A SYMPOSIUM ON THE KINETICS OF HOMOGENEOUS REACTIONS[1]

INTRODUCTION TO THE SYMPOSIUM

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In order to correlate the advances of research in special fields, it is necessary for investigators in related subjects to summarize their findings for the benefit of other scientists who are not familiar with the technicalities involved. For a number of years the Division of Physical and Inorganic Chemistry of the American Chemical Society has endeavored to meet this recognized obligation. It has transmuted its frontier work into more usable form by the organization of symposia and their publication in Chemical Reviews (1 to 4) and elsewhere (5). The present collection of papers on the kinetics of homogeneous reactions is based chiefly on the symposium held before the Division of Physical and Inorganic Chemistry at the eighty-second meeting of the American Chemical Society held at Buffalo, New York, in September, 1931.

Chemical kinetics comprises the study of the velocity of chemical reactions. Although it constitutes one of the oldest fields in physical chemistry the development of theory has been slow. The study of chemical kinetics is seriously complicated by the fact that traces of impurities often exert enormous influences. The industrial chemist has learned, empirically, how to obtain desired results through the control of temperature and concentration, and the use of catalysts. Of the large number of possible reactions which can follow the mixing of reacting materials, he has learned to accelerate the one that he desires and to suppress the others. But he knows little concerning the intermediate steps or the actual mechanisms involved. These things must be stud-

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ied by theoretical chemists who have an intellectual interest in them. It is to them that the present symposium belongs.

No attempt has been made, in this symposium, to cover those individual reactions which have been studied extensively, such as those of nitrogen pentoxide or hydrogen peroxide, but the plan has been rather to study general principles and to bring in specific reactions only as illustrations. It should be pointed out, however, that the important advances have come from the investigation of uniquely simple reactions. For purposes of study a reaction should be free from side reactions and it should have the slowest step—the rate-determining step—so slow that all the other steps can be neglected in comparison with it.

The field of kinetics is large. Therefore a discussion of heterogeneous reactions, which take place at the surface of a solid, has been excluded. Such reactions have been treated adequately elsewhere (6, 7).

Another field closely connected with kinetics is that of photochemistry. Much information concerning the mechanism of a reaction may be gained by giving to the molecules abnormal amounts of energy as in photochemical reactions.

The study of homogeneous reactions is itself divided sharply into reactions in the gas phase and reactions in solution. The gas reactions are simpler because they are not complicated by the presence of a solvent and they have a great advantage in that the collision frequency can be calculated from the kinetic theory of gases. Few kineticists have studied both gas reactions and reactions in solution and little attempt has been made thus far to correlate the theories. Reactions in solution are profitably divided into those which involve non-polar compounds and those which involve polar compounds or ions. Non-polar, organic reactions are simple in that they do not involve electrostatic charges, but the ionic reactions are sometimes simplified for study if the charge becomes the predominating factor. For decades, velocities of organic reactions have been measured and valuable information concerning specific reactions has been accumulated. However, some of the data are of lesser importance in kinetics because they are not sufficiently accurate or because the reactions are too

complex. Many reactions between ions are too rapid to measure, but some are slow and a new impetus has been given to their study by recent theories of solutions and catalysis.

The early history of the theoretical study of reaction velocities began with the formulation of the mass law in 1867. The mathematical description of simple reaction rates, according to first or second order reactions, came next. In 1889 Arrhenius advanced the concept of active and passive molecules and gave an important formula connecting reaction rate with temperature. In 1915 statistical mechanics was applied to the problem and the constant, E, in the Arrhenius equation

$$\frac{d \log_e k}{dT} = \frac{E}{RT^2} \quad \text{or} \quad k = se^{-E/RT}$$

was more closely associated with the energy of activation. In this equation k represents the specific reaction rate, T the absolute temperature, and R the gas constant. The physical significance of the integration constant s will be discussed in papers which follow.

Before 1918 information was accumulating regarding specific reactions and the phenomenon of catalysis, but the theoretical work did not progress rapidly because there was no underlying hypothesis concerning the mechanism. In 1918 and 1919 the radiation hypothesis (8) was proposed, and although it survived but a few years it was extremely active in promoting the theory of chemical kinetics. When this hypothesis failed to explain unimolecular reactions on the basis of radiation from the walls of the containing vessel the collision hypothesis, formerly regarded as inadequate, was reëxamined and found to be satisfactory.

The study of unimolecular gas-phase reactions has constituted one of the most active fields of research in kinetics. For a few years after its discovery in 1921 the unimolecular decomposition of nitrogen pentoxide (9) was the only example of this type of reaction, but now there are more than a dozen. They seem to be satisfactorily explained on the basis of collisions, assuming that a time lag exists between activation and collision. This hypothesis, originally proposed by Lindemann and elaborated by Hinshel-

wood, Christiansen, and Fowler and Rideal, has been most extensively developed by O. K. Rice and Ramsperger and by Kassel.

