

The Absolute Rate of Reactions in Condensed Phases

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zero point is supplied from the energy of the bond formed. The case of no orientation we have discussed in detail in our former paper.² In general, unless the process of activation involves some special mechanism such as we assumed in the preceding paper in the case of the decomposition of azomethane, we may assume that \mathfrak{E}_a lies between the values given by (6) and (10), and all present indications are that these will be rather close together, since $\Delta\epsilon_0$ will be of the order of the zero point energy of only a few vibrations (those changed to translations or rotations in the decomposition) most of which are of the bending type. In the case of exact orientation $\epsilon_{a,0}$ may be evaluated from the observed ϵ_a by Eq. (5). The first integral on the right of (5) is less than kT , the other is equal to kT . In this case, therefore, $\epsilon_{a,0}$ may be taken for all practical purposes to be equal to ϵ_a , and $\epsilon_{a,0}$ is a fair measure of \mathfrak{E}_a which is really the fundamental quantity.

If the process of activation does involve a special mechanism such as assumed in the preceding paper for the decomposition of azomethane, then no direct relation exists between the energy of activation and the energy necessary to break the bond.

If we consider the reaction from the point of view of an activation complex, we may say that Kassel's quantum theory of unimolecular reaction is equivalent to the assumption that the frequencies of the activation complex are the same as those of the molecule which is decomposing; the quantum theory of Rice,⁹ on the other hand, corresponds to a general lowering of frequencies in the activation complex. The evidence now at hand favors Kassel's hypothesis as the basis of an approximate method for calculating the rate of a unimolecular reaction as a function of pressure.

⁹ O. K. Rice, Proc. Nat. Acad. Sci. **14**, 114 (1928).

The Absolute Rate of Reactions in Condensed Phases

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The theory of absolute reaction rates is developed for condensed phases. The equation for the rate of a reaction of any order in any phase where the slow process is the passage over an energy barrier consists of the product of a transmission coefficient κ , a frequency kT/h , an equilibrium constant between an activated complex and the reactants and an activity coefficient factor. Previous theories of reaction rates such as Brönsted's, the collision theory of Mc C. Lewis, etc., are seen to be special cases of the general theory. A variety of examples are considered.

IN a previous paper one of us¹ outlined the theory of the absolute rate of reactions in terms of the activated complex and the probability of its formation from the reacting substances. Here we propose to consider in greater detail the properties of the activated complex and, by application of the equation already derived, to show how the rates of reaction in solution and at interfaces may be calculated. The relation of this treatment to certain empirical generalizations will be considered and the existence of numerous

anomalous reaction rates will be explained.

Reaction rates in solution have usually been considered as too complex to yield to any simple treatment and the work of Christiansen² and of Norrish and Smith³ seemed to show that rates in solution were abnormally slow. Moelwyn-Hughes⁴ from an examination of a large mass of data showed that for many reactions the rate was not far from that calculated on the simple kinetic

² Christiansen, *Zeits. f. physik. Chemie* **113**, 35 (1924).

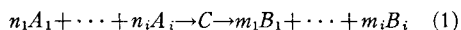
³ Norrish and Smith, *J. Chem. Soc.*, 129 (1928).

⁴ Moelwyn-Hughes, *Kinetics of Reactions in Solution*, Oxford Univ. Press.

¹ Eyring, *J. Chem. Phys.* **3**, 107 (1935).

theory using a collision diameter of the same magnitude as for gaseous reactions. However, this attempt to explain reaction rates yields in general only the same qualified success that the method would give if applied to a calculation of equilibrium constants and, since we know that, for the latter, the method is quite crude, we must clearly seek for a more exact treatment of reaction rates.

In the reaction



nA and mB represent n moles of the reacting species A and m moles of the species B , respectively, while C represents the activated complex. The activated complex, C , differs markedly from an ordinary molecule only in that degree of freedom in which it is flying to pieces, that is to say, it has 4 instead of the usual 3 translational degrees of freedom. We can therefore write for the equilibrium between the reacting molecules and the activated complex

$$K = K^\ddagger \frac{(2\pi m^\ddagger kT)^{1/2}}{h} = \frac{a^\ddagger}{a_1^{n_1} \cdots a_i^{n_i}} \frac{(2\pi m^\ddagger kT)^{1/2}}{h} \quad (2)$$

where a^\ddagger is the activity of the activated complex and a_1 to a_i the activities of the species A_1 to A_i . Later we consider the definitions of the standard state and introduce activity coefficients but first we shall consider states for which the activity may be identified with the concentration

$$K^\ddagger = c^\ddagger / (c_1^{n_1} \cdots c_i^{n_i}).$$

We now consider more closely the significance of K and K^\ddagger . The fact that the activated complex has a fourth translational degree of freedom does not affect the uniqueness of the expression we must write for the specific reaction rate but it does introduce an interesting arbitrariness into the expression for the concentration of the activated complex not present for molecules with but three degrees of freedom. Thus in (2) we have introduced K and K^\ddagger both of which might be interpreted as equilibrium constants. For unit concentration of reactants K gives the concentration of activated complexes which would lie within a length of a cm along the fourth internal translation if for the whole cm the density in

phase space were just that at the point of passage across the barrier. On the other hand K^\ddagger is the equivalent expression for the concentration of activated complexes lying in a single unit, h , of the phase space along this internal translation instead of in the $(2\pi m^\ddagger kT)^{1/2}/h$ units for K . In (2) and throughout the paper we have chosen to define K^\ddagger as our equilibrium constant. The advantage is that K^\ddagger has the usual dimensions so that the specific rate of any reaction is simply obtained by multiplying by a transmission coefficient κ and the universal frequency kT/h . The rate equation is then:

$$\begin{aligned} k' &= \kappa \cdot K \cdot \left(\frac{kT}{2\pi m^\ddagger} \right)^{1/2} \\ &= \kappa \cdot K^\ddagger \frac{(2\pi m^\ddagger kT)^{1/2}}{h} \cdot \left(\frac{kT}{2\pi m^\ddagger} \right)^{1/2} \\ &= \kappa \cdot K^\ddagger \cdot kT/h. \end{aligned} \quad (3)$$

