

## 89. On Bimolecular Reactions in Solution.

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To a high degree of approximation, the rate of chemical reactions is represented by the Arrhenius equation, which, for our present purpose, is best written in the form : number of molecules reacting =  $PZe^{-E/RT}$ ,  $Z$  being the collision number, and  $P$  a factor independent of temperature. The interpretation of  $P$  has been the subject of much experiment and theory. The study of gas reactions revealed the existence of a considerable number of cases where  $P$  approaches unity, thus providing a form of behaviour where activation is not only necessary but also sufficient for reaction. The mechanism of the first-order decomposition of complex organic molecules is, however, much less simple, and factors other than the communication of activation energy play an important part. The same is true of some bimolecular association reactions in gases, and, especially, of many bimolecular reactions in solution, which tend, on the whole, to involve considerably more complex structures than most of those concerned in second-order reactions accessible to measurement in the gaseous state.

Attention was first directed by Christiansen (*Z. physikal. Chem.*, 1924, **113**, 35) to the fact that for these solution reactions  $P$  may be much smaller than unity. In other cases it may approach unity (Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford, 1933, Chap. IV), though usually only for reactions involving an ion (Grant and Hinshelwood, *J.*, 1933, 258). It seemed possible that chemical changes might fall into two well-defined classes of slow and fast, determined by the presence or absence of some special factor, such as a quantum-mechanically forbidden electronic transition; but experiments have not supported this idea (Hinshelwood and Legard, *J.*, 1935, 587; Hinshelwood, *J.*, 1935, 1111; *Bull. Soc. chim.*, 1935, **2**, 1786). We are inclined now to the opinion that there is no sharp division between the two classes, and, moreover, that the whole of the continuous range of behaviour can, if necessary, be interpreted along more or less classical lines. This conclusion is based upon the statistical survey given in a later section (p. 375). Before discussing these statistics, it is desirable to examine the appropriateness of the representation of reaction velocity in the form  $PZe^{-E/RT}$ . Other methods of treatment are used, and, in particular, the analysis of the temperature-independent factor of the Arrhenius equation into a collision factor and a steric factor has been criticised. Alternative methods of treatment are therefore first considered, the relation of these to the collision method being in any case a matter of some interest. We shall reach the conclusion that the discussion of the problem in terms of the factor  $P$  has an interest of its own, and that we are justified in basing our survey upon it.

*The Transition-state Method.*—In this method (Eyring, *J. Chem. Physics*, 1935, **3**, 107; Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875) the activated molecules are treated as an independent species in equilibrium with the reactants. Statistical mechanics already provides an expression for the absolute value of such an equilibrium constant. The calculation (Fowler, "Statistical Mechanics," Cambridge, 1929, Chap. 5) is an elaboration of that by which the Maxwell-Boltzmann law is derived. One works out the total number of complexions of the system, taking into account, not only all the ways in which all the atoms and molecules present can be assigned to the different energy levels, but also the number of ways in which the various atoms can be free or distributed among the various molecules present. In doing this, a special hypothesis must be made. The number of molecules in a given quantum state is a perfectly definite number: the number in a given non-quantised translational state is an indefinite number, depending upon what limits are allowed in defining the state. To introduce a definite correspondence, a range of space and velocity co-ordinates such that  $m \cdot du \cdot dx = h$  is taken as the equivalent of a single quantum state. The condition that the number of complexions shall be a maximum gives the equilibrium constant. The expression is of simple form, each concentration term in the chemical equilibrium constant is replaced by the energy-partition function of the corresponding molecular species, and the product is multiplied by  $e^{-E/RT}$  where  $E$  is the energy absorbed in the reaction. Each partition function is itself a product of separate partition functions for translational, vibrational, and rotational energy. For

a translational degree of freedom, the partition function assumes the form  $\sqrt{2\pi mkT}/h$ , for a vibrational degree  $1/(1 - e^{-h\nu/kT})$ , for a two-dimensional rotational motion  $8\pi^2IkT/h^2$ , and for a three-dimensional rotation  $8\pi^2(8\pi^3I_1I_2I_3)^{1/2}(kT)^{3/2}/h^3$ , where  $I$  is a moment of inertia,  $m$  a mass, and  $\nu$  a vibration frequency. (Statistical weights are omitted.)