In the following article Kassel gives a critical survey of the theories of unimolecular gas reactions, and considers various mechanisms for the activation which follows collision. The interesting influence of foreign gases is discussed also. His rather conservative attitude is desirable at a time when things are moving so rapidly and when almost anything new is too readily accepted.

The collision theory of unimolecular gas reactions gained considerable support from the prediction that the specific reaction rates would decrease at low pressures—a prediction which has been borne out by many experimental measurements. Ramsperger has been active in establishing these facts; in the next article of this series he reviews all the theoretical and experimental material. The facts show that the collisions and the normal decomposition rates are maintained at low concentrations in the presence of an excess of certain inert gases.

Chain reactions, originally proposed by Bodenstein and Nernst, have recently taken a place of importance in kinetics. Sometimes the energized products of an exothermic reaction are able to activate new reactants by collision and thus pass their energy along in a chain involving many molecules. Such reactions have been the object of a great deal of research within the past five years, particularly in the study of explosions. The field is covered in a comprehensive manner by Lewis, who gives the theoretical background and then applies the theory to eight typical explosion reactions, going into considerable detail in the case of the reaction between hydrogen and oxygen. It has been realized for some time that reaction chains can be stopped by collisions with the walls, and that the explosion is profoundly affected by the dimensions of the containing vessel and by the pressure and composition of the reacting gases. The influence of foreign gases is particularly interesting here as well as in the unimolecular reactions. Not only are chains stopped by the walls of the vessel but in some reactions they appear to be initiated by adsorbed ions and atoms. This field was covered in special detail by Alyea at the symposium.

Progress in chemical kinetics has advanced and will continue to advance through the study of especially simple systems. Most of our reactions involve the activations of molecules, but reactions involving atoms comprise simpler phenomena. Reactions of halogen atoms and of alkali atoms have been investigated by Polanyi and others. It has been supposed that exothermic reactions between free atoms require no further activation. Kistiakowsky ably reviews this field and shows that in many reactions additional energy must be supplied to make free atoms react. He emphasizes the fact that not every collision is effective and that the low efficiency varies greatly with different reactions. This steric hindrance factor must be considered in interpreting the experimental results. The contributions of quantum mechanics are shown to be helpful in deciding between different mechanisms.

There is a feeling that quantum mechanics can aid in the solution of many chemical problems. Substantial progress has already been made in chemical kinetics. Eyring has been successful in calculating certain energies of activation and reaction rates with the help of a few simple assumptions. In the review given here he has been unusually successful in explaining things in non-mathematical language. The concepts on which the calculations are based are made clear with simple illustrations.

The mechanism by which energy is exchanged in molecular collision is the object of a critical study by O. K. Rice. He considers vibrational frequencies and other mechanical properties, and calculates the probability of energy transfer at collision for several different gases. He then compares these probabilities with the relative influence of hydrogen and other gases on the falling-off of the unimolecular constants at low pressures.

Physical chemical theories often find their most fertile testing grounds in organic chemistry, where considerable information on molecular structure is already available and where the complicating influence of electrostatic charges is minimized. The review by F. O. Rice on the decomposition of organic molecules will be found complete and suggestive. The manner in which a complex molecule ˙breaks up, whether into new molecules or into free

radicals, is a matter of great interest.   Free radicals are known to exist and to give characteristic band spectra.   Their existence is now accepted by organic chemists.   Whether they play a vital part in kinetics is still undecided, but the reactions of lead tetraethyl and other metallo-organic compounds are cited in favor of the view that free radicals are formed.   A different viewpoint is advanced in some of the other reviews.   The subject of pyrolysis is treated at some length, not from the point of view of descriptive organic chemistry, but from the point of view of the kineticist who is interested in learning how the ruptures occur.   The cracking of paraffins and olefins and the decomposition of ketones, nitrogen compounds and various other types of organic molecules are discussed in some detail.

The order of a reaction, as determined from experimental measurements of velocities, often gives important information regarding the mechanism of the reaction, but it must be borne in mind that the measured rate is the rate of the slowest step in a series of steps.   The intermediate compounds involved in such steps may be fleeting and difficult to identify, but it is possible in some cases to obtain considerable information regarding them. In this field the work of Bray has been outstanding.   He summarizes here the various methods which can be used and illustrates them with specific cases involving thermodynamics, reverse reactions and consecutive reactions.

The review just mentioned and all the others which follow it are concerned with reactions in liquid solutions.   Aqueous solutions of ions have been studied thoroughly in physical chemistry, but the kinetics of reactions between electrolytes is a comparatively unexplored field.   The ions already contain an excess of energy and often do not require time to become activated.   As a result most ionic reactions are immeasurably fast and cannot be studied from a kinetical standpoint.   Important progress has been made, however, in some reactions which are sufficiently slow to permit experimental measurements.   La Mer is particularly qualified to review this field on account of his contributions to the theory of electrolytes and his attempts to measure these fast ionic reactions.

