_i$. The weighted sum of states for the two degrees of rotation of a linear molecule is

$$\sum_{j=0}^{\infty} (2j+1) \cdot \exp\left(\frac{-j \cdot (j+1)h^2}{8\pi^2IkT}\right).$$

Here I is the moment of inertia. Now there are cases for which the position of the activated state on the potential surface depends on the quantum number j . Certain cases of this type will be treated in another place. If the critical configuration does not depend in an important way on j and if $j \cdot (j+1)h^2/8\pi^2I \ll kT$, we can in the well-known way substitute for the summation the integral

$$\int_0^{\infty} 2 \cdot \left(j + \frac{1}{2}\right) \cdot \exp\left(\frac{-(j + \frac{1}{2})^2 h^2}{8\pi^2IkT}\right) dj = \frac{8\pi^2IkT}{h^2}.$$

For a non-linear molecule we can write for the weighted sum of states the expression $8\pi^2 \cdot (8\pi^3ABC)^{1/2} (kT)^{3/2}/h^3$ (if the moments of inertia are small we should sum over the energy levels for a symmetric or asymmetric top). The expression

$\sum(2j+1) \cdot \exp\left(-j(j+1)h^2/(8\pi^2 \cdot (ABC)^{\frac{1}{3}}kT)\right)$ is satisfactory if the moments of inertia differ only a little and the corresponding integral

$$\int_0^{\infty} 4 \cdot \left(j + \frac{1}{2}\right) \cdot \exp\left(\frac{-(j + \frac{1}{2})^2 h^2}{8\pi^2(ABC)^{\frac{1}{3}}kT}\right) dj$$

yields the classical weighted sum given above.

We now suppose that we have a great number of systems in thermal equilibrium and want to know the relative probability of any system being at points 1 and 2 on a potential energy surface. We assume points 1 and 2 are of such a kind that we know the corresponding normal coordinates and that the energy of point 2 is greater by \mathcal{E}_0 than that of point 1. The ratio of the corresponding weighted number of states of points 2 to 1 (which is the relative probability) is obtained by multiplying $\exp(-\mathcal{E}_0/kT)$ into the ratio of the product of the weighted sum for each normal mode for point 2 to the corresponding product for point 1. This very brief discussion of the equilibrium constant is sufficient for our purposes. For a rigorous deduction one may consult the work of Fowler previously referred to. The next conception we will require is the rate at which the systems at point 2 are moving along a particular normal coordinate. In our considerations point 2 will in general correspond to the activated state which we now consider in more detail. We call a system at the activated point an *activated complex*.

THE ACTIVATED COMPLEX

The activated state is because of its definition always a saddle point with positive curvature in all degrees of freedom except the one which corresponds to crossing the barrier for which it is of course negative. Further, the barriers are so flat near the top that tunneling may be neglected without appreciable error. A configuration of atoms corresponding to the activated state thus has all the properties of a stable compound except in the normal mode corresponding to decomposition and this mode because of the small curvature can be treated statistically as a translational degree of freedom. Thus a non-linear activated complex with n atoms ($n \geq 3$) has three regular translational degrees of freedom corresponding to motion of the center of mass in addition to the one corresponding to passage over the top of the barrier. It also has three rotational degrees of freedom for the molecule as a whole, and the remaining $(3n - 7)$ degrees of freedom correspond to internal rotations or vibrations. A linear molecule differs from this in that one of the degrees of freedom which were a rotation is instead a bending vibration. Now the calculation of the concentration of activated complexes is a straight forward statistical problem, given the moments of inertia of the complex and the vibration frequencies. This information is given with sufficient accuracy, even by our very approximate potential surfaces, to give good values for the partition functions.

The procedure for calculating the specific rate is the following: One first calculates the concentration of activated complexes per unit length and with momentum p lying between p and $p+dp$, both these quantities taken for the degree of freedom corresponding to decomposition. This is then multiplied by the associated velocity p/m^* and summed for all values of momenta which correspond to passing over the barrier in the forward direction, i.e., for $p = 0$ to ∞ . We now formulate the particular expressions for the various cases.