If we write the equilibrium constant expressing the concentration of activated molecules in terms of that of the reactants in the form

$$K = \left( \frac{\text{Product of partition functions for active complex}}{\text{Product of partition functions for reactants}} \right) \times e^{-E/RT}$$

where  $E$  is the activation energy, then the rate of reaction may be set proportional to this expression, which is called the probability of the activated state. Without going into the question of the validity of the interesting method by which Eyring seeks to obtain the absolute reaction rate by multiplying such an expression by a thermal translational velocity, it may be said that valuable information can be obtained by considering the relative values of  $K$  for different types of case. For example, one may compare  $K$  for a reaction involving the union of two complex molecules, with the value  $K_a$  for the union of two atoms to form a diatomic molecule (Evens and Polanyi, *loc. cit.*; Bawn, *Trans. Faraday Soc.*, 1935, **31**, 1536).  $K$  will contain three translational partition functions, a three-dimensional rotational, and  $n$  vibrational partition functions for the active transition complex of the two reactants, divided by six translational, two three-dimensional rotational, and  $l$  vibrational partition functions for the two separate reactants. We may represent this symbolically by  $T^3R^3V^n/T^6R^6V^l$ . Since the total number of degrees of freedom before and after union of the reactant molecules to the complex must be the same,  $l = n - 6$ .  $K_a$ , on the other hand, will contain  $T^3$  and  $R^2$  and  $V$  for the diatomic molecule, divided merely by  $T^6$  for the two atoms, giving  $T^3R^2V/T^6$ . (We are not formulating one of the vibrations here as a translation along a co-ordinate in which decomposition occurs: this is unnecessary, since the corresponding terms will cancel in the ratio  $K/K_a$ .) If the energies of activation are equal for the two kinds of reaction under consideration,  $K/K_a$  becomes of the form  $V^5/R^5$ , *i.e.*, a product of five one-dimensional vibration functions divided by a three-dimensional and a two-dimensional rotation function. The vibrational functions are those of the new vibrational degrees of freedom which come into being when half the translations and rotations of the reacting molecules lose their individuality in the complex. If  $h\nu$  is fairly small,  $V$  reduces to the form  $kT/h\nu$ ;  $R$ , apart from a small numerical factor, is  $\sqrt{2\pi IkT}/h$  (the exact product  $R^3R^2$  is easily worked out). Bawn (*loc. cit.*), taking  $kT/h\nu$  as equal to unity for each of the  $V$  terms, and all the moments of inertia to be  $10^{-39}$ , shows that  $V^5/R^5$  may be very small. Thus if  $P$  were unity for the atomic reaction, it would be very small for the reaction of the complex molecules.

*Comparison of the Transition-state Method and the Collision Method.*—The question is whether the transition-state method can be regarded as superseding the collision method. It is objected that the collision diameter used in calculating  $Z$  is an unsuitable quantity to deal with, because it is the distance at which transfer of momentum occurs, and, although significant in the discussion of transport phenomena, is only arbitrarily related to chemical interaction. This, however, is a matter of taste. In the collision method we consider the two molecules at the distance for momentum transfer (which, incidentally, is fairly well related to crystallographically-determined distances), and inquire what further conditions of orientation and internal state, relative velocities of pairs of atoms, and so on, must be fulfilled. These conditions are evidently difficult to specify. In applying the transition-state method, however, the difficulties are really as great, and the arbitrariness of the assumptions which must be made to obtain a numerical answer is only less apparent. In the problem discussed in the last section,  $kT/h\nu$  was taken as unity, while the moment of inertia was so chosen that  $R$  was a quantity of the order 10. With these values a very small  $P$  followed naturally. But the vibrations concerned are those of newly-formed degrees of freedom in an active molecule where the binding may be very loose: thus  $kT/h\nu$  might in fact be much greater than unity, and when five such terms are multiplied together a whole range of different results can be obtained. Again, three of the  $R$  terms refer to the active

