A SYMPOSIUM ON THE KINETICS OF REACTION[1]

INTRODUCTION TO THE SYMPOSIUM

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Fundamental physical chemistry in America has shared in the pioneering investigations which are even now being turned to practical advantage. America is responsible for the modern concepts of surface reactions, through the illuminating studies of Langmuir. From America, outwards, have spread the accepted concepts of the catalytic surface and the scientific interpretation of the industrially important phenomena of poisons and of promoters, and of the nature of gaseous activation at surfaces which is so important in technical catalysis. American physical chemistry has fertilized the field of chain reactions, which are fundamental in processes of deterioration and in the operation of the internal combustion engine. The physical chemistry of nitrocellulose, of cellulose esters, and of other plastics provided the basis for the technical development of nitrocellulose paints and enamels, and for improvements in the fields of photography, artificial fibers, and cellophane. Abundant evidence of a dispassionate nature from foreign lands testifies to the fact that the high standards of American chemical science rest to a large extent on the excellence of its fundamental research in physical chemistry rather than on its contributions to other branches of the subject. It is a matter for meditation and discussion whether the American chemical industry has utilized to the fullest possible extent this abundance of excellent physical chemical material.

The effect of earlier discoveries on subsequent technical development should therefore stimulate our interest in the symposium which we hold

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[1] The papers included under this title form part of an all-day symposium on "Kinetics of Reaction," which was presented by the Division of Physical and Inorganic Chemistry at the Eighty-ninth Meeting of the American Chemical Society in New York City on April 22, 1935. The morning session, which included the papers by H. S. Taylor, G. B. Kistiakowsky, F. O. Rice, V. K. La Mer and H. Eyring, was arranged by H. S. Taylor, and the introduction refers specifically to that session. The afternoon session, which included the papers by F. Daniels, H. A. Liebhafsky, W. F. K. Wynne-Jones, and L. P. Hammett, was arranged by L. P. Hammett.

today. We shall learn this morning of those newest studies in the field of reaction mechanism and reaction kinetics that are now issuing from prominent centers of our physical chemical science. They comprise, we believe, the beginnings of new and significant chapters in their special field, of decisive implications for applied science. In the review of new work in the field of thermal decomposition we shall learn of the important developments now taking place through the investigations of Professor Rice of Johns Hopkins University and those from the Harvard University Laboratories which Professor Kistiakowsky will report. These studies will serve to emphasize the importance of molecular fragments, atoms or free radicals, in many forms of chemical reactions. They have opened up an entirely new field of study of reactions hitherto thought to be simple unimolecular reactions. Much of the early work in this field will now, of necessity, be reëxamined and reinterpreted in the light of concepts developed by Rice. It would be superfluous to emphasize the fundamental significance of these studies in the technically important pyrolytic reactions and explosion reactions. The fundamental studies have, at once, a technical implication.

In addition, however, we shall hear of the limitations of the present theoretical treatment of chemical kinetics. Professor La Mer will present experimental evidence of the inadequacy of current concepts in interpreting already available experimental material, especially in the realm of reaction velocities in solution. It will be shown that many reactions proceed at speeds which differ greatly from those calculable on the basis of simple collision theories, the efficiency of which collisions is governed by an exponential factor expressive of the energy of the fruitful collisions. It will be shown that rates of reaction varying a millionfold from normal expectation are not uncommon. The causes of such deviations will be presented by Professor Eyring. It will be shown that the technique of reaction rate measurements has been refined to a point where the classical theories of reaction kinetics are no longer adequate. Classical kinetics is based on a collisional mechanism, the molecules of which collisions have been assigned a nineteenth-century billiard-ball immutable structure. The wave-mechanical concepts of atomic structure have provided a more intimate picture. With their aid we can not only deduce the most favorable configurations of atomic or molecular approach but can interpret such approach in terms of the individual translational, rotational, and vibrational energies of the impinging molecules. With the aid of the quantum mechanics, for simple processes, the conversion of the kinetic energy of approach into the potential energy of the collisional system as a whole can already be charted on a contour map, from which the easiest path to reaction can be deduced with the facility with which the aviator can choose his airway through a mountain range with the more familiar geographical charts and maps of the regions which he traverses. The new methods provide a more intimate interpretation of the activated complex, the intermediate high energy stage in the process of reaction, and with the aid of statistical mechanics, it is now possible, as Professor Eyring will show, not only to deduce theoretically all the results of the classical kinetics, but also to indicate in what directions our previous knowledge fails and how the newer concepts provide a satisfactory interpretation of the deviations found. The work is specialized. It is a beginning in the application of the newer pictures of the atom and the molecule to the central problem of the chemist,—reaction speed and reaction mechanism.

It is for such reasons that the Division of Physical and Inorganic Chemistry proudly sponsors its symposium on this anniversary occasion. Our service to the chemistry of the future, fundamental and industrial, is to provide a finer structure of chemical theory than has hitherto obtained. We are confident that, in our efforts to provide our science with a more comprehensive theoretical basis for the mechanics of reaction, we lay the foundations for a more skillful achievement of all reactions, in laboratory or factory. The years ahead will yield rich store of chemical progress. The present achievements of synthetic organic chemistry are but a faint indication of the syntheses which yet shall be achieved. We will play our part also in such developments. The synthetic reactions of the laboratory are, in comparison with processes *in vivo*, labored and inefficient. Progress towards the goal set by vital processes in the simplicity and ease of synthesis, metathesis, and decomposition is something to which we will contribute by our more penetrating analyses. For us to scale successfully the less accessible heights, our charts of reaction path will become ever more indispensable.