

*Recent Advances in the Theory of Reaction Kinetics in Solution.*

TILDEN LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY ON DECEMBER 17TH, 1942.

By R. P. BELL.

A LARGE part of the work which has been done on reaction velocities in solution has been concerned with the use of kinetic measurements for obtaining information about the physical or chemical constitution of solutions, or the mechanism of reactions. For example, the evidence for the classical theory of electrolytic dissociation depended to a considerable extent on measurements of the velocity of hydrolysis of esters and the inversion of cane sugar, and more modern views on the nature of electrolyte solutions have received valuable support from the work of Brønsted and his school on reaction kinetics in solution. From a rather different point of view, measurements of kinetic order have often been used to tell us something about the consecutive steps of complicated reactions, only one of which normally determines the observed velocity. In recent years this kind of analysis has proved very fruitful in the hands of Ingold and his collaborators for investigating the mechanism of many of the reactions of organic chemistry, especially in relation to modern electronic theory.

In all these cases the reaction velocities are used primarily as a tool for obtaining useful information, and until fairly recently few workers in this field attempted to develop a theory which would account for the absolute values of the observed velocities for different reactions and different solvents. As has been recently pointed out by Polanyi,<sup>1</sup> indifference to this aspect of the subject seems to have been almost deliberate in some quarters. However, during the last ten years there has been a determined attack on the fundamental problems of reaction velocities in solution, both on the theoretical and on the experimental side. In this lecture I shall try to show how far this attack has succeeded.

For a long time the theoretical approach was confined almost entirely to gas reactions, which was understandable in view of the successes of the kinetic theory of gases, and the failure of attempts to account for the properties of liquids along similar lines. The reason for modern departures from this conservative attitude was originally probably an experimental one, as it was soon found that the simplicity of gas reactions was more apparent on paper than in the laboratory. Very few gas reactions are wholly free from both chain reactions and surface reactions, and even in the absence of these complications it is often found that the kinetic order of the reaction is not a simple integral one, but varies, for example, between the first and the second order. In solution, on the other hand, surface and chain reactions are very rare, and almost all reactions follow accurately, either first- or second-order kinetics, unless there are chemical reasons for departures.

On the theoretical side, the fear of complications in solution has rested to some extent on misapprehensions. Although our general knowledge of the liquid state is still very incomplete, many of the difficulties involved are irrelevant when dealing with reactions between solute molecules in fairly dilute solutions. In this there is a close analogy with the thermodynamic properties of solutions, where the behaviour of solutes is frequently just as simple as that of gases at comparable concentrations, even in solvents such as water which themselves exhibit complex properties. Modern theories of solution have concentrated particularly on deviations from such simple behaviour, and the success of some of these theories (notably the Debye-Hückel treatment of electrolytes) may have resulted in a tendency to ascribe too great an importance to such deviations in general. Moreover, the use of reactants showing abnormal thermodynamic behaviour by no means always entails corresponding kinetic complications. For example, in reactions between an ion and a neutral molecule the simple kinetic law of mass action is obeyed up to concentrations where the thermodynamic behaviour of electrolytes is far from ideal.<sup>2</sup> The same state of affairs occurs in reactions between non-electrolytes: thus the reaction between acetic anhydride and ethyl alcohol in benzene solution is a simple bimolecular reaction over a concentration range in which the apparent degree of association of the alcohol (derived from freezing-point measurements) doubles itself.<sup>3</sup> Only in reactions between ions are deviations from simple kinetic behaviour of primary importance, and even in this case they can be largely avoided by working in very dilute solution, or by maintaining a high and constant salt concentration. The high accuracy and reproducibility of kinetic measurements in solution has made it possible to investigate special phenomena such as salt effects, and consecutive or reversible reactions showing complicated kinetics, a circumstance which may sometimes have obscured the large amount of simple kinetic material available for theoretical interpretation.

Before dealing with the different methods of theoretical approach, it is convenient to summarise the experimental material which has to be accounted for.<sup>4</sup> I shall deal only with second-order reactions, since it is only in this case that significant progress has been made. All theoretical treatments involve the temperature dependence of the reaction velocity, and almost all the experimental data have been analysed in terms of the simple Arrhenius equation

$$k_2 = Ae^{-E/RT}$$

where  $k_2$  is the bimolecular velocity constant,  $E$  the activation energy, and  $A$  the collision factor.  $E$  has the dimensions of energy, and is usually expressed in kilogram-calories per gram-molecule.  $A$  has the same dimensions as  $k_2$ , *i.e.*, (concentration)<sup>-1</sup> (time)<sup>-1</sup>, and different authors express it in different units. We shall take the concentration in moles per litre and the time in seconds. In using the above equation it is commonly assumed that both  $A$  and  $E$  are independent of temperature, and we shall see later that this is only true as a first approximation. However, theory indicates that it is likely to be a fairly good approximation, and this is

borne out by the experimental data, which are rarely sufficiently accurate to detect any temperature variation of these quantities. The simple assumption is certainly adequate for the broad generalisations which will form the chief subject of this lecture.

