

Remarks on the Generalization of Activated Complex Theory

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Activated complex theory has been very useful to chemists in their treatment of chemical reaction rates: For any given potential energy surface one can calculate the rate constant of a reaction if the assumptions of activated complex theory are correct. In effect, activated complex theory is principally used nowadays to calculate the pre-exponential factor A in the Arrhenius expression for rate constant, $k = A \exp(-E/kT)$. The activation energy E is usually too difficult to calculate *a priori* except for a few reactions.

The assumptions of activated complex theory are now being examined more rigorously than before and one should have a good idea of their correctness or error in the not too distant future, partly as a result of electronic computer calculations.

The principal assumptions of activated complex theory are (1) an equilibrium between reactants and those activated complexes that are moving in the forward direction along the reaction coordinate q , and (2) a treatment of the motion along q as being rectilinear. Several additional, usually minor approximations are also usually made (e.g., neglect of centrifugal potential on the course of motion along the reaction coordinate).

Assumption (2) has been made largely for convenience. It is an unnecessary one and has recently been removed [1], by using a curvilinear reaction coordinate and translating the usual derivation into one for which a curvilinear metric is appropriate at every stage of the derivation.

Assumption (1) is under current active investigation. Some years ago several authors [2] pointed out that if, somehow, the reacting system remained in the same quantum state for the vibrational-rotational motion, as the system moved along the reaction coordinate, a striking consequence would occur: If the distribution of quantum states of the reactants were one of thermal equilibrium then the distribution of quantum states of activated complexes moving *in the forward direction* along the reaction coordinate q would also be an equilibrium one. Since the former type of thermal equilibrium is expected to be achieved in typical experiments, the latter type of equilibrium would also be achieved then, and so assumption (1) would be justified. The condition that the system remain in the same vibrational-

rotational quantum state during the motion along q might well be called the "vibrationally-adiabatic" condition: The process would be quantum mechanically adiabatic with respect to the vibration-rotation degrees of freedom.

Clearly, the investigation of the correctness of this condition must be one of analytical mechanics — quantum mechanical or classical. The entire concept of "remaining in the same vibrational-rotational state" must be more sharply defined, as must the nature of the reaction coordinate curves throughout the configuration space. To this end, the analytical mechanics of linear collisions was investigated recently [3], with the aid of a coordinate system which passed smoothly from one suited to reactants to one suited to products during the reactive collision. The coordinate system is not one of the usual ones, that is, it is not tied to "separation of variables", but has been used in treatments of orbits of particles in accelerators.

More recently, this analytical mechanics was extended from linear collisions to collisions in ordinary space [3b]. In this case it was necessary to study in some detail the evolution of the various degrees of freedom during the course of the collision. A "vibrationally-adiabatic" approximation was used to solve the various equations of motion. This evolution may be described as follows:

In a 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 .

Extensive numerical integrations of the classical mechanical equations of motion of the atoms during the collision have been performed by several research groups, particularly by those of KARPLUS and those of BUNKER [4]. (Pioneering work was done by WALL and his collaborators [5].) An analysis [6] of the numerical studies [4a] for the $H + H_2 \rightarrow H_2 + H$ reaction provides encouraging results for assumption (1) of activated complex theory, for this reaction at least. (There are also reactions for which one would not expect the vibrationally adiabatic assumption to be valid.) Reasoning in this direction has also led to a statistical dynamical theory of chemical reaction cross-sections [7].

Nowadays, very detailed results on chemically reactive collisions are being obtained experimentally, due to the use of molecular beam techniques, to the study of light emission from exothermic reactions in flow systems and in flash photolyses, to the investigations of ion-molecule reactions, and to others. Thus, theories are needed which are much more detailed than those used for rate constants of reactions at thermal equilibrium. Indeed, these new experimental sources of information represent the main motivation for the numerical integrations and for the analytical mechanics studies.

Hopefully, from such studies one can learn about a variety of problems including (1) contribution of vibrational excitation to the reaction rate, (2) accuracy of the activated complex theory, (3) extent of vibrational excitation of the reaction products, (4) angular distribution of reactant and product molecules in molecular scattering, (5) extent of quantization of the various degrees of freedom in the actual complex theory, (6) calculation of atom tunneling contribution to the reaction rate, (7) nonadiabatic contributions (vibrational, rotational excitation), (8) relation between classical and quantum mechanical cross-sections, and (9) relation of threshold energy [8] of a reaction to other properties (e.g., to activation energy).

The potentialities for future investigators in this field are clearly considerable.

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