317. *The Mechanism of Chemical Reactions.*

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THE object of this paper is to point out that two contrasted groups of chemical reactions may possibly prove to correspond to a quantum-mechanical classification of physical processes. In a considerable number of chemical changes the rate of reaction can be shown to be equal to the rate of activation of the molecules, and in still further examples the energy of activation is clearly the most important factor controlling the rate, even if there is no exact quantitative relation.* These may be called reactions of the first group. There are other reactions which appear to occur at only a small fraction of the rate at which the necessary energy can be communicated to the molecules. These may be called reactions of the second group. Possibly there is a continuous transition between the two types, but the available information is not extensive enough for a statistical investigation of this. For preliminary theoretical discussion, however, there is nothing lost by contrasting the extreme examples only.

It is possible that the apparent slowness of the chemical change in the second group is sometimes illusory, and depends upon wrong assumptions about the nature of the reacting species, or upon the neglect of corrections which should be applied to the constant of the Arrhenius equation to obtain the true heat of activation.† Nevertheless, having regard to the considerable variety of types of reaction in which such behaviour is found, it is probably justifiable to say that in the second group the rate is largely determined by a probability factor independent of temperature, as well as by activation.

Nearly all real chemical reactions are too complex to be treated in detail by quantum mechanics, which usually idealises them as, *e.g.*, a simple change in displacement of two masses, or the passage of a single mass through a potential barrier. The great value of quantum-mechanical considerations, however, is qualitatively to indicate what general types of behaviour we may expect to encounter. In quantum-mechanical calculations about atomic systems two types of case arise. The first is exemplified by the calculations of Eyring and Polanyi (*Z. physikal. Chem.*, 1931, *B*, **12**, 279) on the energy of activation of reactions of the type $XY + Z = XZ + Y$, which occur whenever Z approaches XY with the requisite energy. The whole treatment involves nothing characteristically quantum mechanical except the calculation of the forces between the various atoms. The second type is exemplified in the numerous calculations of transition probabilities between states of equal energy. Transitions occur by "resonance," and the probability depends upon the magnitude of an integral containing the potential energy due to a "perturbation" to which the system is subjected. One of the most recent investigations of this type is that of Zeuer (*Proc. Roy. Soc.*, 1933, *A*, **140**, 660), who deals with transitions between excited attractive states of diatomic molecules and "crossing" repulsive states of different symmetry. Ordinarily such transitions are improbable, but are strongly favoured by a powerful external electric field.

The question now arising is the following: can we correlate the first group of chemical reactions with the first type of molecular process, and the second group with the second type? To do this we should have to satisfy ourselves that a principle something like the following held good: whether the rate of reaction is equal to the rate of activation (or rate of passage through a potential barrier) or not, depends upon whether a large perturbing force is necessary, and upon whether or not the requisite perturbation is present. The available evidence is hardly complete enough, and the best use of the principle would be as a guide to further experiment, but some characteristic examples may be considered briefly.

In the first group occur principally simple gaseous decompositions or interactions (Hinshelwood, *op. cit.*), and a considerable number of bimolecular reactions in solution (Moelwyn-Hughes, *Chem. Revs.*, 1932, **10**, 241), to which must be added certain reactions depending on collisions between solvent and solute molecules. In the second group are a few gas reactions such as the interaction of sodium vapour and cyanogen (von Hartel and Polanyi, *Z. physikal. Chem.*, 1930, *B*, **11**, 97), certain bimolecular reactions in solution (Christiansen, *ibid.*, 1924, **113**, 35; Norrish and Smith, J., 1928, 129; Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.*, 1931, *A*, **131**, 177; J., 1932, 230), and unimolecular gas reactions, the condition for the existence of which is that the rate of activation must be considerably greater than the rate of chemical transformation.

In the simplest gas reactions the perturbation may well be the collision itself, since

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* Hinshelwood, "Kinetics of Chemical Change," 3rd edition, 1933.

† An example of one type of complicating factor is to be found in the preceding paper.