The experimental values of  $E$  cover a wide range (about 7—40 kg.-cals./mole), and do not show any general correlation with the type of reaction or solvent. More theoretical interest attaches to the absolute value of the constant  $A$ . The data do not at first sight appear to encourage any generalisations, since in the units which we have chosen  $A$  varies over the range  $10^2$ — $10^{19}$ : moreover, the values do not, as was at one time supposed, fall into a few narrow categories, but are distributed over the whole range. However, when reactions are divided into classes, the following rough generalisations emerge:

*Reactions between two uncharged molecules.* (a) Most organic reactions have  $A = 10^2$ — $10^7$ , with considerable variations from one solvent to another. (b) A few reactions involving non-polar reactants and products have  $A = 10^7$ — $10^{11}$ , independent of the solvent.

*Reactions between an ion and an uncharged molecule.* (c) Most reactions of this class have  $A = 10^9$ — $10^{11}$ , varying little with the solvent.

*Reactions between two ions.* (d) For ions of opposite charge,  $A = 10^{13}$ — $10^{19}$ . For ions of like charge  $A = 10^2$ — $10^8$ . In each case the deviation from  $A = 10^{11}$  increases with increasing valency of the reacting ions.

The reactions under (a) include those of organic halides with bases to give salt-like products (*e.g.*, the Menschutkin reaction), substitution in aromatic compounds by uncharged reagents, and catalysis by uncharged acids and bases. Class (b) includes the small number of reactions which have been studied both in the gas phase and in solution, *e.g.*, polymerisation reactions of unsaturated hydrocarbons, and a few typical gas reactions like the decomposition of ozone and chlorine monoxide.<sup>5</sup> Class (c) includes the large number of reactions in which an organic halide reacts with an anion in solution, and also the many reactions catalysed by hydrogen or hydroxyl ions, or other charged acids and bases. Almost all the reactions for which data are available fall into one of the above classes.

There are two types of theoretical treatment which have been used to explain the values of  $A$  summarised in the above table, and although their essential unity is gradually becoming more apparent, it is still convenient to treat them separately.<sup>6</sup> In the simple form of the *collision theory* the velocity expression is written in the form

$$k_2 = PZe^{-E/RT}$$

$Z$  is the kinetic theory collision number arrived at by assigning definite radii to the reacting molecules: in the units we have chosen it will always be of the order of magnitude  $10^{11}$  at ordinary experimental temperatures. The Boltzmann factor  $e^{-E/RT}$  gives the fraction of colliding pairs which will possess sufficient energy to lead to reaction, and  $P$  is the factor expressing the probability that other conditions (such as the favourable orientation of the colliding molecules) will be fulfilled. In the *transition state theory* attention is focused on the state of lowest probability through which a pair of molecules pass during the process of reaction, and this state,  $X$ , is termed the transition state or the critical complex. It is then possible to express the reaction velocity in terms of the equilibrium constant  $K$  for the equilibrium  $A + B \rightleftharpoons X$ . The expression for the bimolecular velocity constant  $k_2$  is

$$k_2 = \frac{1}{2}Kv$$

where  $v$  is a thermal velocity which will not vary greatly from one reaction to another. (Other apparently different formulations are possible, but are equivalent to the above equation.)  $K$  is formally related to the free energy of activation  $F$  by the equation  $RT \log K = F$ , and if  $F$  is split up into an energy and an entropy term by the usual equation  $F = E - TS$ , the equation for the velocity becomes

$$k_2 = \frac{1}{2}ve^{S/R}e^{-E/RT}$$

$v$  and  $S$  can be calculated in principle by the methods of statistical mechanics, though the information needed for this calculation is equivalent to that needed to predict  $P$  and  $Z$ , and is not available in our present state of knowledge. The derivation of all the above equations indicates that  $P$ ,  $Z$ ,  $v$ , and  $S$  will all vary only slowly with the temperature, thus agreeing to a first approximation with the simple Arrhenius equation. On the other hand, some caution is necessary in identifying values of  $A$  and  $E$  obtained by applying the Arrhenius equation to experimental data with those occurring in more exact expressions, since barely detectable deviations from the Arrhenius equation may cause considerable discrepancies between the two sets of values.<sup>7</sup>

Much has been written recently about the comparative status and usefulness of these two theories, and I shall make no attempt to go into the question here, especially as the controversial element in these discussions has largely disappeared. It may, however, be of interest to mention my own attitude as far as practical procedure is concerned. In attempting to account qualitatively for a new kinetic phenomenon I should think first along the lines of the collision theory, but having found a possible explanation I should check it by considering the same problem in the light of the transition state theory. Moreover, if and when data became available for a quantitative treatment, I should use the equations of the transition state theory. However, at present a semi-quantitative treatment is the most which can be attempted, and the use of both methods will be illustrated in the following discussion.