THREE ATOM REACTIONS

Consider the reaction



where the activated complex $A - B - C$ is linear. We write for the specific reaction rate constant

$$k_1 = \bar{p}/m^* \quad (2)$$

$$= c \frac{g_a i_a}{g_n i_n} \left(\frac{m_3}{m_1 m_2} \right)^{\frac{3}{2}} \frac{I_3 \sigma_2}{I_2 \sigma_3} \frac{h^2}{(2\pi)^{\frac{3}{2}} (kT)^{\frac{1}{2}}} \frac{(1 - \exp(-hv_2/kT)) e^{-\mathcal{E}_0/kT}}{\prod_{i=1}^3 (1 - \exp(-hv_i^*/kT))}$$

$$\cdot \left\{ \frac{c g_a i_a \cdot \frac{(2\pi m_3 kT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 I_3 kT}{\sigma_3 h^2} \prod_{i=1}^3 \left(1 - \exp\left(\frac{-hv_i^*}{kT}\right)\right)^{-1} e^{-\mathcal{E}_0/kT} \frac{(2\pi m^* kT)^{\frac{1}{2}}}{h}}{g_n i_n \cdot \frac{(2\pi m_1 kT)^{\frac{3}{2}}}{h^3} \frac{2\pi m_2 kT}{h^3} \left(1 - \exp\left(\frac{-hv_2}{kT}\right)\right)^{-1} \frac{8\pi^2 I_2 kT}{h^2 \sigma_2}} \right\}$$

The subscript 1 refers to atom A , 2 to BC and 3 to the activated complex. \mathcal{E}_0 is the difference in energy between the initial substances and the activated state at the absolute zero. The quantities $m_j, I_j \sigma_j$ are the mass, moment of inertia and symmetry number respectively of the particle j . The three frequencies v_i^* (for $i = 1, 2, 3$) are for the activated complex and v_2 is the vibration frequency of AB . The latter $g_a i_a$ and $g_n i_n$ are the products of weights arising from electronic states and nuclear spin for the activated and ground state respectively. Frequently $g_a = g_n$ and i_a and i_n need only be considered for reactions in which there is a change in ratio of ortho and para forms. m^* and \bar{p} are the reduced mass and average momentum along the normal coordinate corresponding to decomposition. The quantity in equation (2) which multiplies \bar{p}/m^* (the average velocity of activated complex along the normal coordinate corresponding to passing over the barrier) is of course the concentration of activated complex per cm of length normal to the barrier when there is unit concentration of reactants per cc. Now

$$\begin{aligned} \bar{p}/m^* &= \frac{\int_0^\infty \exp(-p^2/2m^*kT) p/m^* dp}{\int_{-\infty}^\infty \exp(-p^2/2m^*kT) dp} \\ &= kT/(2\pi m^*kT)^{\frac{1}{2}} \end{aligned}$$

Thus we see that the terms for the activated complex associated with the normal coordinate along which decomposition occurs give simply $\left((2\pi m^*kT)^{\frac{1}{2}}/h\right) \bar{p}/m^* = kT/h$. This factor will of course come in in the same way for every type of reaction.

For some reactions it will happen that the same activated complex may cross the barrier and return without decomposing. This fact reduces the actual reaction rate. It is taken care of by the factor c which is the reciprocal of the average numbers of crossings required for each complex which reacts.⁹ It will generally be about unity. There are methods available for estimating the factor c . The other symbols appearing in equation (2) are well known and if we introduce our constants in grams cm sec. units, k_1 is given in cc molecules⁻¹ sec.⁻¹. If we want k_1 in cc moles⁻¹ sec.⁻¹ we must multiply the k of equation (2) by Avogadro's number \mathcal{N} . A form frequently used for writing experimental specific reaction rates is

$$k_2 = BT^{\frac{1}{2}} \cdot \exp(-\mathcal{E}/kT) = BT^{\frac{1}{2}} \exp\left(-\left(T \cdot \frac{d \log k_2}{dT} - \frac{1}{2}\right)\right). \quad (3)$$

The activation energy \mathcal{E} in equation (3) is written as $kT^2 d \log k_2/dT - \frac{1}{2}kT$ as this is the way it is calculated from the temperature increment.