Further substitution of

$$K^\ddagger = e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}$$

gives

$$k' = \kappa \cdot e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} kT/h. \quad (4)$$

These equations give the rate of a reaction in any phase provided that the slow process is the surmounting of a potential energy barrier. This is simply an alternative way of expressing Eq. (10) of the previous paper. We here employ the symbol κ instead of c for the transmission factor in order to avoid confusion with concentration.

The equivalence of Eqs. (3) and (4) to (10) of the previous paper is seen when we write the equilibrium constant K^\ddagger in terms of the partition functions for the normal molecules and the activated complex

$$K^\ddagger = (F_a'/F_n) e^{-E_0/kT},$$

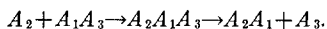
where F_a' is the partition function for all the degrees of freedom of the activated complex except the one along which decomposition is occurring, and F_n the partition function for all the reactants. Since the thermodynamical and statistical mechanical formulations are exactly equivalent, we shall be able, in our subsequent discus-

sion, to use whichever equation happens to be the more convenient for our purpose. This is particularly valuable for reactions in solution as many of the properties of solutions have been experimentally determined and correlated on a thermodynamical basis although their interpretation by statistical mechanics has not often been possible except in rather general terms.

As previously indicated, whenever it is justifiable to regard the reactants simply as hard spheres, this treatment reduces exactly to the usual kinetic theory treatment, but we can show that such conditions will be rare and more or less accidental.

THE TRANSMISSION COEFFICIENT

The transmission coefficient, κ , represents the probability of the activated complex forming the products after crossing the barrier, i.e., not returning. If the activated complex makes on the average n crossings of the barrier before decomposition then $\kappa = 1/n$. From the shape of the potential surface for a given reaction it is possible to estimate the value of κ and frequently this value is very close to unity. The effect of the relative masses of the reacting atoms will be illustrated by consideration of the reaction of an atom with a diatomic molecule.



Eyring and Polanyi⁵ discussed this reaction in detail and pointed out that for the three atoms colliding along a straight line the mechanics of the reaction can be represented by a mass point moving on a surface made by plotting the potential vertically and using as horizontal axes the two distances between the atoms A_2 to A_1 and A_1 to A_3 . These distances must be plotted not at right angles, however, but at an angle of $\theta = 90^\circ - \sin^{-1} [(m_2m_3)/(m_1+m_2)(m_1+m_3)]^{1/2}$, where the m 's are the masses of the three atoms. Thus we see that if either m_2 or m_3 is small compared with the other two masses, the acute angle, θ , approaches 90° . The surface itself consists of two confluent valleys parallel to the two axes. A mass point, representing our system, coming up one valley will, after passing over the intermediate low

barrier, either be reflected and return or else pass into the second valley. In the latter case we have reaction. Which of these cases will arise depends on θ and therefore upon the relative masses. How much the two valleys round off into each other at their junction will also have its effect on κ and, as this rounding off will be the greater the more the coulombic or additive binding exceeds the exchange binding, κ should more nearly approach unity as the reactants become more metallic (since the coulombic energy then becomes notably great). Just how near κ approaches unity is thus seen to depend on the ratio of the colliding masses and the nature of the binding forces. Our present knowledge comes from consideration of the approximate surfaces available for some of the simpler reactions for which we can say that κ is of the order unity.

On the other hand a type of reaction for which κ is often small is the adsorption of molecules on solid surfaces. Here the transmission coefficient is to be identified with the accommodation coefficient for that fraction of the molecules which strikes the surface with more than the necessary activation energy for adsorption.

NATURE OF EQUILIBRIUM IN THE ACTIVATED STATE

There is an important point regarding the activated complex which perhaps more than any other has been generally misunderstood. *It is not necessary that a large fraction of the activated complexes must fail to react in order that the equilibrium concentration be maintained. The activated state is not in general a state of indecision in which the activated complex is uncertain which way to proceed.* When κ is nearly unity an activated complex formed from the reactants will almost certainly decompose into products and whether it will do this or not is entirely independent of how fast the reaction is proceeding in the reverse direction. To say that activated complexes formed from reactants and from products collide and thus help to maintain equilibrium is without meaning as they are moving in spaces corresponding to different coordinates much as two trains passing on parallel tracks. By definition, for a gas reaction all molecules which are together at the activated state are included in the activated com-

⁵ Eyring and Polanyi, *Zeits. f. physik. Chemie* **B12**, 279 (1931).