The meagre experimental data for homogeneous bimolecular gas reactions give values of  $A = 10^9$ — $10^{11}$  for simple molecules, falling to  $10^7$ — $10^8$  for a few reactions between complex molecules. From the point of

view of the collision theory this corresponds to  $P$  values of  $10^{-2}$ —1 for simple molecules and  $10^{-4}$ — $10^{-3}$  for complex ones, values which are quite plausible from a geometrical point of view. If the reaction takes place in solution instead of in the gas, the position will be modified to some extent by the interaction between the solvent and the reacting system, which will be at a minimum when the reacting molecules and the transition state are both of low polarity. In this case the effect of the solvent may be pictured merely as a kind of physical interference, and the value of  $P$  will be the same in solution as in the gas phase. On the other hand, the collision number  $Z$  should be somewhat greater in solution than in the gas, since the free space between the solvent molecules is less than the total volume of the solution. An exact evaluation of this free space factor would demand a much more exact knowledge of the structure of liquids than we yet possess, but various idealised models indicate that  $Z$  should be increased by a factor not exceeding 4.<sup>8</sup>

This conclusion agrees with experiment for the class of reactions (b) above, where the range of  $A$  values,  $10^7$ — $10^{11}$ , is the same as for the bimolecular gas reactions. In these reactions not only are the reactants of low polarity, but the probable mechanisms involve only the making and breaking of homopolar bonds, without any considerable separation of charge at any stage. Direct comparison of  $A$  values in the gas phase and in solution has rarely been possible, and the only data of any accuracy are those of Wassermann<sup>9</sup> on the dimerisation of cyclopentadiene in the gas phase and 8 different solvents. The values of  $A$  were identical within the experimental error, *i.e.*, they did not differ by a factor of more than 3. Further interesting evidence is obtained from the conversion of para- into ortho-hydrogen, catalysed by oxygen or nitric oxide.<sup>10</sup> This catalysis is not chemical in nature, but depends on the paramagnetic properties of the oxygen or nitric oxide molecules. Only a small fraction of the collisions between the para-hydrogen and the paramagnetic molecules result in conversion, but this fraction is independent of temperature (*i.e.*, does not involve an energy of activation) and would be expected theoretically to be unaffected by the presence of the solvent. Experiment shows that the conversion takes place 1.2—2 times as fast in aqueous solution as in the gas phase, from which it can be safely concluded that the collision numbers on the two phases are in approximately the same ratio.

The transition state theory arrives at the same result for reactants of low polarity, though by an apparently less direct route. For gas reactions, if the two reactants A and B are pictured as structureless spheres of known radii, statistical mechanics can be used to calculate the entropy change in forming the complex X. When this is substituted in the equation for the reaction velocity the resulting expression is identical with that of the collision theory, if  $P$  is put equal to 1. When the actual structure of the colliding molecules is taken into account it is still possible to write down the expressions for  $S$  and  $v$ , but they now contain a number of distances and frequencies which can only be estimated roughly. However, the formation of X from complex molecules A and B will always involve the conversion of some rotational degrees of freedom into vibrational ones, and it can be shown that this circumstance will make the term  $e^{+S/R}$  smaller than it is for the idealised spherical molecules. This reduction may amount to several powers of 10, and will appear in the factor  $A$  of the Arrhenius equation, thus agreeing with the experimental results for complex molecules in the gas phase.<sup>11</sup> Just as in the collision theory, the effect of the solvent can be calculated from first principles only by making simplifying assumptions about the structure of the solvent. If the only effect of the solvent is to reduce the space available to a fraction  $\sigma$  of the whole volume, this will increase the entropy change  $S$  by an added term  $-R \log \sigma$ , since in the reaction  $A + B \rightarrow X$  the number of molecules decreases by one.  $v$  will be unaffected by the presence of the solvent, so that the collision factor  $\frac{1}{2}ve^{+S/R}$  is increased by a factor  $\sigma$ , just as before. There is also an alternative procedure, which does not make use of any model of the liquid state, but estimates the effect of the solvent upon  $S$  from experimental data on the entropy of solution of non-polar molecules in general.<sup>12</sup> This method, when correctly applied,<sup>13</sup> predicts that the factor  $A$  will be 2—3 times greater in solution than in the gas, in excellent agreement with the conclusions already reached.