complex, and the assumption that this has a normal moment of inertia is equivalent to specifying fairly exactly the distance of the molecules at the instant of chemical transformation. To obtain a small value of  $P$  we also had to assume that  $h\nu/kT$  was not very small compared with unity, the new vibrations in the critical complex being those of not too loosely bound atoms. In other words, each pair of atoms which form a new link must be not too far from their stable positions—not stretched apart, for example, so that the vibrations are near a convergence limit. This, therefore, seems to be equivalent to demanding a rather exact orientation of the colliding molecules as a whole, and probably also a fairly exact definition of the exact phase of their motion which certain atoms are in. To specify the five  $V$  terms correctly and obtain the exact value of  $P$  is in essence as difficult as to specify the orientations and phases correctly.

It seems, then, that the collision theory is not really at a fundamental disadvantage, if, as a matter of taste, we prefer to approach the problem in that way. The conclusion is that we should seek all the help we can obtain by applying both methods. Though the transition-state method works in terms of quantities which are themselves of a more general significance, assuming that we know them, the specification of the collision conditions must always retain some independent interest.\*

*Consideration of Entropy Changes.*—The entropy change in a chemical reaction is related to the equilibrium constant by the well-known thermodynamic equations  $\log K = U/RT + S/R$  (where  $U$  is the difference of the activation energies for the two opposing reactions), and  $K = k_1/k_2$ . Hence  $\log k_1 - \log k_2 = S/R - E_1/RT + E_2/RT$ . Since  $\log k = A - E/RT$ , it follows that  $A_1 - A_2 = S$ . Very interesting relations between  $S$  and the separate values  $A_1$  and  $A_2$  may be observed (cf. Soper, J., 1935, 1393; Rice and Gershinowitz, *J. Chem. Physics*, 1934, 2, 853; Rodebush, *ibid.*, 1933, 1, 440), but it does not seem possible in any generally valid way to derive  $A_1$  and  $A_2$  from  $S$ . It may be possible to split  $S$  into two terms such that  $S = f(S_1) - f(S_2)$ , where  $f(S_1)$  and  $f(S_2)$  are respectively functions of reactants only and products only, but these two quantities will not necessarily equal  $A_1$  and  $A_2$ ; for we might have  $A_1 = f(S_1) + C$  and  $A_2 = f(S_2) + C$ , and  $C$  may be as important as any of the other terms. Thus we cannot, without special justification, calculate  $P$  from  $f(S)$ . This was clearly stated by van 't Hoff ("Lectures," English transl., p. 214) in his discussion of the influence of solvents on reaction velocity. He pointed out that the solvent has two effects, one acting on the two opposing reactions to an unequal extent and producing the thermodynamically calculable equilibrium shift, and the other operating equally, to an unknown extent, on the forward and the reverse reaction.