plex so that the direction in which the activated complex proceeds is a mechanically determined question and is not influenced by the number of activated complexes moving in the reverse direction. For solutions, the direction of decomposition is equally determined by mechanics if we include the solvent molecules in our activated complex. This is also true when we treat the effect of the solvent molecules as an external potential and integrate over the external coordinates of the reacting molecules to obtain K^\ddagger in the way usual for equilibrium constants. The solvent molecules simply modify our potential surface but leave unchanged the concept of a mass point passing over a barrier. Now, since we can use equilibrium statistics when there are an equal number of activated complexes proceeding in both directions, we can still use it if those in one direction are completely suppressed, provided, of course, there is no autocatalysis. Thus if $\kappa=1$ and we start out with reactants but no products the number of activated complexes going in the forward direction is exactly the equilibrium number and there are none going in the reverse direction. If some activated complexes collide with the surface and then return, the number moving in the forward direction will be fewer than the equilibrium number by the factor κ . If there is autocatalysis there are then two separate mechanisms which are important; one in which the activated complex contains the reaction products and one in which it does not. The previous considerations apply then to each separate mechanism whether there be one or a dozen. Chain reactions are simply built up of a series of successive reactions each of which is to be treated as we have indicated. This aspect of the theory of the activated complex is given particular prominence, as it is in sharp contrast with the commonly held view in which it is assumed that, only when most of the activated complexes fail to react (i.e., $\kappa \ll 1$), can one assume that the equilibrium numbers are moving in a given direction. The nature of the activated complex thus becomes clearly apparent when considered in terms of a potential surface.

REACTION IN A CONDENSED PHASE

As we have seen, we can write for the specific reaction rate constant

$$k' = \kappa \cdot K^\ddagger kT/h \dots \quad (3)$$

$$\text{or,} \quad k' = \kappa \cdot (F_a/F_n) e^{-E_0/RT} kT/h \dots, \quad (5)$$

providing our standard state has been defined so that the activities a_i can be identified with the concentration c_i . In the present unsatisfactory condition of the theory of condensed phases there is a real advantage in choosing the dilute gas as the standard state. Then for any condensed state we must write:

$$K^\ddagger = a^\ddagger / (a_1 \dots a_n) = \alpha^\ddagger c^\ddagger / (\alpha_1 \dots \alpha_n \dots c_1 \dots c_n)$$

and for the rate $(c_1 \dots c_n k')$

$$= \kappa \cdot c^\ddagger \cdot kT/h,$$

giving the specific rate

$$k' = \kappa \cdot K_0^\ddagger \cdot (\alpha_1 \dots \alpha_n / \alpha^\ddagger) \cdot kT/h \dots, \quad (6)$$

where the a 's are the activities and the activity coefficients α_i and α^\ddagger approach unity as the gas becomes infinitely dilute. When the reaction proceeds in a phase other than the gaseous we still retain the gaseous state as the standard and as long as the gas phase is sufficiently near the ideal the α 's have the significance of distribution coefficients between the two phases.

Our choice of the infinitely dilute gas as the standard state irrespective of the phase in which the reaction is proceeding has the great advantage that in the statistical mechanical calculation for the standard state we can restrict our attention to the reacting particles. If it is desirable to use statistical mechanics to calculate the activity coefficients, two avenues are open: we may treat the adjacent molecules either as entering into a larger activated complex, or as constituting a field in which the reacting molecules move. Either treatment simply has the effect of increasing the number of degrees of freedom for which the potential energy must be considered and leaves unchanged the general problem of the passage of an activated complex across a potential barrier.

For a reaction proceeding in solution we see that the rate is greater than in the dilute gas by the factor $(\alpha_1 \dots \alpha_n) / \alpha^\ddagger$ and it is clear that exact cancelation of the activity coefficients will be fortuitous and that, in general, a reaction is likely to proceed at a different rate in solution

than in the gaseous state. For the exact calculation of the rate, a knowledge of distribution coefficients is essential and we will indicate briefly the method of introducing into our equation certain empirical generalizations.

For the distribution of a substance between its pure liquid phase and the gaseous phase several rules have been advanced of which the most valuable are Trouton's rule, its modification by Hildebrand and a more recent formulation by Langmuir.⁶ Using Langmuir's Eq. (29) for the vapor pressure in atmospheres one readily obtains the equation $p = 2.5e^{\frac{1}{2}T^{\frac{1}{2}}e^{-\Delta H/RT}}$, which together with an average value of 0.027 for the concentration in moles per cc in the liquid phase, gives as a general equation for the distribution ratio between the liquid and gaseous states for nonassociated liquids

$$\alpha = 5.0T^{\frac{1}{2}}e^{-\Delta H/RT}. \quad (7)$$

Over a temperature range extending from a few degrees absolute to some thousands of degrees, although α is of the order 10^3 , this equation represents the data within 2 or 3-fold for such diverse substances as fused salts, the halogen acids and the elements both metallic and nonmetallic. If, instead of the value 0.027, the actual liquid concentration is employed, Langmuir's calculations show that the discrepancy is usually not more than 40 percent. For certain associated liquids, however, such as water and ammonia, the numerical constant in the above equation is about 30 instead of 5.⁷

While these considerations apply to pure liquids we may readily extend them to solutions. If the solutions are ideal then clearly Eq. (7) applies; even if the solutions are nonideal, if the deviation arises principally from variation in the heat of vaporization then the equation is still applicable.

Frequently instead of using the approximate equation we may employ more accurate experimental data such as are available in the form of solubility coefficients of gases and vapor pressures.