The interaction between solvent and solute is often too intimate to be described in terms of a free-space factor, and this is particularly so in the case of ions. Apart from the possibility of chemical solvation, the powerful electrostatic field will tend to orient solvent molecules round the ion, and this may be expected to modify the simple behaviour described above. It therefore seems at first sight surprising that reactions between an ion and an uncharged molecule [class (c) above] have  $A = 10^9$ — $10^{11}$ , *i.e.*, the same as for a bimolecular gas reaction between simple molecules. However, it is important to realise that the significant factor in determining the reaction velocity is not the actual extent of the solute-solvent interaction, but the extent to which this interaction changes when the two reactants collide to form the transition state. If one of the reactants is charged and the other uncharged, the reacting system will have the same net charge throughout the process of forming the transition state, and to a first approximation there will be no change in solvation. The solvent thus plays no direct part in the collision process, and contributes nothing to the entropy change in the process  $A^+ + B \rightarrow X^+$ . Hence according to both collision theory and transition state theory the collision factor should be little affected by the solvent, as is found experimentally.

There are, however, many cases in which the reaction process involves a change in the extent of solvation, and it is in fact changes of this kind which are usually invoked to explain all the major differences between gas and solution kinetics.<sup>14</sup> As an example we may consider the reaction between two ions of opposite charges,  $A^+$  and  $B^-$ . Before reaction, both ions will be solvated, but when they come together the collision complex formed will have zero net charge, and will therefore be solvated to a much smaller extent. In this case, therefore, the formation of the transition state involves the de-solvation of a number of solvent molecules, and it is necessary to include these solvent molecules in any theoretical considerations about the reaction

velocity. From the point of view of the transition state theory this means that the equilibrium to be considered is not simply  $A^+ + B^- \rightleftharpoons X$ , but  $AS_m^+ + BS_n^- \rightleftharpoons X + (m+n)S$ , where  $S$  is a solvent molecule. When a solvent molecule becomes detached from the ion, it exchanges vibrational and librational movement for translation and rotation, and passes from a state of comparative order into one of comparative disorder. This decrease of order is accompanied by an increase of entropy, and the effect of the solvent is thus to make the term  $e^{+S/R}$  greater than it would be in the absence of solvent. This agrees with the experimental finding that reactions between oppositely charged ions have  $A$  greater than  $10^{11}$ .

Statistical mechanics gives expressions for the entropy of desolvation, which could be evaluated if the distances and force constants of the solvated ion were known, as well as the structure of the solvent. Although this is not possible, the observed values of  $A$  up to  $10^{19}$  can be accounted for on the basis of plausible assumptions. It should be pointed out that the increase of entropy associated with desolvation can easily be understood qualitatively without recourse to a detailed treatment. The energy levels predicted by the quantum theory for a molecular vibration are fairly far apart, whereas for rotation they are considerably closer together, and for translation they are so close together that they cannot be directly detected. A change in which vibrations are converted into rotation and translation therefore produces a large increase in the number of energy levels which are available within a given energy range, and thus increases the probability (or entropy) of the system. The simplest application of this principle is, of course, in the equilibrium between a diatomic molecule and free atoms,  $A_2 \rightleftharpoons 2A$ , where one degree of freedom of vibration and two of rotation are converted into three translational degrees of freedom. For this reason the ratio (atoms)/(molecules) is much greater than the Boltzmann factor  $e^{-Q/RT}$ ; *i.e.*, the dissociation into atoms is accompanied by an increase of entropy.

It would seem at first sight that the collision theory could never account for values of  $A$  considerably greater than  $10^{11}$ , since if the factor  $P$  is taken to represent additional restrictions due to orientation, it must be less than unity. However, the actual collision which takes place is between two unsolvated ions, and not between the original solvated reactants. In order to calculate the number of these collisions it is necessary to consider first the equilibrium between solvated and unsolvated ions, where the effect of the entropy change will again be apparent.