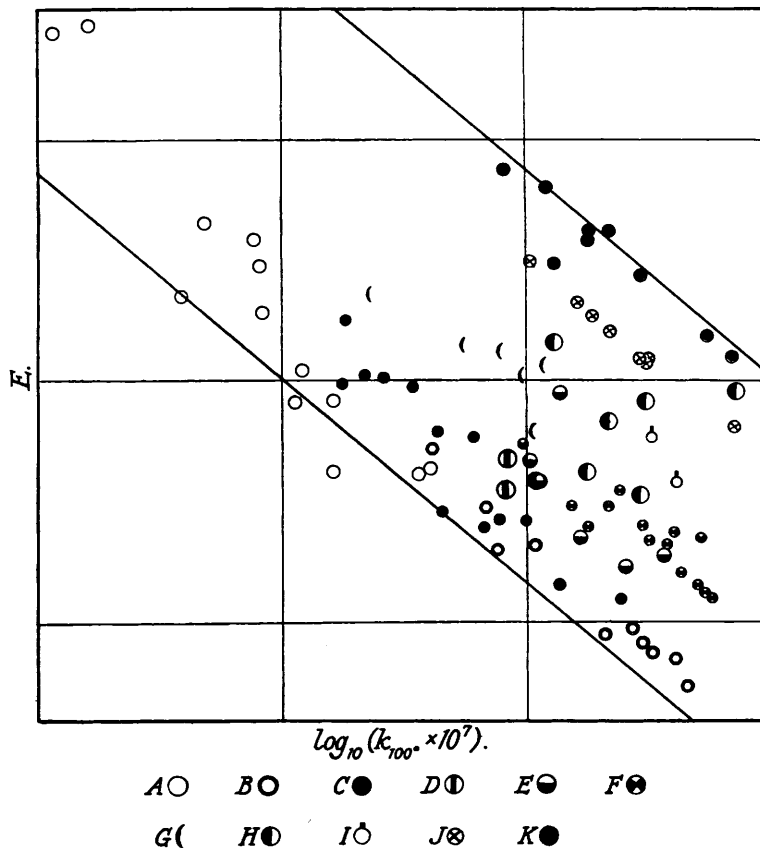
That the limitation of the thermodynamic method is real and not merely formal, is shown by the fact that  $P$  may be a function of the catalyst employed, e.g., in esterification

\* The present method of approach is not inconsistent with the view that the reactive species is sometimes a definite complex (see, e.g., Conant and Bartlett, *J. Amer. Chem. Soc.*, 1932, 54, 2881). The concentration of such complexes will vary with temperature, and this introduces a difference between the observed activation energy, obtained from the Arrhenius equation, and the activation energy which the complex itself must possess in order to react. This fact might seem to call for a modification of the ordinary collision treatment, but the difference is really only a formal one. If two reactants, X and Y, form reversibly a complex XY with evolution of heat  $Q$ , then the concentration of XY, as long as it is small compared with that of X and Y, is given by van 't Hoff's equation,  $[XY] = \text{const. } [X][Y]e^{Q/RT}$ . If the complex itself requires an activation energy  $E_c$  for further change, its rate of reaction will be proportional to  $[XY]e^{-E_c/RT}$ , and thus the rate expressed in terms of the reactants will be  $\text{const. } [X][Y]e^{-(E_c - Q)/RT}$ . The Arrhenius activation energy will be  $E_c - Q$ , i.e., less than  $E_c$ . This, however, does not explain why the reaction proceeds at a smaller rate than might have been expected from the observed value,  $E_c - Q$ . For molecules which bring only  $E_c - Q$  can form a complex, which, by hypothesis, will now contain  $E_c - Q + Q$ , and thus possesses the activation energy necessary for further reaction. Why it does not react immediately but persists and is perhaps later resolved into its products once more, is the same problem as before. The same argument applies *mutatis mutandis* to the case of an endothermically formed complex. We have then the state of affairs that molecules which bring the *observed* activation energy into a collision can give a complex possessing the algebraic sum of the observed activation energy and the heat of formation of the complex, i.e., the true activation energy of the complex, yet reaction does not occur except in a fraction of the encounters. This fraction, as before, is  $P$ .

reactions (Williamson and Hinshelwood, *Trans. Faraday Soc.*, 1934, 30, 1145; Hinshelwood and Legard, J., 1935, 587, 1588), or in the acetone-iodine reaction (Smith, J., 1934, 1744). Since the equilibrium constant cannot be altered by the catalyst,  $P$  cannot be calculated in these cases from thermodynamic quantities alone. This does not preclude the existence of striking correlations between  $P$  and the position of equilibrium in certain types of reaction (compare Evans and Polanyi, *loc. cit.*).