Putting equation (2) in the same form as equation (3) we find for comparison

$$\mathcal{E} = \mathcal{E}_0 + \sum_{i=1}^3 (hv_i^*/\exp(hv_i/kT) - 1) - (hv_2/\exp(hv_2/kT) - 1) - kT, \quad (4)$$

⁹ Also referred to as the transmission coefficient.

and

$$\begin{aligned}
 BT^{\frac{1}{2}} = c \cdot \frac{g_a i_a}{g_n i_n} \left(\frac{m_3}{m_1 m_2} \right)^{\frac{3}{2}} \frac{I_3 \sigma_2}{I_2 \sigma_3} \frac{h^2}{(2\pi)^{\frac{3}{2}} (kT)^{\frac{1}{2}}} \frac{(1 - \exp(hv_2/kT)) \mathcal{N}}{\prod_{i=1}^3 (1 - \exp(-hv_i^*/kT))} \quad (5) \\
 \cdot \exp \left\{ \sum_{i=1}^3 (hv_i^*/kT) (\exp(hv_i^*/kT) - 1)^{-1} \right. \\
 \left. - hv_2/kT \cdot (\exp(hv_2/kT) - 1)^{-1} - 1 \right\} .
 \end{aligned}$$

In equation (5) and in the preceding expressions the masses m_j refer to the masses of a single atom or molecule. If the masses are taken in atomic weight units and written with primes we get:

$$\begin{aligned}
 BT^{\frac{1}{2}} = 1.41 \cdot 10^{12} (300/T)^{\frac{1}{2}} c (g_a i_a / g_n i_n) (m'_3 / m'_1 m'_2)^{\frac{3}{2}} (I_3 \sigma_2 / I_2 \sigma_3) \\
 \cdot (1 - \exp(-hv_2/kT)) \\
 \cdot \prod_{i=1}^3 (1 - \exp(-hv_i^*/kT))^{-1} \cdot \exp \left\{ \sum_{i=1}^3 (hv_i^*/kT) (\exp(hv_i^*/kT) - 1)^{-1} \right. \\
 \left. - (hv_2/kT) (\exp(hv_2/kT) - 1)^{-1} \right\} \quad \text{in cc mole}^{-1} \text{ sec.}^{-1} \text{ units.} \quad (5')
 \end{aligned}$$

For many simple reactions all the terms in $BT^{\frac{1}{2}}$ except $1.41 \cdot 10^{12}$ are of the order of magnitude of 1 so that this factor multiplied by the activation energy term gives approximately the rate of the reactions and actually agrees to this approximation with the known experimental values. We here have an exact theoretical collision diameter for reaction rates which replaces the rough kinetic theory value and provides in addition a theory for predicting and explaining divergences.

The inverse dependence on temperature of B is to be noted. This will be the case for molecules for which there are two more fairly stiff quantized vibrations in the activated complex than in the unactivated particles. Partition functions for fairly stiff vibrations depend only slightly on temperature. It is difficult to test this dependence of B upon T experimentally but for this same case there is a predicted dependence of isotopic reactions on mass which may be more readily detected. For the moment of inertia of the activated complex we have $I_3 = m_1 a^2 + m_4 c^2 - (m_1 a - m_4 c)^2 / m_3$ where m_1 and m_4 are the masses of atoms A and C , respectively, and m_3 is the sum of the masses of the three atoms; a is the distance between A and B , and c the distance between B and C . Now $I_2 = m_4 m_5 d^2 / (m_4 + m_5)$ where d is the distance between B and C whose masses are, respectively, m_5 and m_4 . If all three atoms are alike $I_3/I_2 = (a+c)^2/d^2$, i.e., the ratio is independent of the mass of the atoms so that for protium or deuterium mass enters explicitly into B only in the term $(m'_3/m'_1 m'_2)^{\frac{3}{2}}$. Thus from this cause alone the protium reaction should go faster by a factor of $2^{\frac{3}{2}}$ instead of $2^{\frac{1}{2}}$ as is found if one assumes the only difference lies in the relative velocities of colliding particles. If the two extra bending frequencies in the activated complex

