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R. A. Marcus
University of Illinois
Urbana, 61801

Recent Developments in Theoretical Chemical Kinetics

In the post-war years there have been a variety of new experiments in kinetics, and these have stimulated new theoretical developments. In the present brief article I have listed some of these experiments, and considered some selected topics and new questions in theoretical kinetics.

The experiments are many and varied. They include some on the chemical physics of gas phase reactions of small molecules, some on fast reactions in solution and at electrodes, a number on unimolecular reactions, and some which might be regarded as half experiment and half theory, namely electronic computer calculations of classical mechanical collision trajectories.

The first group includes studies of crossed-molecular beams (*1*), and studies in shock-tubes (*2*), in flash photolyses (*3*), and in gaseous flow systems (*4*). In the beam investigations, the angular distribution and kinetic energy distribution of the reaction products have been measured as a function of initial velocity of reactants. At present, to be sure, almost all of the beam experiments involve alkali metal atoms as one reactant because of detection problems. The rotational energy of the products has also been estimated. In the shock, flash photolysis and flow systems the vibrational energy distribution of the reaction products has often been estimated spectroscopically. Mass spectrometers and ionic beams have been used to study gaseous ion-molecule reactions and their dependence on the ion velocity (*5*).

This "chemical physics" group of experiments has re-attracted many chemical physicists to kinetics, not only in experiment but in related theory. This work has been concerned mainly with the "physics" of chemical reactions. It has led to a closer relation between kinetics and physicists' studies on electron and nuclear scattering, as well as to studies on collisional translational, vibrational, and rotational energy transfer.

The study of fast reactions in solution (*6*) has been stimulated by the enhanced post-war familiarity of chemists with electronic instrumentation. One group of reactions studied involves only the transfer of an electron (*7, 8*). This group forms a unique one in chemistry: no chemical bonds are broken or ruptured, a circumstance which has permitted their theoretical study to be quite far-reaching and has led to a number of predicted relationships among homogeneous and electrochemical rate constants. Study of these reactions was also furthered by the post-war availability of isotopes and, to a lesser extent, by the presence of spin resonance line broadening experiments.

The unimolecular reaction study was itself a rebirth of a field that was very popular in the late 1920's until it was inundated at that time by the complexities of free radical discoveries and effects. With the new insight afforded by the next twenty years of free radical studies, various unimolecular reactions became amenable to study since 1950. Both chemical and thermal activation have been used (*9*).

In the computer field, the classical mechanical equations of motion have been integrated numerically for atoms and molecules undergoing chemically reactive collisions. With the aid of assumed potential energy functions, both bimolecular (*10, 11*) and unimolecular (*10*) reactions have been investigated.

The Theory

The 1920's and 1930's were golden years in theoretical chemical kinetics, involving applications of quantum mechanics to the mechanisms of chemical reactions and names such as Polanyi, Wigner, London, Eyring, Rice, Kassel, Hinshelwood, Hirschfelder, and others. The developments included, among others, the concept of reactive motion on a potential energy surface, activated complex theory, unimolecular reaction rate mechanism, atom recombination mechanism, and generally a more detailed insight into the nature of a reaction.

Post-war theoretical chemical kinetics has included progress in unimolecular reactions (*12*), atom recombination in the presence of third bodies (*12a*), electron transfer reactions in solution and at electrodes (*8*), inorganic (*7, 13*) and organic reaction mechanisms, gaseous ion-molecule reactions (*14*), molecular dynamics of particular reaction types (spectator and other models (*1*), vibrationally-adiabatic reactions (*15*), etc.), optical model for scattering (*1, 16*), statistical-dynamical (*17*) or statistical (*18*) theories of certain reaction cross-sections, and generalization of activated complex theory (*19*).

At one time, rate constants were the main concern of theoretical chemical kinetics, together with their dependence on temperature, pressure, molecular structure and, if they occurred in solution, electrolyte and solvent. Such is still the case in reactions in solution. In the chemical physics and computer gas phase studies mentioned earlier, reaction cross sections or other detailed properties have become a main concern. In contrast, the concept of reaction cross section is not quite as well defined in solutions as in gases and is currently not used there.

The interplay of experiment and computer-experiment has already been very fruitful for small molecule systems. The three-way comparison between experiment, computer-experiment, and approximate theory is just in its infancy but holds much promise. Two uncertainties in the approximate theory are the potential energy function and the assumed dynamics. One uncertainty in the computer-experiment is the potential energy function. The three-way comparison provides information on these uncertainties and helps extend the reach and implications of the computer-experiments in an inexpensive way. It also serves to make approximate theories "honest": In pre-computer days, often one could merely juggle a parameter to obtain an apparent fit between theory and experiments. Computers have reduced this latitude in some domains at least.

A major problem which remains to be solved in the area of computer calculations for reactive collisions is the numerical integration of the *quantum* mechanical equations of motion on any potential energy surface.

Activated Complex and More Detailed Theory

Whereas theoretical and experimental reaction kinetics was once largely concerned with rate constants, it has now also become quite concerned with bimolecular reaction cross sections, with the extent of vibrational, rotational, and translational excitation of the reaction products; and with the role of vibrational excitation of the reactants in influencing the reaction rate.

Where does activated complex theory stand here? In analyzing these problems one finds that even if one wished to apply activated complex theory to each of them, one cannot—or at least not in the usual form. The usual formulation of activated complex theory simply does not provide enough dynamical or statistical information on the molecular level to answer these questions. One is led, thereby, to inquire into the analytical mechanics of the individual reactions, as well as into the possible dynamical justification for activated complex theory.