It is also possible for the formation of the transition state to be accompanied by an *increase* of solvation, and this is the case for a large number of reactions between unchanged molecules. In many of these the products of reaction are ionic, for example in the Menshutkin reaction  $R_3N + RI \longrightarrow [R_4N]^+[I]^-$ , and many analogous reactions between an organic base and a halogen compound. The transition state in these reactions, although not bearing any net charge, is likely to involve a considerable separation of charge, with the production of a dipole. It will therefore have a more powerful external field than the reacting molecules separately, and will orient more solvent molecules. The low values of  $A$  observed for this type of reaction are undoubtedly connected with this increase of solvation.<sup>15</sup> From the point of view of the transition state theory the problem is just the converse of that mentioned above: conversion of rotation and translation into vibration involves an increase of order, a decrease of entropy, and hence a low value for  $e^{+S/R}$ . In the collision picture the act of reaction involves not only the collision and orientation of the two reactant molecules, but also the simultaneous presence and orientation of a number of solvent molecules, which naturally reduces the steric factor  $P$ .

When two uncharged molecules react, the formation of a transition state of high polarity is not confined to those reactions in which the final products are ions. A large proportion of the reactions of organic chemistry are now believed to take place by an ionic mechanism; *i.e.*, the electronic displacements involved in the reaction process resemble those which would lead to the formation of ions, though actual free ions need not be formed either as final products or at any intermediate stage.<sup>16</sup> These reactions will have a transition state of higher polarity than the initial reactants, and low values of  $A$  are to be expected. This is in fact the case for the great majority of reactions between uncharged molecules [group (a) above], most of the exceptions being the few "typical gas reactions" already mentioned, where the reaction mechanism is not believed to be ionic. An interesting single exception is the reaction of lead tetra-acetate with glycols, where an  $A$  value of approximately  $10^{11}$  is coupled with independent evidence that the reaction mechanism involves free radicals rather than ions.<sup>17</sup>

Since the orientation of solvent round the polar transition state constitutes an unfavourable factor for the completion of the reaction, it might be asked why reactions of this type do not take place without the occurrence of solvation, thus removing the reasons for a low value of  $A$ . However, the co-operation of the solvent affects not only the value of  $A$ , but also the value of  $E$ , and in the present case the orientation of the solvent decreases the energy necessary to produce the charge separation in the critical complex. The effect of solvation is therefore to decrease  $A$  but to increase  $e^{-E/RT}$ , and in practice the latter effect usually appears to be the greater, thus favouring the reaction mechanism involving solvation. Correspondingly it is found that the velocity of this type of reaction varies considerably from one solvent to another, the variation involving both the  $A$  and the  $E$  factor. If the solvent used is of low polarity, the addition of small concentrations of a polar substance often has a marked effect on both  $P$  and  $E$ .<sup>18</sup> This polar substance may in some cases be one of the reactants or the products, in which case the reaction will not follow simple kinetics.<sup>19</sup> The accelerating effect of polarisable material appears particularly clearly when attempts are made to study reactions of this type in the gas phase. It is invariably found that any homogeneous reaction which may be taking place is completely obscured by a much faster wall reaction, the energy necessary to produce the polar transition state being presumably lowered by the proximity of the material of which the reaction vessel is made.<sup>20</sup>

A semi-quantitative treatment resembling that already given shows that reactions between ions of like charge also involve a transition state which is solvated to a greater extent than the initial reactants, thus explaining the experimental values of  $A \sim 10^{11}$ . The general problem of reactions between ions can also be approached from an electrostatic standpoint, the solvent being regarded as a uniform medium of dielectric constant  $D$ . This leads to the equation

$$\log P = (z_1 z_2 e^2 / k r D^2) \cdot dD/dT$$

where  $e$  is the electronic charge,  $r$  the distance of closest approach of the reacting ions, and  $z_1$  and  $z_2$  the algebraic valencies of the ions. ( $P$  is the "experimental" value obtained by applying the simple Arrhenius equation to the experimental data. In principle it will vary slightly with temperature, but the variations will normally be too small to detect by experiment.) For polar solvents  $dD/dT$  is negative, and this treatment therefore predicts  $P < 1$  for reactions between ions of like charge and  $P > 1$  for reactions between ions of opposite charge. This is of course in agreement with experiment, and the experimental values of  $P$  can be accounted for by assuming plausible values for the distance  $r$ .<sup>21</sup> At first sight this method of treatment appears to bear no relation to the one given above, which appeals to changes in the orientation of solvent molecules. However, this orientation presupposes that the solvent molecules have a dipole moment, and it is the dipole moment which determines the magnitude of the factor  $dD/dT$  in the above equation: hence the two methods have essentially the same physical basis, in spite of their apparent diversity.

The electrostatic treatment can also be formally applied to reactions involving uncharged molecules, giving an equation which involves the dipole moments and radii of the reactants and of the transition state.<sup>22</sup> However, the dipole moment of the transition state is not known, and the radii enter the equation to the third power, so the treatment does not yield anything of quantitative value. Qualitatively it agrees with experiment and with the orientation picture in predicting  $P < 1$  for reactions with a transition state of high polarity.