*The experimentally observed values of P for Bimolecular Reactions in Solution.*—A convenient way of representing experimental results is to plot  $\log k$  against  $E$  for series of related reactions, examples being chosen in each series to cover as wide a range of velocity as possible. In this way it is easy to decide whether relations between  $k$ ,  $E$ , and  $P$  are

FIG. 1.



significant and characteristic or merely accidental. Several series have now been studied in this way, and the results are collected together in Fig. 1. The series included are the following :

A. Esterification in alcoholic solution, the catalyst being the undissociated acid molecule (Hinshelwood and Legard, *loc. cit.*).

B. Benzoylation of aniline as modified by nuclear substituents (Williams and Hinshelwood, J., 1934, 1079; Newling, Staveley, and Hinshelwood, *Trans. Faraday Soc.*, 1934, 30, 579).

C. Quaternary ammonium salt formation in benzene solution (Winkler and Hinshelwood, J., 1935, 1147).

D. Two examples only : interaction of acetic anhydride and alcohol in two solvents (Moelwyn-Hughes and Hinshelwood, J., 1932, 230).

E. Esterification with hydrion as catalyst (Hinshelwood and Legard, *loc. cit.*).

F. Halogenation of phenolic ethers (Bradfield and Jones, J., 1928, 1006, 3073; 1931, 2903, 2907. Here about half the available points, chosen at random, are plotted).

G. Reaction between trinitroanisole and ring-substituted dimethylanilines (Hertel and Dressel, *Z. physikal. Chem.*, 1935, B, 29, 178).

H. Oxidation of cyclic compounds by potassium permanganate (preceding paper).

I. Two examples only: additions to dienes (Wassermann, J., 1935, 828).

J. Alkaline hydrolysis of substituted benzoic esters (Ingold and Nathan, this vol., p. 222. We are indebted to Prof. Ingold for advance communication of these results).

K. Interaction of alkyl halides and negative ions. [Three of the points refer to the results of Grant and Hinshelwood for the reaction of potassium hydroxide with ethyl halides (J., 1933, 258), and the others are the first five values given by Moelwyn-Hughes (*op. cit.*, table, p. 79). They could be supplemented by others from this same table, but the range of  $E$  values would not thereby be extended, nor would the degree of departure of the points from a single line be appreciably changed. The values given are justly representative of the whole set.]

Of these, D and I transgress the principle that a whole series should be available, but they are included as examples of interesting types of reaction, meriting further study.

The values of  $k$  are all calculated to  $100^\circ$  and expressed in g.-mol./l./sec. The two diagonal lines in Fig. 1 are of the standard slope,  $2.303RT$ , and in positions corresponding to  $P = 1$  and  $P = 10^{-8}$  respectively.

In any given series the tendency of the points to group themselves about a line of the standard slope is evident, except that in series A there is an increase in the slope towards the higher values of  $E$ . Both the position of the mean standard line for any series and the deviations of the individual points from it are of interest. The following simple statistical analysis was therefore made. By the method of least squares the best line of slope  $2.303RT$  was drawn through the points for a given series, only the two points for the highest  $E$  values in series A being omitted. This line cuts the ordinate corresponding to  $\log k \times 10^7 = 0$  at a value  $b$ . Since  $k \times 10^7 = cPZe^{-E/RT}$ , where  $c$  is a constant for the conversion of units,  $2.303RT \cdot \log(k \times 10^7) = 2.303RT \cdot \log(cPZ) - E$ , whence  $b = 2.303RT \cdot \log(cPZ)$ . For series K we know that  $P$  is almost exactly unity. The variations of  $Z$  from case to case are small and are neglected: hence from the value of  $b$  for series K we find  $c$ , and hence the absolute values of  $P$  for the other series.

To convey an idea of the distribution of the individual values in a series about the mean, the Gauss curves shown in Fig. 2 have been constructed. Although there are not enough examples in any series to establish the exact form of the frequency distribution curve, the assumption of the symmetrical form is unobjectionable in representing the range of the deviations. The constant  $a$  in the equation of the curves  $y = e^{-a^2x^2}$  is found for each series by measuring the range of  $\log P$  which includes approximately half the points, and then using a table of error functions and their integrals.