are small, the term $(1 - \exp(hv_i/kT))^{-1}$ approaches the value kT/hv_i , and remembering that $v_i = (1/2\pi)(f_i/m_i)^{1/2}$ where f_i is the corresponding force constant and m_i the reduced mass, we see that B will be dependent upon temperature and depend on mass in the way previously supposed, i.e., $B \sim T/m^{1/2}$. The actual dependence will lie between this extreme and $B \sim 1/T^{3/2}$. The results of Topley and the present author, soon to be published, indicate that actually the system should more closely approach the latter dependence. These authors have calculated values of B for both the ortho-para-hydrogen conversion and the reaction $\text{Br} + \text{H}_2$ which agree with experiment.

It should be emphasized that in the particular formulation (2) of our specific reaction rate constant all the quantities may be calculated from the appropriate potential surface which can always be constructed at least approximately. However, in cases where any part of the partition functions is more accurately known from some other source such information can of course be incorporated.

If one realizes that the term $(2\pi mkT)^{1/2}/h$ for a translational degree of freedom has a value of the order of 10^8 for a light atom at ordinary temperature, one sees that the replacement of two terms like this in the initial products by two bending vibrations in the activated complex introduces a factor in k of the order 10^{-16} . This factor is of course the analog of the collision area in the rough kinetic picture and explains why the kinetic picture works approximately, since the other terms in (2), except the average velocity, \bar{v}/m^* , are not very different from unity for many reactions. A discussion showing when the general statistical treatment reduces to the usual kinetic theory treatment is given farther on.

In the case where the least activation energy corresponds to a non-linear activated complex the terms

$$8\pi^2 I_3 kT / (\sigma_3 h^2) \prod_{i=1}^3 (1 - \exp(-hv_i^*/kT))^{-1}$$

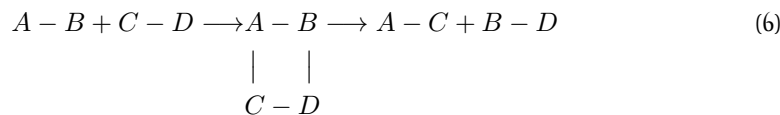
in equation (2) are replaced by the quantity

$$8\pi^2 (8\pi^3 A^* B^* C^*)^{1/3} (kT)^{3/2} h^{-3} \prod_{i=1}^2 (1 - \exp(-hv_i^*/kT))^{-1}$$

In this case we see a vibrational degree of freedom has become a rotational one. The letters $A^* B^* C^*$ now correspond to the principal moments of inertia of the activated complex. The calculation of the reaction rate and of B and E then proceeds exactly as before.

FOUR ATOMS

Consider the reaction:



$$k_6 = c g_a i_a (2\pi m_3 kT)^{\frac{3}{2}} h^{-3} 8\pi^2 (8\pi^3 A_3 B_3 C_3)^{\frac{1}{3}} (kT)^{\frac{3}{2}} \sigma_3^{-1} h^{-3} \quad (7)$$

$$\cdot \prod_{i=1}^5 (1 - \exp(-hv_i/kT))^{-1} kT/h \cdot \exp(\mathcal{E}_0/kT)$$