To illustrate some of these points let us consider some features at the various levels. For rate constants, which the activated complex theory was originally formulated to calculate, one needs to know the potential energy surface (and from it the nature of the reaction coordinate) in two regions of configuration space only: the activated complex region and the reactants' region. In fact, the reaction coordinate has normally never been defined in the intermediate region. Somehow, one also assumed, there is a mysterious equilibrium between reactants and activated complexes.

Thus far, there have been only two tests of this quasi-equilibrium assumption using computer calculations. In one of these, the $H + H_2 \rightarrow H_2 + H$ reaction was examined. The results are encouraging (*11, 19b*). Computer calculations have also been used to test theories of the unimolecular reaction of a vibrationally-excited molecule, in one of which a quasi-equilibrium between the energetic molecule and activated complexes of the same energy is assumed. Here, again the results are encouraging (*10*). We return to the quasi-equilibrium postulate later.

Beyond this rate constant level, a more detailed theory is needed, even to make a calculation. For example, recently a statistical-dynamical theory was formulated for chemical reaction cross sections as a function of the velocity, the vibrational state and the rotational state of the reactants (*17*). In this theory, designed for nearly "vibrational-adiabatic" reactions, the quasi-equilibrium approximation was supplemented by postulates closer to the basic molecular dynamics. The theory leads to a simple expression for the reaction cross-section. Comparison with computer results on the $H + H_2 \rightarrow H_2 + H$ reaction yielded encouraging results without adjustable parameters.

To theorize about still more detailed properties (differential rather than total reaction cross section; excitation of vibrations, rotations, and translations of products), a still more detailed dynamical analysis is needed (*20*). Some of our own current thoughts have proceeded along the following lines.

We first recall the fact that except for some special cases there has been almost no published work on the analytical mechanics of chemical reactions (*20*). One of the difficulties in treating bimolecular reactions in the past has stemmed from the absence of a suitable coordinate system for describing in a continuous way the course of the collision. Very recently we were able to find a coordinate system which passes smoothly from one suited to the reactants to one suited to the activated complex, and finally to one suited to the products during the course of the collision (*15*). In applying these coordinates to a class of chemical reactions, use was made of a "vibrationally adiabatic hypothesis" (*21*) as a first approximation (preservation of quantum number of each quasi-periodic degree of freedom), and nonadiabatic corrections were calculated. In one type of approximation the following picture of a reactive collision emerges (*15b*).

In a head-on reaction $A + BC \rightarrow AB + C$ the BC vibration evolves into an ABC symmetric stretching vibration of the activated complex and finally into an AB vibration. The initial radial relative translational coordinate of A with respect to BC evolves into the usual asymmetric translational coordinate in the activated complex (reaction coordinate) and finally into the radial relative translational coordinate of the products. The two orbital relative translational coordinates of A with respect to BC evolve into two rotations of the activated complex and finally into the two orbital or relative translational coordinates of C with respect to AB. The two rotations of BC evolve, after some coupling with the orbital motions, into the two bending modes of a linear activated complex and finally into the two rotations of AB.

The vibrationally-adiabatic hypothesis, in conjunction with the cited coordinate system, should provide insight into problems such as the following, for the case of nearly vibrationally-adiabatic reactions: contribution of vibrational excitation to the reaction rate, accuracy of the activated complex theory (*21*), extent of vibrational excitation of the reaction products, angular distribution of reactant and product molecules in molecular scattering, extent of quantization of the various degrees of freedom in the activated complex theory, calculation of atom tunneling contribution to the reaction rate, nonadiabatic contributions (vibrational, rotational excitation), relation between classical and quantum mechanical cross-sections, and relation of threshold energy of a reaction to other properties (e.g., to activation energy).

At present, I believe, an "almost vibrationally-adiabatic" approximation has some real merit for some reactions, while for some others it should be replaced by an opposite extreme. The latter for a certain class of reactions are reactions in which the system strikes the curved portion of the usual potential energy contour diagram in skewed-axes coordinates with a high velocity. Also, it should work best for the vibrational coordinate. For the rotational-bending motion one expects at best some distribution of quantum numbers about the adiabatically determined value. Calculations in progress should reveal the actual situation.

A connection between "vibrational-adiabaticity," at least in some statistical sense, and the justification of the quasi-equilibrium postulate of activated complex theory has been recognized (*15, 21*). Here, one should not think of an actual equilibrium between reactants and activated complexes, but rather of an apparent equilibrium between reactants and only those activated complexes that are moving in a forward direction—from reactants to products. In another item mentioned above, calculation of atom tunneling contribution to reaction rate, the effects of a curvilinear reaction coordinate were calculated (*15a*) and were found to be large when the tunneling energy is appreciably below the barrier height. The usual tunneling formulae, it was found, led to too high a predicted tunneling rate in such cases.

Conclusion

We have seen a substantial increase in molecular and dynamical detail in which experiment and theory are now interested. It is, as one writer said, a type of molecular spectroscopy of chemical reactions. Answers are gradually becoming available on some of the currently used postulates, but the complete picture is not yet known. To appreciate the new developments the chemist needs familiarity with potential energy surfaces, with elements of mechanics, with coordinate systems, and with various aspects of modern collision theory.

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