⁶ Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932).

⁷ This equation applies only up to pressures of a few atmospheres. At the critical point α is of course unity. A more exact equation would take account of the decrease in the temperature dependence of α by including terms in the denominator of the general form $\{1 - \exp(-h\nu/kT)\}^{-1}$.

UNIMOLECULAR REACTIONS

For any unimolecular reaction in the liquid phase we may write Eq. (6) in the form

$$k' = \kappa \cdot K_0^{\ddagger} \alpha_1 / \alpha^{\ddagger} \cdot kT/h \quad (8)$$

and we can distinguish three cases: (1) If the activated complex and the normal molecules both form ideal solutions in a solvent then, since by definition there is no heat of mixing, we see from Eq. (7) that $\alpha/\alpha^{\ddagger} = 1$ hence

$$k' = \kappa \cdot K_0^{\ddagger} \cdot kT/h,$$

that is to say, the reaction will proceed at the same rate as in the gaseous state. (2) If the deviations from ideality are due mainly to changes in the heat of vaporization (ΔH) then the α 's may not cancel but their ratio will introduce a factor giving the equation

$$k' = \kappa \cdot K_0^{\ddagger} \cdot e^{-(\Delta H - \Delta H^{\ddagger})/RT} \cdot kT/h$$

and the exponential term simply leads to a change in the apparent activation energy. (3) If the numerical factor is affected and to a different extent for the reacting molecules and the activated complex, as would happen if solvation of the various species occurred, we have the case where not only the apparent activation energy but also the factor multiplying it may be considerably altered.

If we know the reaction rates in solution and in the gas phase together with the partial pressures of the reactants we can deduce the partial pressure of the activated complex: this is true for reactions of any order. With the knowledge of the vapor pressure of the activated complex thus obtained we can go very far in excluding certain types of mechanism. Thus, if the data lead to a value of the vapor pressure of the activated complex which is compatible with Eq. (7) using a value of ΔH which is at least approximately in agreement with Langmuir's⁸ ideas of molecular surface energy, it is highly probable that the activated complex in solution is unchanged and homopolar. A change in mechanism as between the two phases will in general lead to an abnormal value for the apparent vapor pressure of the activated complex.

⁸ Langmuir, Chem. Rev. **6**, 451 (1929).

The classical example of a unimolecular reaction which has been studied in several phases by Daniels and his collaborators^{9, 10} is the decomposition of N_2O_5 which in a variety of "inert" solvents proceeds with the same specific reaction rate as for the gas. By reference to the last column of Table V of the paper by Eyring and Daniels we see that α/α^\ddagger for saturated solutions of N_2O_5 in nitromethane, carbon tetrachloride and liquid N_2O_4 are 1.71, 2.32 and 2.01, respectively, whereas the next to the last column shows us that the corresponding values of α for nitromethane and carbon tetrachloride are 740 and 1108, respectively. These values of α are about what one would expect for an ideal solution. The values for the ratio α/α^\ddagger indicate that the activated complex likewise has the vapor pressure of a practically normal molecule. N_2O_5 does not decompose in the interior of a crystal in spite of the fact that the activity of the normal molecule is the same as that in the gas so that the activity coefficient is approximately the same as in concentrated N_2O_5 solutions. The reason is that the activity coefficient of the activated complex is enormously high, since, for a molecule in a lattice to form the activated complex, it must displace a great number of molecules thus placing the complex itself under tremendous pressure and leading to a correspondingly high value for the activity coefficient, α^\ddagger .

Our reaction rate Eq. (3) in the form

$$k' = \kappa \cdot K \cdot (kT/2\pi m)^{\frac{1}{2}}$$

applies equally well for the process of sublimation, vaporization or desorption. When the activation energy is equal to the latent heat then K is the ratio of equilibrium concentrations of gas, c , to condensed molecules, c_s . The actual rate will then be given by

$$k'c_s = \kappa \cdot (K \cdot c_s) (kT/2\pi m)^{\frac{1}{2}}, \quad (9)$$

where the quantity $(K \cdot c_s) = c_1$ is simply the value deduced from vapor pressure measurements. The rate equation owes its simple form in this case to the fact that the activated complex is to be identified with the vapor molecules.

N_2O_5 decomposes at 45°C in nitric acid at

0.042 times and in propylene chloride at 0.155 times the rate in the gas; hence, we deduce that, for these solvents, either the vapor pressure of the normal molecules is low or the vapor pressure of the activated complex is high by comparison with the normal solvents. Eyring and Daniels' suggestion that the slow rate was due to the formation of a stable complex assumes, of course, that the low value of α/α^\ddagger is due to α being low. Vapor pressure or solubility measurements will resolve this question. In general we should expect that abnormal solubility, which of course makes α low, will arise from abnormal solvation thus encasing the molecule in a sheath which may make α^\ddagger high for the same sort of reasons as for a molecule in the interior of a crystal. Whether α^\ddagger is increased or decreased depends on whether the solvent adds to the reactant in such a way as to strengthen or weaken the bond to be broken. There is a further point to be discussed in connection with this reaction. Since we know the actual rate of the reaction and also the heat of activation our theoretical equation enables us to evaluate the entropy of activation. The experimental results for the decomposition of N_2O_5 in the gas phase are represented by the equation

$$k' = 5.08 \times 10^{13} e^{-24,700/RT}.$$

We take the transmission coefficient as unity, since it can hardly differ materially from this value for this reaction, and, by equating the above experimental result to the theoretical value for k' , we find that the activated complex is 4.27 units richer in entropy than the normal molecules. This is a typical result for many unimolecular reactions.¹¹

We will now use our general theory to calculate the steric factor for one of the elementary processes of a chain reaction postulated by F. O. Rice.¹² The reaction is the formation of a five-membered ring and a methyl radical from the normal hexyl radical: the activated complex will be an almost closed five-membered ring with the methyl radical in the act of leaving the ring. From the data of Parks and Huffman¹³ we find that the

¹¹ Polanyi and Wigner, *Zeits. f. physik. Chemie* Haber Band, 439 (1928).