It is of interest now to consider the reasons why reactions in solutions have proved in many respects more tractable than reactions in gases, both from an experimental and from a theoretical point of view, in spite of the additional complications introduced by the presence of the solvent. The almost complete absence of surface reactions is easily explained, since the solvent molecules, present in very large numbers, are likely to have the monopoly of adsorption on any surfaces which are present. Similarly, a chain reaction is unlikely to occur, since the usual chain carriers, atoms or free radicals, are likely to react with a solvent molecule before they are able to continue the chain by meeting another solute molecule. Much more important, however, is the rôle of the solvent molecules in maintaining the equilibrium distribution of energy among the reacting molecules. This distribution is bound to be disturbed to some extent by the reaction process, which removes molecules having an abnormally high energy, or an unusual distribution of energy among different internal degrees of freedom. Whether or not this disturbance is appreciable depends upon the rate at which the equilibrium distribution is re-established by the transfer of energy by collision, or among internal degrees of freedom. In gas reactions collisions are relatively rare, and the reaction velocity may be considerably affected by the rate at which energy is transferred, thus leading to apparent reaction orders between 1 and 2. In solution, on the other hand, the molecules of the reactant are colliding very frequently with solvent molecules, and it is probably safe to assume that there are no appreciable deviations from the equilibrium distribution. This assumption is in fact made, explicitly or implicitly, in all the theoretical considerations so far advanced. This is obvious in the case of the transition state method, which applies primarily only to a system in complete equilibrium, *e.g.*,  $A + B \rightleftharpoons X \rightleftharpoons C + D$ . Its application to observed velocities in systems not at equilibrium assumes that the velocity constants do not depend on the distance from equilibrium. It is perhaps not always realised that the equations of the simple collision theory are equally dependent on an equilibrium distribution, since expressions like  $e^{-E/RT}$  are derived on the assumption of statistical equilibrium. The success of the general survey given above thus provides a further reason for supposing that equilibrium considerations are adequate for treating reaction velocities in solution. It should, however, be mentioned that many of the points already dealt with can be given an alternative explanation by assuming that the transfer of energy is a rate-determining factor.<sup>23</sup> The question cannot be regarded as definitely settled, but the non-equilibrium explanation seems unlikely in view of the frequent collisions with solvent molecules, and the many points of analogy between kinetic and thermodynamic data for reactions in solution.<sup>24</sup>

We have just seen that any deviations from equilibrium energy distribution are likely to be much less important in solution reactions than in gas reactions. The act of reaction will also tend to disturb the equilibrium spatial distribution of the reacting molecules, since it removes pairs of molecules which are close together, and it can easily be seen that this disturbance will be more serious in solution than in the gas phase. The production of fresh colliding pairs depends on the rate at which distant molecules can move towards each other, and this movement will be obstructed by the presence of solvent molecules. Under extreme conditions this process may not take place fast enough to maintain the equilibrium number of colliding pairs, and the reaction rate will then be partly controlled by the rate of diffusion through the solvent.<sup>25</sup> Such a state of affairs will arise if the viscosity is high, or if a large proportion of the collisions lead to reaction, *i.e.*, if the activation energy is low. It should be noted that this conclusion does not conflict with the previous statement that the collision number in solution does not differ greatly from that in the gas. In the absence of any reaction the total number of collisions is not much affected, but the presence of the solvent molecules causes them to occur in groups, so that when two solute molecules meet they are likely to collide a large number of times before part-

ing company.<sup>26</sup> It is because of this grouping that the removal of molecules by reaction may cause the collision number to fall below its equilibrium value.

Fortunately, rough calculations show that the lowering of the equilibrium collision number will not be appreciable in ordinary bimolecular reactions in solution. If  $E = 20$  kg.-cals., the viscosity would have to approach that of the vitreous state before deviations became important, and for media of ordinary viscosity  $E$  would have to be less than 2 kg.-cals.<sup>27</sup> This last value corresponds to a bimolecular reaction much too fast to be observed. There are, however, some observable phenomena in which a large proportion of collisions are effective, notably the coagulation of colloids under certain conditions,<sup>28</sup> and the quenching of fluorescence by solute molecules.<sup>29</sup> In both these cases the velocity should depend on the number of collision groups, rather than on the total number of collisions, and it is in fact found experimentally that the viscosity of the medium is an important factor. It should be emphasised that this class of phenomenon cannot be treated by the transition state theory. It is necessary to consider a kinetic picture of the collision process, taking into account the way in which the solvent modifies the simple picture used for gas reactions.