$$\cdot \left[g_n i_n (2\pi m_1 kT)^{\frac{3}{2}} h^{-3} (2\pi m_2 kT)^{\frac{3}{2}} h^{-3} \right.$$

$$\cdot (1 - \exp(-hv_1/kT))^{-1} (1 - \exp(-hv_2/kT))^{-1}$$

$$\left. \cdot 8\pi^2 I_1 kT \sigma_1^{-1} h^{-2} 8\pi^2 I_2 kT \sigma_2^{-1} h^{-2} \right]^{-1}$$

$$= c g_a i_a (g_n i_n)^{-1} (m'_3/m'_1 m'_2)^{\frac{3}{2}} (\sigma_1 \sigma_2 / \sigma_3) 1.92 \cdot 10^{12} (300/T) (A'_3 B'_3 C'_3)^{\frac{1}{2}} (I'_1 I'_2)^{-1}$$

$$\cdot \prod_{i=1}^5 (1 - \exp(-hv_i/kT))^{-1} (1 - \exp(-hv_1/kT))$$

$$\cdot (1 - \exp(-hv_2/kT)) \exp(-\mathcal{E}_0/kT)$$

in cc mole⁻¹ sec.⁻¹ units.

The subscripts 1, 2 and 3 refer to the species $A - B$, $C - D$ and the activated complex respectively. Primed symbols as before mean that atomic weights are to be used as masses, and atomic weights $\cdot (\text{Ångstroms})^2$ are the units in which moments of inertia are to be given. The significance of the other symbols will be clear from the definitions in connection with equation (2). Since all the quantities in (7) are of the order of unity for most reactions except the numerical factor and $e^{-\mathcal{E}_0/kT}$ we see again why the kinetic theory picture agrees approximately.

Clearly, for any bimolecular reaction, we can immediately write down the expression corresponding to k_6 . If A , B , C and D instead of being atoms are radicals there will simply be additional vibration and internal rotation terms with the expression for moments of inertia of the initial substances in the appropriate cases, taking the form for non-linear molecules. The same reasons for approximate agreement with kinetic theory will remain. Now the activated complex for the type of reactions we are considering is the same for the forward or the reverse reaction. So that in calculating the specific reaction rate constant k for a unimolecular reaction which is bimolecular in the reverse direction we simply modify the denominator of the reverse reaction constant to correspond to the new initial reactants.

UNIMOLECULAR REACTIONS

Suppose we have a non-linear molecule of n atoms decomposing unimolecularly. We then write, cancelling out factors common to the initial and activated states:

$$k_8 = c^* \sigma / \sigma^* (A^* B^* C^* / ABC)^{\frac{1}{3}} \prod_{i=1}^{3n-7} (1 - \exp(-hv_i^*/kT))^{-1} \quad (8)$$

$$\cdot \prod_{i=1}^{3n-6} (1 - \exp(-hv_i/kT))$$

$$\cdot (kT/h) \exp(-\mathcal{E}_0/kT).$$

Quantities referring to the activated state in equation (8) are starred. Now in the particular case where $hv_i \ll kT$, i.e., all vibrational degrees of freedom approach a classical behavior we have $(1 - \exp(-hv_i/kT))^{-1} = kT/hv_i$; and equation (7) takes the form:

$$k_9 = c^* (\sigma/\sigma^*) \prod_{i=1}^{3n-6} \prod_{i=1}^{3n-7} (v_i^*)^{-1} (A^* B^* C^*)^{\frac{1}{3}} (ABC)^{-\frac{1}{3}} \exp(-\mathcal{E}_0/kT). \quad (9)$$

c^* has the same meaning as the c defined in connection with equation (2). We of course come to this same result (9) directly if we integrate the appropriate classical expressions for vibration over phase space. Thus for each vibrational degree of freedom:

$$(1/h) \cdot \int_{-\infty}^{\infty} \exp(-p^2/(2m_1kT)) dp_i \cdot \int_{-\infty}^{\infty} \exp(-f_i g_i^2/(2kT)) dq_i = kT/hv_i$$