quantum mechanics shows that collisions readily induce transitions of various kinds. But the duration (cf. Born and Weisskopf, *Z. physikal. Chem.*, 1931, *B*, **12**, 206) of a collision is small, and if the molecules leave the impact with energy divided among a large number of degrees of freedom, then the probability of the requisite internal transformations of this energy is small. This is shown rather strikingly by the fact that molecules such as nitrous oxide and acetaldehyde can be activated in several distinct ways (Fletcher and Hinshelwood, *Proc. Roy. Soc.*, 1933, *A*, **141**, 41), presumably depending on the location of the energy, for the same chemical transformation. Thus the internal redistribution of energy after collision must be difficult. In contrast with the small probability of decomposition of a complex molecule activated by ordinary collisions, we have the very effective activation sometimes caused by a collision with the right kind of catalyst molecule. For example, in the decomposition of certain organic compounds under the catalytic action of iodine, the rate of reaction approaches the rate of activation (and the activation mechanism is simplified to involve only two square terms of energy). The highly polarisable molecules of halogens are the best catalysts for such changes, and all the organic compounds susceptible to their action appear to possess dipole moments in the neighbourhood of the bond which has to be broken in the chemical change (Bairstow and Hinshelwood, *Proc. Roy. Soc.*, 1933, *A*, **142**, 77). Another fact which may not be without significance is that one of the " slowest " of the unimolecular gas reactions is the isomeric change of methyl maleate (Nelles and Kistiakowsky, *J. Amer. Chem. Soc.*, 1932, **54**, 2208) which involves, not a decomposition, but the more delicate process of an internal rearrangement. The interaction of cyanogen and sodium must involve some rather important transitions of carbon valency electrons, and it is easy to believe that the process is improbable in the quantum-mechanical sense even in a collision.

Of bimolecular reactions in solution, it may be significant that the great majority of those at present known to take place at a rate given by the simple formula *number of collisions* $\times e^{-E/RT}$, involve collisions between a molecule and an ion (Grant and Hinshelwood, this vol., p. 258; for list, see Moelwyn-Hughes, *loc. cit.*), *e.g.*, an alkyl halide and an ethoxyl ion. The enormous perturbation due to the ionic field may be of much more than secondary importance in creating the right condition for the " efficiency " of the collisions. Examples of slow reactions of the second group are, as far as is known, much commoner among interactions of neutral molecules, for example, the combination of tertiary amines and alkyl halides (Menschutkin; also Christiansen, Norrish and Smith, Moelwyn-Hughes and Hinshelwood, *locc. cit.*), the esterification of acetic anhydride by alcohol (Moelwyn-Hughes and Hinshelwood, *loc. cit.*), the chlorination of phenolic ethers and anilides (Roberts and Soper, *Proc. Roy. Soc.*, 1933, *A*, **140**, 71), the benzoylation of aniline (preceding paper), the rearrangement of *N*-bromoacetanilide (Bell, *Proc. Roy. Soc.*, in the press) under the influence of undissociated acid molecules in chlorobenzene solution. Reactions of this kind may be more complex than they appear at first sight and only long and detailed investigation can settle the matter, but they are certainly characterised by very small apparent heats of activation and a difference between possible rate of activation and actual rate varying from 10^4 to 10^8, in contrast with almost exact agreement in some of the examples of the other class. One possible explanation, at least, is that the transition probabilities in the encounters are so small that a low energy of activation does not lead to a correspondingly rapid reaction. These reactions are very sensitive to the environment of the molecules. A rough qualitative parallelism between dielectric constant and rate of reaction in a given solvent has long been known, though there is nothing like a systematic relation. Solvent molecules with a large electric moment are of the kind to provide the necessary perturbing actions. The presence of water in non-aqueous solvents, and the action of polar surfaces may also be regarded as providing electrostatic perturbing fields. (Roberts and Soper point out that in some of the " slow " bimolecular reactions referred to there is a large difference in polarity between the reactants and the products, a fact which may be of importance.)

In connexion with the possible importance of electrostatic perturbations, it is interesting to consider the electronic displacements which, according to the theories of Robinson and others, play so great a part in many of the reactions of organic chemistry. We can conceive a class of reaction where the requisite disturbance of the participating molecules is produced so much more easily by an intense local field than by the thermal oscillations that the activation factor ceases to be all-important or may even in extreme cases become insignificant.

The whole picture must remain a very complicated one, and there will doubtless be many apparent contradictions. For example, the oxidation of picric acid by potassium permanganate (Musgrave and Moelwyn-Hughes, unpublished results) seems to be a reaction of the "slow type," despite the fact that one of the reactants at least is an ion, but this is a complex case, and apart from anything else, the possibility that the reactants are two negative and repelling ions has to be considered. The decomposition of chlorine monoxide in solution, as in the gas, has about the normal rate : but here, although we have two neutral molecules, we have a fairly simple decomposition reaction.

The object of the present note is certainly not to propose any premature generalisations, but simply to suggest that ultimately some contribution to the systematisation of chemical kinetics may be extracted by considering a possible classification of thermal reactions into those where activation is of primary importance and those where the action of perturbing fields is of great influence in affecting the probability of transitions. As far as we can see at present, the former class would be the larger and more important, but the latter by no means negligible; or, if we regard all reactions as intermediate between these two ideal classes, we may expect the majority to conform more nearly to the former than to the latter.

In the former class the energy factor, and in the latter, environmental influences, would be of primary importance. This consideration suggests the line of experimental approach.

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