¹² F. O. Rice and K. K. Rice, *Aliphatic Free Radicals* (1935).

¹³ Parks and Huffman, *Free Energies of Some Organic Compounds* (1932).

⁹ Lueck, *J. Am. Chem. Soc.* **44**, 757 (1922).
¹⁰ Eyring and Daniels, *J. Am. Chem. Soc.* **52**, 1473, 1486 (1930).

entropy of cyclopentane is about 21 units less than that for normal pentane at 25°C; the formation of the ring changes 4 rotations into vibrations so that the difference in entropy should increase with temperature approximately as $4/2 R \ln T$. This leads to an entropy change for this ring closure at 650°C of about 25.6 units which corresponds to a steric factor of 2.5×10^{-6} as compared with Rice's estimate of 10^{-6} . This approximate calculation could be improved by taking account of the vibration frequencies in the ring by the formula $\prod_{i=1}^4 1/(1 - e^{-h\nu_i/kT})$. However, as it stands, it is certainly correct to better than a power of ten. Thus, such a calculation gives a quantitative theory for the change of the steric factor with temperature, something quite impossible on previous ideas about reaction rates.

There is another type of unimolecular reaction occurring in solution which, although requiring an activation energy of as much as 35,000 calories, still proceeds at a measurable rate at room temperatures. In the past this has been interpreted on the assumption that the slow process is the transfer of energy in collision yielding an activated molecule with the energy, E , distributed among $F+1$ classical degrees of freedom giving the equation

$$k' = Ze^{-E/RT}(E/RT)^{F+1}/F!,$$

where Z is the number of collisions. This point of view forces Moelwyn-Hughes,¹⁴ in order to explain the rapid reaction rate, to assume that the slow process is the transfer of energy between solvent molecules and the molecule decomposing. That, in solution, this should be the slow process, seems highly improbable when we realize that here if ever we should have the high pressure rate. That it is necessarily the mechanism is certainly untenable, as we see from our conception of an activated complex.

Although the theory invoking a collision and $F+1$ degrees of freedom is on the whole highly arbitrary it does at least take into account more degrees of freedom than are considered in the simple collision theory. Eq. (4) shows that the effect of these other degrees of freedom mani-

TABLE I. *Decomposition of Et₃SBr in benzyl alcohol-glycerol mixtures.*

% Benzyl alcohol	ΔS	ΔS^\ddagger
100	20.85	20.42
90.23	17.25	15.86
80.39	13.14	12.91
69.39	6.80	11.07

fested in the entropy of activation must be considered in chemical reactions.

An example of this type of reaction is the decomposition of triethylsulphonium bromide in various solvents. Taking the data of Corran,¹⁵ which have been used by Soper¹⁶ for demonstrating the analogy between the rate of the reaction and the entropy of the equilibrium process, we have calculated the entropies of activation which are given in column 3 of Table I.

The striking correspondence between the entropy change for the reaction (column 2) and the entropy of activation shows us that the activated complex must resemble closely the products of the reaction. This is in marked contrast to the behavior of the N_2O_5 molecule where the activated complex had an entropy close to that of the decomposing molecule.

BIMOLECULAR REACTIONS

When we come to bimolecular reactions in solution we find that there are reactions which according to the collision theory proceed too fast, too slow and at a normal rate.

Of the first type we have the reverse reaction to that considered above, the association of diethyl sulphide and ethyl bromide to form triethylsulphonium bromide. This reaction proceeds at a reasonable rate at 80°C in pure benzyl alcohol although it has the rather high activation energy of 28,400 calories as deduced from Corran's equilibrium measurements. A kinetic theory calculation yields for the collision diameter the value 1.14×10^{-7} cm instead of the normal value of 2 or 3 Angstroms. Such an interpretation throws the entire responsibility on the translational coordinates and so leads to this impossibly large collision diameter. The conception of the activated complex places a part of the responsi-

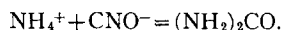
¹⁴ Moelwyn-Hughes, *Kinetics of Reactions in Solution* (1933), p. 163.

¹⁵ Corran, *Trans. Faraday Soc.* **23**, 605 (1927).

¹⁶ Soper, *Chem. Soc., Discussion* 45 (1931).

bility on the internal coordinates and we see at once that, since the unimolecular decomposition has an entropy of activation practically equal to the total entropy change for the equilibrium process, the bimolecular reaction must proceed with zero entropy of activation instead of the 7 units for a bimolecular reaction in solution¹⁷ required to give agreement with kinetic theory.