if we use the relationship $v_i = \frac{1}{2}\pi (f_i/m_i)^{\frac{1}{2}}$. In using (8) it must be remembered that for certain molecules some of the degrees of freedom treated as vibrations can better be treated as internal rotations. In any particular case there is no particular difficulty in doing this. equation (9) is sufficiently near to that found for unimolecular reactions at high pressures that there seems no doubt of the wide applicability of both equation (8) and (9). A formula very similar to equation (9) was obtained by an approximate method in a paper by Polanyi and Wigner.¹⁰

¹⁰ M. Polanyi and E. Wigner, Z. Phys. Chem. A (Haber Band), 439 (1928).

General case

Cases could of course be multiplied almost indefinitely but enough examples have been given to leave no doubt of the proposed method of procedure in a particular case. We may write for the specific reaction rate constant for a reaction of any order

$$k_i = c(\mathcal{F}_a/\mathcal{F}_n)(\bar{p}/m^*) = c(\mathcal{F}'_a/\mathcal{F}_n)(kT/h) e^{-\epsilon_0/kT} \quad (10)$$

where \mathcal{F}_a is simply the partition function (or Zustandssumme) for the activated state and \mathcal{F}_n is the same quantity for the normal state. \mathcal{F}'_a is the partition function for the activated complex for all the normal coordinates except the one in which decomposition is occurring. The partition function for this normal coordinate is included in the factor $(kT/h) e^{\epsilon_0/kT}$. The other quantities have been defined.

The frequently observed negative temperature coefficient of trimolecular reactions has a ready explanation from the point of view presented here. Since the formation of an activated complex from three molecules involves a great loss in entropy, a reaction which goes with a reasonable rate at ordinary temperatures will necessarily have a low activation energy. Further in forming the complex a number of translational and rotational terms with direct dependence on temperature are converted into vibrational terms with very low temperature dependence. Thus the rate will vary inversely with the temperature to a comparatively high power so that if the activation energy is low enough, the k will have a negative temperature coefficient. Kassel¹¹ has discussed such reactions also.

The extremely low rates, as compared with expectations from kinetic theory, observed in solutions are to be thought of as associated with a change of translational or rotational degrees of freedom of the original molecules into vibrational or oscillatory states of the activated complex. These changes may of course be in the enveloping solvent molecule. Any advantage of this formulation of the problem for solutions over any other consideration of entropy and heat content must come from a happy choice of the mechanism of reaction.

When the rate determining step shifts to the collision process as it does for "unimolecular reactions" at low enough pressure we again use well-known statistical methods, but our slow process is now connected with energy transfer in collision.

KINETIC THEORY DIAMETERS

It becomes a matter of considerable interest to show under what circumstances the preceding general statistical method reduces to the simple kinetic theory scheme as ordinarily applied. We first calculate the number of collisions between two kinds of hard spheres A and B with radii r_1 and r_2 , and masses m_1 and m_2 , respectively. We use our general method. The respective concentrations per cc of A and B are N_1 and N_2 . Our procedure is to calculate the number of pairs of molecules per cc per second which come closer to each other than $(r_1 + r_2 + \epsilon)$. We then let ϵ approach zero. Our collision complex then has three degrees of freedom associated with translational motion of the center of gravity; one degree corresponding to relative translation along the line of centers; and two degrees corresponding to motion

¹¹ L. S. Kassel, J. Phys. Chem. 34, 1777 (1930).

perpendicular to the line of centers, i.e., two degrees of rotation. Before collision there are six translational degrees of freedom, i.e., three for each sphere. The expression for the number of collisions when there is one molecule of each kind per cc may then be written at once:

$$k_{11} = \frac{\left[(2\pi(m_1 + m_2)kT)^{\frac{3}{2}} / h^3 \right] \sum_0^{\infty} (2j + 1) \exp(-j(j+1)h^2/8\pi^2IkT) (kT/h)}{\left[(2\pi m_1 kT)^{\frac{3}{2}} / h^3 \right] \cdot \left[(2\pi m_2 kT)^{\frac{3}{2}} / h^3 \right]} . \quad (II)$$

The significance of each term will be clear from our previous discussion.