Figs. 1 and 2 both show that there is a fairly continuous transition from the fast to the slow type of reaction. Fig. 2 shows further that there is considerable variation in the degree of conformity to the mean type of behaviour.

*Factors influencing P.*—We may now attempt to estimate the range over which  $P$  might theoretically be expected to vary. For this purpose we tabulate first a series of factors which tend to make  $P$  small, and assign a rough but, we think, not unreasonable figure for the ratio in which perfect efficiency of activating collisions might be reduced by the operation of each.

(1) The reactive groups of the colliding molecules must be presented to one another in correct orientation. We might plausibly take 1/10 of each molecular surface as active in an unfavourable case. Thus according as two or three molecules are involved (three, for example, with acid, catalyst, and alcoholic solvent), the inefficiency factor could be anything from unity down to  $10^{-2}$  or  $10^{-3}$ .

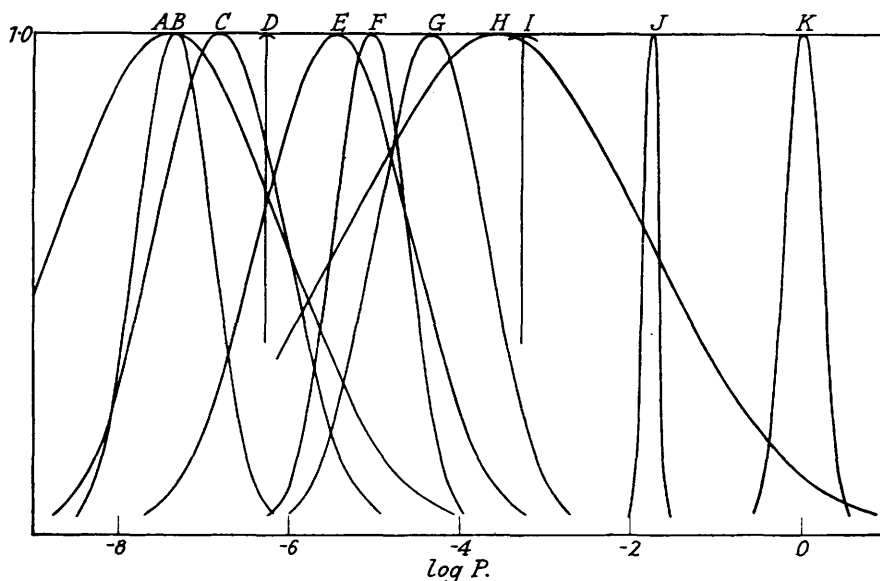
(2) New linkings must be formed and existing ones broken. A link is most easily broken when the two atoms are at the extreme of the amplitude of their vibration. Thus, even when the link is activated, there may be only a comparatively narrow range of phase in

which actual rupture occurs. This might easily correspond to 1/10 only of the whole period. Changes in at least two links are usually involved, so that a factor of  $10^{-2}$  would not be surprising.

(3) Groups may be present in the molecules which impede access to the reactive centres. Although steric hindrance is overcome mainly by increased activation energy, approach to the active centres may still only occur when the hindering groups are in that phase of their bending oscillations which opens the widest angle of access. A factor of  $10^{-1}$  is reasonable here.

(4) In some reactions the solvent must play an intimate part which does not appear in the chemical equation. Several attempts have been made to study typical solution reactions in the gas phase, and the reaction has usually been proved to occur not homogeneously but in an adsorbed film (cf. J., 1932, 230; *Trans. Faraday Soc.*, 1935, 31, 1739). The continuous medium round the reacting molecules is thus in some way highly important. Moreover, the value of  $P$  varies over a considerable range from solvent to solvent. Thus

FIG. 2.



the orientation of the solvent molecules round the activated complex can be of great importance. For example, in a reaction such as quaternary ammonium salt formation the solvent dipoles might need to be orientated in such a way as to produce a field capable of stabilising the polar form of the transition complex. The probability of the correct orientation is very difficult to estimate, but as a rough approximation we may take each active complex to be surrounded by an octahedral distribution of solvent molecules, each one of the six having a "right" and a "wrong" orientation. The chance that all are right is  $1/64$ , from which we will only conclude that a factor of the order  $10^{-2}$  is possible.