This lecture has been concerned chiefly with the general way in which reaction velocities in solution can be accounted for theoretically. Quantitative predictions are in most cases out of our reach at present, but there are a few points of detail on which notable success has been achieved, chiefly by using the transition state theory and by making use of the close relation which it indicates between kinetic and thermodynamic properties. I shall do little more than mention some of them here. The most notable instance is the primary salt effect in reactions between ions, which in dilute solutions can be quantitatively predicted by applying the Debye-Hückel theory. The correct expressions were given first by Brönsted in 1921, but during the following ten years there was much dispute about their theoretical basis.<sup>30</sup> The transition state theory composes these differences of opinion, and brings the problem into close relation with the secondary salt effect, *i.e.*, the effect of ionic concentration on the dissociation of a weak electrolyte.<sup>31</sup> The same kind of treatment can be extended to the effect of the dielectric constant on the velocity of ionic reactions,<sup>32</sup> the effect of salt concentration and dielectric constant on reactions involving dipole molecules,<sup>33</sup> and the effect of pressure on reaction kinetics in solution.<sup>34</sup> In all these cases, however, the resulting expressions involve unknown properties of the transition state, *e.g.*, its size and charge distribution, so no quantitative prediction is possible. It is more useful in these cases to regard the study of these different effects as a means of measuring the properties of the transition states in different reactions, with the ultimate aim of defining them as closely as we can stable molecular species.

In conclusion, I should like to mention three problems which have attracted a good deal of attention, but which are still far from being solved. When a reaction is studied in a series of solvents it is frequently found that the factors  $A$  and  $E$  of the Arrhenius equation change in a parallel manner. The transition state theory connects this behaviour in a natural manner with the parallelism between heats and entropies of solution which is found experimentally in many cases. In neither case, however, can any satisfactory molecular explanation be given.<sup>35</sup> Similarly, relations are often found to exist between reaction velocities and equilibrium constants in related series of reactions, corresponding to relations between free energies of activation and free energies of reaction. Examples of this kind of relation are the Brönsted equation for catalysis by a series of acids or bases, and the Tafel relation for over-voltage. In these cases it is possible to obtain a plausible explanation in terms of molecular potential-energy curves, but the detailed working out of this picture is far from satisfactory.<sup>36</sup> Finally, a strict theoretical treatment indicates that the observed activation energy should vary slightly with temperature, just like the energy of reaction in a chemical equilibrium.<sup>37</sup> At present there are very few pieces of experimental work in which this variation can be estimated, or even detected with certainty. Further work along these lines should give valuable information about the modes of vibration and rotation of the transition state, and the possibility of the kind of non-classical behaviour known as the "tunnel effect."<sup>38</sup>

The Tilden lectures are supposed to deal with recent advances in some branch of chemistry, and I may seem to have transgressed this requirement by attempting to give a complete survey of the theory of reaction kinetics in solution. My excuse must be the very rapid growth of the subject, and in fact almost every piece of work which I have mentioned has been done during the last ten years. It may also have been noticed that I have mentioned very few names in the course of the lecture. This is because a large number of workers in different countries have made significant contributions to the subject, and it is impossible to pick out one or two as specially worthy of mention. The recent history of this subject provides a very good example of the efficiency of unplanned collaboration, and several of the advances have been due to contributions from apparently irrelevant sources. Another ten years of work will inevitably fill out and modify many of the details, but I believe that the general outlines of the subject are now sufficiently well established to justify an attempt to review the position at this stage.

<sup>1</sup> *Nature*, 1942.

<sup>2</sup> Brönsted, *Chem. Rev.*, 1928, **5**, 231.

<sup>3</sup> Soper and Williams, *J.*, 1931, 2297.

<sup>4</sup> Cf. Hinshelwood and Winkler, *J.*, 1936, 371.

<sup>5</sup> For references see Bell, *Ann. Reports*, 1939, **36**, 86.

<sup>6</sup> Cf. discussions in *J.*, 1937, 629, and *Trans. Faraday Soc.*, 1938, **34**, 1—267.

<sup>7</sup> Bell, *ibid.*, p. 232.

<sup>8</sup> Jowett, *Phil. Mag.*, 1929, **8**, 1059; Rabinowitch, *Trans. Faraday Soc.*, 1937, **33**, 1224; Fowler and Slater, *ibid.*, 1938, **34**, 91; Bell, *ibid.*, 1939, **35**, 324.