Now if the temperature is not too low we have $j(j+1)h^2/8\pi^2I \ll kT$; so that we can make the usual approximation for the two rotational degrees of freedom, i.e.,

$$\sum_0^{\infty} (2J + 1) \exp(-j(j+1)h^2/8\pi^2IkT) = 8\pi^2IkT/h^2 .$$

Also kT/h is just the term $\left[(2\pi m^*kT)^{\frac{1}{2}} / h \right] \bar{p}/m^*$ of course. The moment of inertia $I = (m_1 m_2 / m_1 + m_2) \cdot (r_1 + r_2)^2$, so that we have after simplification

$$k_{11} = 2(r_1 + r_2)^2 (2\pi kT (m_1 + m_2) / m_1 m_2)^{\frac{1}{2}} . \quad (12)$$

The number of collisions per cc per second is then

$$Z = N_1 N_2 k_{11} = 2N_1 N_2 (r_1 + r_2)^2 (2\pi kT (m_1 + m_2) / m_1 m_2)^{\frac{1}{2}} \quad (13)$$

which is the usual expression for the number of collisions. Our method of treatment of collisions neglects certain of the refined features arising from the wave nature of the atoms. These are not of interest to us in our present treatment of reaction rates since here we make no explicit use of kinetic theory diameters. For an exposition of these features see a series of papers by Massey and Mohr.¹² For identical colliding systems a symmetry number should be included in equation (II) to (13).

It is now easy to see when we are justified in using the simple kinetic picture. If the two colliding molecules have (a) none of their internal frequencies appreciably modified in the activated state and (b) if the two degrees of freedom replacing translation, which are not themselves translation, correspond to a rotation (as in the very special case of two colliding atoms) or if they are bending frequencies with force constants of practically zero, then we are justified in applying the simple kinetic theory. Even then there will be some difference arising from the fact that $(r_1 + r_2)$ for transfer of momentum is in extreme cases as much as 2.5 times as large as for the corresponding activated complex. Thus approximate agreement with simple kinetic theory will occur in particular cases, but much lower as well as higher values are to be expected in other reactions.

In general it does not seem useful to separate our formulas into a collision factor and a steric factor, but if this is to be done we should associate the kinetic theory diameter with the changes occurring in the particular six degrees of freedom which correspond to translation before the molecules collide. The changes in the other degrees of freedom would then be

¹² H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. A141, 434 (1933); A144, 188 (1934) and subsequent papers.

interpreted as the steric factor. It is interesting to note that if the two bending frequencies arising from translational terms are stiff enough so that the system lies almost entirely in the corresponding lowest states, the reaction diameter as just defined will be less than the kinetic diameter by the factor $8\pi^2IkT/h^2$ which may reach a value of the order of 100 for heavy atoms and moderately high temperatures.

The present formulation of the calculation of absolute rates of chemical reactions has certain features in common with a number of more intuitive previous treatments,¹³ but has more in common with the treatment of Pelzer and Wigner. It goes beyond these in formulating the general problem in a way susceptible to treatment with our present potential energy surfaces and in pointing out the consequences of quantization on the temperature coefficient and the difference in rate for isotopes. The fact that the activated complex is much like any other molecule except in the degree of freedom in which it is flying to pieces makes possible our comparatively simple formulation. A number of investigations are now in progress in which the absolute rate of reaction is being calculated.

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¹³ W. H. Rodebush, *J. chem. Phys.* 1, 440 (1933); V. K. La Mer, *ibid.*, 1, 289 (1933); O. K. Rice and H. Gershinowitz, *ibid.*, 2, 853 (1934)