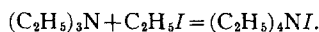
A further example of an abnormally rapid reaction is the conversion of ammonium cyanate into urea



The energy of activation for this reaction in aqueous solution is 23,170 calories and from equation (4) we have $\Delta S^\ddagger = 0.9$.¹⁸

Moelwyn-Hughes¹⁹ has compiled a list of reactions in solution which proceed at nearly the rate calculated from the collision theory. For reasons of space we will not include here the complete table of entropies of activation which we have computed for these reactions but merely state that where the reaction rate is just equal to that calculated by Moelwyn-Hughes the entropy of activation is 7 units. A departure by a factor of ten in either direction gives a corresponding change of 4.6 units in ΔS^\ddagger . These "normal" reactions involve a neutral molecule and an ion as reactants and consequently the activated complex will carry the same charge as the ion and hence we should expect that the entropy due to solvation would not be much changed as between the reactants and the activated complex. It is, therefore, to be expected that such reactions should involve about the same entropy of activation as analogous gas reactions.^{19a}

Of the reactions which proceed at an abnormally slow rate, one large class is that involving salt formation as in the Menshutkin reaction



A number of these reactions have been tabulated

TABLE II. $(\text{C}_2\text{H}_5)_3\text{N} + \text{C}_2\text{H}_5\text{Br}$ in acetone-benzene mixtures.

% Acetone	ΔH^\ddagger	$-\Delta S^\ddagger$
100	11,710	41.29
80	12,100	40.32
50	12,040	41.64
20	12,180	42.42
0	11,190	48.09

by Moelwyn-Hughes²⁰ and the values we have calculated for their entropies of activation range from 25 to 50 units. In general, if for a given equilibrium there is a large entropy change, it is inevitable that either the forward or the reverse reaction proceeds at an abnormal rate. Not many equilibrium data are available but from the results of Essex and Gelormini²¹ for the reaction



occurring in nitrobenzene at 60°C we calculate the entropy change for the equilibrium is 54.1 units while $-\Delta S^\ddagger$ is 37.5. This suggests that the activated complex is strongly polar and has many solvent molecules oriented around it. In a nonpolar solvent instead of orientation of solvent molecules there will be orientation of the reactants and products. This change in behavior on going from a polar to a nonpolar solvent is well exemplified by the data for the reaction between triethylamine and ethyl bromide in mixtures of acetone and benzene. We see from the figures in column 3 that the entropy of activation remains nearly constant so long as there is an appreciable number of acetone molecules which can be oriented around the activated complex but in pure benzene there is a markedly greater decrease in the entropy of the activated complex.

The known behavior of electrolytes in different solvents and in particular the investigations of Kraus and his co-workers²² into the properties of electrolytic solutions in nonpolar solvents is in harmony with these suggestions of solvent orientation and solute association.

Quite recently Williams and Hinshelwood²³

¹⁷ For a bimolecular reaction at about 50–100°C a kinetic theory collision diameter of 2A is equivalent to an entropy of activation of 6.9 while a diameter of 3A corresponds to 5.3 entropy units.

¹⁸ Walker and Hamby, *J. Chem. Soc.* **67**, 746 (1895).

¹⁹ Moelwyn-Hughes, *Kinetics of Reactions in Solution* (1933), p. 79.

^{19a} Even for a "normal" reaction the rate in solution is greater by the activity factor $\alpha_1\alpha_2/\alpha^\ddagger$. Part of this factor is reflected in a smaller absolute value of the entropy of activation.

²⁰ Moelwyn-Hughes, *Kinetics of Reactions in Solution* (1933), p. 111.

²¹ Essex and Gelormini, *J. Am. Chem. Soc.* **48**, 882 (1926).

²² Kraus and Hooper, *Proc. Nat. Acad. Sci.* **19**, 939 (1933); Kraus and Vining, *J. Am. Chem. Soc.* **56**, 511 (1934); Kraus, *Trans. Electrochem. Soc.* **66**, 179 (1934).

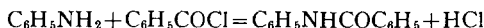
²³ Williams and Hinshelwood, *J. Chem. Soc.*, 1079 (1934).

TABLE III. *Benzoylation of amines in benzene.*

Amine	Acid chloride	ΔH^\ddagger	$-\Delta S^\ddagger$
H	p. NO ₂	5,900	40.22
p. CH ₃	H	6,800	38.54
H	p. Cl	7,000	39.97
H	H	7,350	39.62
H	p. CH ₃	8,000	39.24
p. Cl	H	7,600	41.83
m. NO ₂	H	10,500	39.17
p. NO ₂	p. NO ₂	10,400	42.52
p. NO ₂	H	11,800	39.50

have studied the benzoylation of certain amines and in conformity with the previous work of Bradfield²⁴ have shown that while these reactions proceed at a rate about a million times slower than that predicted by kinetic theory considerations the steric factor that they introduce is nearly the same for each reaction. In Table III we give the values of $-\Delta S^\ddagger$ for these reactions.

The reactions all involve substituted anilines reacting with various substituted benzoyl chlorides and we indicate in column 1 the particular substituent in the aniline molecule and in column 2 the substituent in the benzoyl chloride. The reaction in each case is of the type



and the activated complex will consist of the two reacting molecules linked between the N atom and the carbonyl carbon atom with hydrogen and chlorine ions in the act of splitting off. This activated complex will be strongly polar and the high entropies of activation are in accord with this. It is interesting to note that, whereas the energies of activation vary considerably, the entropy is practically the same for each reaction. This constancy of the entropy of activation is to be expected since the strongly polar portion of the activated complex is the same in each case. On the other hand the variation of the energy of activation receives a simple explanation in terms of the dipole effects of the substituent groupings as has been pointed out by Williams and Hinshelwood who find that the equation of Nathan and Watson²⁵

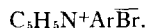
$$E = E_0 \pm c(\mu - \alpha\mu^2)$$

is applicable for these reactions.