- <sup>9</sup> *Nature*, 1936, **137**, 496; 1937, **138**, 368; 1937, **139**, 669; J., 1936, 1028; 1939, 870; *Trans. Faraday Soc.*, 1938, **34**, 128.
- <sup>10</sup> Farkas and Sachsse, *Z. physikal. Chem.*, 1933, B, **23**, 1; Farkas and Garbatski, *Trans. Faraday Soc.*, 1939, **35**, 263.
- <sup>11</sup> Evans and Polanyi, *ibid.*, 1936, **32**, 1333.
- <sup>12</sup> Evans and Polanyi, *ibid.*, 1935, **31**, 875; Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, **3**, 492.
- <sup>13</sup> Bell, *Trans. Faraday Soc.*, 1939, **35**, 324.
- <sup>14</sup> Wynne-Jones and Eyring, *loc. cit.* (12).
- <sup>15</sup> Ogg and Rice, *J. Chem. Physics*, 1937, **5**, 140.
- <sup>16</sup> Cf. Watson, *Ann. Reports*, 1938, **35**, 208.
- <sup>17</sup> Criegee, Kraft, and Rank, *Annalen*, 1933, **507**, 159; Waters, J., 1939, 1805; Bell, Sturrock, and Whitehead, J., 1940, 82.
- <sup>18</sup> Williams and Hinshelwood, J., 1934, 1079; Fairclough and Hinshelwood, J., 1937, 1573.
- <sup>19</sup> Moelwyn-Hughes and Hinshelwood, J., 1932, 231; Pickles and Hinshelwood, J., 1936, 1353; Edwards, *Trans. Faraday Soc.*, 1937, **33**, 295; Holzschmidt and Potapov, *Acta Physicochim. U.R.S.S.*, 1937, **7**, 778.
- <sup>20</sup> Bell and Burnett, *Trans. Faraday Soc.*, 1939, **35**, 208.
- <sup>21</sup> Moelwyn-Hughes, *Proc. Roy. Soc.*, 1936, A, **155**, 308; LaMer and Kamner, *J. Amer. Chem. Soc.*, 1935, **57**, 2662.
- <sup>22</sup> Moelwyn-Hughes and Sherman, J., 1936, 101.
- <sup>23</sup> Hinshelwood, *Trans. Faraday Soc.*, 1936, **32**, 970; Edwards, *ibid.*, 1937, **33**, 295.
- <sup>24</sup> Evans and Polanyi, *ibid.*, 1936, **32**, 1333.
- <sup>25</sup> Leontovitch, *Z. Physik*, 1928, **50**, 58.
- <sup>26</sup> Rabinowitch and Wood, *Trans. Faraday Soc.*, 1936, **32**, 1381; Rabinowitch, *ibid.*, 1937, **33**, 1225; Fairclough and Hinshelwood, J., 1939, 593.
- <sup>27</sup> Evans and Polanyi, *loc. cit.* (24).
- <sup>28</sup> Smoluchowski, *Physikal. Z.*, 1917, **17**, 594; *Z. physikal. Chem.*, 1917, **92**, 129.
- <sup>29</sup> Wawilow, *Z. Physik*, 1929, **53**, 665; Franck and Wawilow, *ibid.*, 1931, **69**, 100; Svesnikov, *Acta Physicochim. U.R.S.S.*, 1935, **3**, 257; 1936, **4**, 453; 1937, **7**, 755; Bowen, *Trans. Faraday Soc.*, 1939, **35**, 15.
- <sup>30</sup> Cf. Bell, *Ann. Reports*, 1934, **31**, 67.
- <sup>31</sup> Wynne-Jones and Eyring, *loc. cit.* (12).
- <sup>32</sup> See Davis and LaMer, *J. Chem. Physics*, 1942, **10**, 585, for references to earlier papers.
- <sup>33</sup> Moelwyn-Hughes, *loc. cit.* (21); Laidler and Eyring, *Ann. New York Acad. Sci.*, 1940, **39**, 303; Amis and Jaffe, *J. Chem. Physics*, 1942, **10**, 599.
- <sup>34</sup> Perrin, *Trans. Faraday Soc.*, 1938, **34**, 144.
- <sup>35</sup> Bell, *ibid.*, 1937, **33**, 496; Hinshelwood, *ibid.*, 1938, **34**, 138.
- <sup>36</sup> Bell, "Acid-Base Catalysis," Chap. VIII (Oxford, 1941).
- <sup>37</sup> Scheffer and Brandsma, *Rec. Trav. chim.*, 1926, **45**, 522; Brandsma, *ibid.*, 1928, **47**, 94; 1929, **48**, 1205; LaMer, *J. Chem. Physics*, 1933, **1**, 289.
- <sup>38</sup> Bell, *Proc. Roy. Soc.*, 1935, A, **148**, 241; Hirschfelder and Wigner, *J. Chem. Physics*, 1939, **7**, 616.
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