If all these adverse factors combine,  $P$  will be of the order  $10^{-8}$ . Their influence, however, may be modified by the following :

(I) Smallness or simplicity of the reacting molecules reduces the effect of all four factors.

(II) Anything which lengthens the duration of collisions will modify (2), (3), and (4). As a special case of a lengthened collision time we may have definite complex formation.

(III) Ionic charges on the reactants may remove the effect of (1) by producing automatically a favourable orientation. They may also affect (4) and enhance (II).

(IV) If, as is possible in certain catalytic gas reactions (cf. J., 1935, 1111), specific kinds

of energy transfer occur in the activating collisions, the molecules may behave as virtually simpler structures than they really are, with consequent increase of  $P$ .

In the most favourable case these factors may raise  $P$  to unity. The balance between them and the adverse factors (1)–(4) may be expected to give any value between unity and  $10^{-8}$ . To decide how the balance is made up in a given reaction is a matter of no small difficulty, but hardly greater than that of assigning the correct values to all the quantities used in the statistical-mechanical treatment. In a general way it may be said that in series K ( $P = 1$ ) factors (I) and (III) are apparently of decisive importance, that factor (III) accounts for the marked difference between A and E, and that in the reactions where polar salts are formed factor (4) is evidently very important. On the whole, it may be said that the results are quite understandable even though they would have been hard to predict in detail. The range of divergence from the averages can also be understood in a general way. When the reactive group is highly localised, or the group modifying the rate is remote from the active group, the departures from the mean will be small. The benzoylation reaction is a good example of this, as also is series J. In the esterification series, the reacting groups are much more closely incorporated in the main structure and the range of variation is correspondingly wider. The same applies with greater force to the ring-breaking oxidation reactions where the structural factor must be as great as to give rise to what is virtually a change in mechanism from case to case. Within the total range of variation of  $P$  in a given series, various regularities, such as correlations between  $E$  and  $P$ , and so on, are possible (J., 1935, 1111; cf. Evans, Morgan, and Watson, *ibid.*, p. 1167).

If second-order gas reactions are regarded from this point of view, factor (I) would seem to be the governing one, though in some catalytic reactions (IV) may play an important part.

First-order reactions, in gases and in solution, present a rather different picture. When only one molecule reacts, the process does not have to be completed in the short time of a collision, and the preactivated molecule may draw upon the energy stored in any of its parts. If the molecule is complex, this may give rise to a rate of reaction far greater than  $Z e^{-E/RT}$ . In this sense  $P$  becomes much greater than unity. Examples are well known for both gases and solutions. The range over which  $P$  may vary is from about unity to  $10^5$ . Thus, taking both first- and second-order reactions into account, we have a continuous range of  $P$  values from  $10^{-8}$  to  $10^5$ . In a general way we are now in a position to say where approximately, though by no means quantitatively, a reaction of a given type will occur in this spectrum of  $P$  values. Though the full interpretation may possibly involve factors as yet unknown, and quantum-mechanical explanations may be necessary for some of the more detailed relations (compare Bell, *Proc. Roy. Soc.*, 1936, in the press), relatively simple ideas can give at least a qualitatively satisfactory explanation of the whole range of observed behaviour.

#### SUMMARY.

The transition-state method and the collision method of treating bimolecular reactions are compared, and it is concluded that the latter method is quite appropriate for a general discussion of the problem. A statistical survey of bimolecular reactions in solution is made in terms of the collision theory.

The factors influencing the value of  $P$  in the equation,  $\text{rate} = P Z e^{-E/RT}$ , are discussed, and the conclusion is reached that the whole range of observed behaviour can, if necessary, be understood, qualitatively at least, in terms of relatively simple classical ideas.

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[Received, January 30th, 1936.]