²⁴ Bradfield, Jones and Spencer, J. Chem. Soc., 2907 (1931).

²⁵ Nathan and Watson, J. Chem. Soc., 2436 (1933).

Baker and Nathan²⁶ have recently published the results of a study of the reaction between various substituted benzyl bromides and pyridine or α -picoline. The values of $-\Delta S^\ddagger$ calculated from their data vary from 20 to 40 units depending upon the particular reaction and the solvent. These values are similar to those quoted above for the Menshutkin reaction and support the idea that the activated complex has a strongly polar structure possibly of the type suggested by Baker and Nathan



One more point should be emphasized in connection with reactions in which the charge on particular atoms changes during the reaction. If the change in charge occurs before or after the system reaches the activated state then our treatment of the slow process as adiabatic is complete. If the change in charge coincides with and is partly responsible for the slow process (i.e., the potential surface for our reacting system is formed from two surfaces corresponding to different atomic charges, intersecting at the activated state) then a part of the chemical inertia which we have included in the term ΔS^\ddagger should be interpreted instead as a slowness of transition from one surface to the other. In the present state of our knowledge of potential surfaces for reaction in solution a more definitive statement can hardly be made. However, when there is a large overall entropy change for the reactions it is very reasonable to assume that the observed slowness arises simply from the low entropy of the activated state. The possibility that a very slow reaction may be nonadiabatic must not be overlooked. If the apparent entropy of the activated state is as high or higher than would be expected for a similar molecule the reaction is probably adiabatic otherwise it is suspect.

ACID AND BASE CATALYSIS

Another group of reactions of great interest is that included under the general description of acid and basic catalysis. These reactions have been intensively studied of recent years especially in the laboratories of Brønsted and Dawson and an excellent review of their main features is given

²⁶ Baker and Nathan, J. Chem. Soc., 519 (1935).

in an article by Pedersen.²⁷ Brönsted and Pedersen first proposed the relation

$$k' = GK^x$$

where k' is the specific rate constant for a reaction which treats the catalyst as a reactant and where K is the dissociation constant of any acid or base. G and x are independent of the catalyst for a given reaction at a definite temperature. If x is independent of the temperature we have

$$d \ln k'/dT = x \cdot d \ln K/dT + d \ln G/dT \quad (10)$$

and, as ΔH for the ionization of many weak acids with a dissociation constant of about 10^{-5} at room temperature is approximately zero,

$$d \ln k'/dT \sim d \ln G/dT,$$

that is to say the energy of activation is nearly the same for different catalysts. This is shown by the work of Kilpatrick, Pedersen and Smith.^{28, 27} Without introducing this approximation we may write (10) in the form

$$\begin{aligned} (\Delta H^\ddagger/RT - \Delta S^\ddagger/R) \\ = x \cdot (\Delta H/RT - \Delta S/R) - \ln G \end{aligned} \quad (11)$$

and set

$$\Delta H^\ddagger = x \cdot \Delta H - \Delta H_G, \quad (11a)$$

$$\Delta S^\ddagger = x \cdot \Delta S + \Delta S_G, \quad (11b)$$

where ΔH_G and ΔS_G are the energy and entropy components of $\ln G$. Pedersen has shown that in the bromination of acetoacetic ester the above Eq. (11a) for the energy of activation holds quite well using the same x for the various basic catalysts that he employed.

The results of Smith for the iodination of acetone enables us to calculate the values of ΔS^\ddagger given in Table IV. The first three columns are self-

TABLE IV. Iodination of acetone in aqueous solution.

Catalyst	ΔH^\ddagger	$-\Delta S^\ddagger$	$-\Delta S$	$-(10.4 + \Delta S/2)$	P/K^\ddagger
OH_3^+	20,680	10.4	0	10.4	0.021
$\text{Cl}_3\text{CH}_2\text{COOH}$	19,230	16.9	(13.0)	(16.9)	0.025
ClCH_2COOH	19,230	21.2	25.1	23.0	0.016
CH_3COOH	20,010	24.2	30.1	25.4	0.033
$\text{C}_2\text{H}_5\text{COOH}$	19,370	26.7	30.9	26.3	0.011

²⁷ Pedersen, *Den Almindelige syre og Basekatalyse*, Copenhagen 1932.

²⁸ Kilpatrick and Kilpatrick, *J. Am. Chem. Soc.* **53**, 3898 (1931); Smith, *J. Chem. Soc.*, 1744 (1934).

explanatory, the fourth contains the value of the entropies of ionization of the various acids calculated from the data of Harned and Embree.²⁹ To make the data consistent with the assumed formula for hydrogen ion OH_3^+ the usual dissociation constants of all the other acids are divided by 55.5. In column 5 we give the values obtained by adding half the entropy of ionization to the entropy of activation for the hydrogen-catalyzed reaction. Columns 3 and 5 now show a very interesting agreement. Column 6 contains the figures given by Smith for the steric factor (which on the collision theory must be introduced to account for the observed rates) divided by the square root of the dissociation constant. The figures given for dichloroacetic acid in columns 4 and 5 are those required to fit the experimental entropy of activation given in column 3. In the absence of accurate data for the dissociation constant of this acid this value of ΔS may be regarded as a provisional estimate.