His review of reaction velocity in ionic systems is unusually comprehensive and timely. Brönsted's theory of critical complexes is properly stressed as the guiding principle and a clear derivation is given for Brönsted's formula. Interionic attraction and the primary and secondary salt effects are discussed, and Christiansen's illuminating treatment of bimolecular reactions in solution is emphasized. Finally, several new and significant experimental researches are reviewed.

The effect of acids and bases in catalyzing certain reactions has been the object of careful investigations for half a century but a new impetus has been given within the last eight years by the proton theory of acids and bases proposed by Brönsted and by Lowry. The studies of Brönsted on the effect of electrolytes on reaction rates, and the influence of the Debye-Hückel theory of strong electrolytes have aided, too. The picture of acid and basic catalysis, as worked out and reviewed by Martin Kilpatrick and Mary L. Kilpatrick, is satisfactory and quite complete. The molecular acid as well as the proton play a part in reactions. The action of the acid with the solvent must be considered also. There is a similarity between the dissociation process of an acid and the catalytic process in which the proton is given to a molecule of reactant. Several factors are involved, as shown by the fact that the energy of activation varies with different catalytic conditions.

The methods of statistical mechanics undoubtedly offer the most exact means for handling problems of kinetics. Scatchard gives a careful analysis of the possibilities as applied to liquid solutions together with the variables that must be considered. Obviously the treatment of liquid solutions is more complicated than the treatment of gases.

Very few attempts have been made to correlate investigations in the gas phase with those in liquid solutions. The rate of decomposition of nitrogen pentoxide has been found to be approximately the same in inert solvents as in the gas phase (10). This result might be expected in the case of unimolecular reactions. The comparison of rates of bimolecular reactions in the gas phase and in solution is a matter of great interest. It is generally conceded that nothing is known concerning collision frequency in the

liquid phase.   On the other hand, with properly chosen reactions, it may be possible to throw some light on the nature and the significance of collisions in liquids.   No direct experimental measurements of the two are available as yet, but, in the last paper of this group, Moelwyn-Hughes gives a comprehensive review of established bimolecular reactions which occur in solution and compares them with the corresponding values calculated for the gas phase.

In conclusion it may be said that real progress has been made in the theory of chemical kinetics during the past few years, but that important advances are still ahead.   Rates of simple reactions can be described in exact mathematical language, but we have been successful in *predicting* reaction rates only in a few cases.   We are still groping for a law that will assign definite energy values to specific valence bonds and permit simple calculations of heats of activation.   Possibly such a goal can never be attained.   At present there is some difficulty in comparing heats of dissociation as obtained from thermochemical measurements with those calculated from spectral data.   The values obtained from spectral data include the extra kinetic energy with which the reaction products are thrown out.

We are looking for more definite physical interpretations of the Arrhenius equation, which has been so successful in representing the experimental facts.   The form of the equation is such that extraordinary accuracy is required in measuring the temperature coefficient of the reaction rate before complete theoretical conclusions can be drawn.   Very few of the measurements of chemical kinetics now available are sufficiently accurate for this purpose.   Furthermore the mathematical methods used in calculating specific reaction rates from experimental data have been unsatisfactory in many cases.   The averaging of a number of logarithmic equations has frequently led to a cancellation process, and, as a matter of fact, graphical methods for evaluating velocity constants are often better.   The use of more exact calculations of rate constants has been discussed recently (11, 12).

Further information regarding diameters and the effectiveness of collisions in chemical reactions is needed.   A good start has

already been made and it seems likely that chemical kinetics may even be able to contribute something to physical kinetics.

In the study of reaction rates in solution every effort should be made by means of physical measurements or otherwise to learn more about the intermediate compounds which determine the mechanism of the reaction.

Progress in research can often be made by pushing experimental conditions to extremes. Thus in chemical kinetics the experiments at very low pressures have already yielded material of considerable importance. Studies of reaction rates at high pressures are needed also. Experimental measurements of extremely rapid reactions, such as ionic reactions or the dissociation of nitrogen tetroxide, would be valuable also. Some progress has been made with fast reactions but new methods may yet be devised. Strange as it may seem, the very slow reactions have been neglected, although the only special technique that they require is patience.

While experimental research is progressing, theoretical calculations must keep pace. Although applications of quantum theory seem difficult it happens, frequently, that the problems become much simpler when the actual attack is made. Already quantum mechanics has offered an explanation for the observed decomposition rate of nitric oxide. A critical evaluation of our present concepts would be welcomed also. The theory of activated molecules, and the calculation of energies of activation from temperature coefficients of reaction rates, seems fairly satisfactory, but it is possible that an entirely new viewpoint might be still more satisfactory.

Research in chemical kinetics has suffered for lack of stimulating hypotheses, but now the greatest need seems to be for accurate and complete experimental investigations of simple reactions.

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