It is not necessarily true that x has the same value in Eqs. (11a) and (11b) and it may well be that some of the departures from linearity in the plots of $\log k'$ vs. $\log K$ are due to this cause.

THE BRÖNSTED EQUATION

We have seen that Eq. (6) gives the rate of a reaction in any phase in terms of that in the gas phase. However, in any given solvent it is convenient to employ activity coefficients which are defined with respect to a standard state in that solvent—the infinitely dilute solution—and consequently we will separate the factor $(\alpha_1 \cdots \alpha_n)/\alpha^\ddagger$ into two terms. The first term will represent the distribution coefficient between the standard states for the liquid and gas whereas the second will give the activity coefficient factor in the solvent. We then rewrite Eq. (6) in the form

$$k' = (\kappa \cdot K_0^\ddagger \cdot ((\beta_1 \cdots \beta_n)/\beta^\ddagger)(kT/h)) \cdot (f_1 \cdots f_n)/f^\ddagger. \quad (12)$$

The factor $(f_1 \cdots f_n)/f^\ddagger$ is simply the Brönsted activity factor and the remarkable success in the interpretation of salt effects which has been achieved by application of the Brönsted equation is too well known to require recapitulation here.

²⁹ Harned and Embree, *J. Am. Chem. Soc.* **56**, 1050 (1934).

The above equation goes beyond that of Brönsted in that it provides a theory for the quantity in parenthesis.

The critical complex of Brönsted's theory has been variously interpreted. Brönsted³⁰ himself refers to it as being formed by collisions between the reacting molecules and as decomposing instantaneously into the products, while Bjerrum³¹ treats it as a molecule with a life which is long compared with the duration of a collision. As we have already stated there is no such ambiguity about the description of the activated complex which is simply a molecule in statistical equilibrium with the reactants and which is actually in the act of flying to pieces having a mean life which we can take as h/kT . The fleeting existence of the activated complex might be regarded as making inapplicable the usual rules for activity coefficients and of course for electrically charged complexes we have the problem that whereas the time of relaxation of the ion atmosphere is of the order 10^{-10} second the life of the activated complex is only 1.6×10^{-13} second at ordinary temperatures. However, this apparent difficulty is not real, since the molecules which come together and form the activated complex will be those which are already within one mean free path and will therefore have reciprocally modified their ionic atmospheres in such a way as to make a combined atmosphere approximating to that of the activated complex. The Brönsted activity factor therefore gives a precise description of the behavior of a reaction with changing medium and the activity coefficients involved are purely thermodynamical quantities. Of course, it is true that localization of charges in the activated complex will make its activity coefficient depend upon the ionic strength in some less simple manner than for symmetrical ions, but this problem is not peculiar to reaction rate studies but occurs equally in ordinary equilibria. La Mer and Kamner³² have made accurate measurements on the rate of the reaction between β -bromopropionate and

thiosulphate ions and have found that, on the mechanism they assumed, the activity factor is of opposite sign to that predicted from the Brönsted equation. They suggest as explanation that the localization of the charge on the bromopropionate ion results in an abnormal activity coefficient for the activated complex. Sturtevant³³ has shown that dissymmetry of the field does not affect the validity of the Debye-Hückel limiting equation for activity coefficients and, since we have shown that the same considerations are valid for the activated complex as for ordinary molecules, we conclude that, if the results of La Mer and Kamner are as accurate as they appear, some other mechanism must be sought for this reaction.

The present theory of rates reduces the problems of kinetics to a thermodynamic calculation of an equilibrium constant for the activated complex and the calculation of a transmission coefficient which is frequently very near unity. The principal problems are thus seen to be those always met in calculating an entropy and a heat of reaction. The difficulties in the simple kinetic picture are thus seen to disappear when viewed in the light of the general theory.

One of us (W. F. K. W-J) is indebted to the Leverhulme Trustees for a fellowship and to the University of Reading for leave of absence.

Note added in proof: Of the two definitions for the equilibrium constant used here and in the previous article¹ Evans and Polanyi (Trans. Faraday Soc. **21**, 875 (1935)), in a paper which has appeared while this article was in press have employed the one which requires multiplication by the velocity normal to the energy barrier (and of course the transmission coefficient κ) to give the absolute rate. We also have chosen this definition for processes (such as vaporization or adsorption) where the energy barrier is localized between two phases. For processes inside a single phase we use the definition for which the equilibrium constant must be multiplied by the frequency kT/h and the transmission coefficient κ to give the absolute rate. This difference in choice of the equilibrium constant is a formal one which will be ultimately decided on the basis of utility.

Our value of $5T^\ddagger = 87$ at room temperature (see Eq. (7)) for the apparent ratio of bimolecular collisions in the liquid to the gaseous state agrees with their factor of about 100.

³⁰ Brönsted, *Zeits. f. physik. Chemie* **102**, 109 (1922); **115**, 337 (1925).

³¹ Bjerrum, *Zeits. f. physik. Chemie* **108**, 82 (1924).

³² La Mer and Kamner, *J. Am. Chem. Soc.* **53**, 2832 (1931).

³³ Sturtevant, *J. Chem. Phys.* **3**, 295 (1935).