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THEORY OF CHEMICAL KINETICS

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Technical Scope of Research

Research is proposed in the theory of chemical dynamics where we shall study the application of Franck-Condon factors to a variety of rearrangement collisions. In the area of chemical instabilities, we propose to study the kinetics of first-order phase transitions and the formation of macroscopic structures in colloidal systems.

During the recent contract period we have made extensive progress in research in the theory of chemical kinetics. A publication list of the Principal Investigator is appended. The superscript "star" on a number on the publication list denotes research support by the Department of Energy.

A. Chemical Dynamics

1. Franck-Condon factors in studies of dynamics of chemical reactions.

The Franck-Condon approximation of treating an electronic transition in a molecular system at essentially fixed nuclear coordinates has a basic physical similarity to the chemist's intuitive and useful notion of thinking about bond rearrangements during the chemical reaction without explicit analysis of the nuclear motion. We have studied this approach in some detail in connection with relatively simple chemical rearrangement reactions. We start with the formal theory of scattering in which the reaction cross section is expressed as a square of a transition matrix. Then by applying the Born-Oppenheimer approximation and the Franck-Condon approximation, we obtain very simple expressions for the transition matrix which can, with still further simplifications, be evaluated by back-of-envelope calculations. In Ref. 120 we studied the general theory of rearrangement collisions for reactions which occur on a

simple adiabatic surface and determined the proper description of such reactions by means of a quasi-adiabatic formulation in which a curve crossing occurs. We then provide a variational method for the choice of such quasi-adiabatic surfaces so that the Franck-Condon approximation becomes most applicable. In Reference 139 we begin a study of reactions in which electronic transitions occur so that the reaction may be described by a curve crossing of adiabatic surfaces. Computationally simple, analytic formulas are developed to describe the energy dependence of quenching of electronically excited atoms by atoms and molecules. These formulas include the dependence of the Franck-Condon factors on the translational wave functions as well as the wave functions for the internal degrees of freedom. We use these formulas to evaluate the translational energy dependence of the fine structure transition cross sections for $F(^2B_{3/2}) + X \rightarrow F(^2P_{1/2}) + X$ where $X = Xe, H^+$ and H_2 . The cross sections generally increase as the initial translational energy increases. Our results agree semi-quantitatively (or better) with those obtained from other theoretical techniques. In the case of $F + H^+$ we find that the absolute cross section is sensitive to the analytic form used for the non-adiabatic coupling but our model gives the correct energy dependence. At the energies of our calculations we find only a small amount of vibrational excitation of H_2 . Finally, we use our expressions to interpret some

trends of available experimental results on the quenching of Hg ($^3P_2 \rightarrow ^3P_1$) by several molecules. We find that collisional excitation of the internal modes of the molecule becomes more important as the initial translational energy increases. However, these modes do not contribute to the quenching cross section in a statistical fashion.

We have in progress a study of the validity of the Franck-Condon approach unencumbered by other approximations. This requires numerical analysis of the transition matrix with and without the Franck-Condon approximation. We have nearly finished the work on the calculations of the transition matrix made with the Franck-Condon approximation and use for comparison exact classical and quantum mechanical calculations previously published by others. We find the Franck-Condon approximation to provide appropriate predictions of trends of behavior of the transition matrix with initial energy and gratifyingly find that the calculations are not very sensitive to choices of quasi-adiabatic surfaces given the adiabatic surface for the reaction.

We have studied the process of collision-free unimolecular decomposition of large molecules at a given total energy by means of the theory of mean first passage times. The theory is intermediate between the dynamical and statistical theories. We find that the rate

of decomposition is given in terms of a series, the leading term of which has the form used in the RRKM theory. We analyze the conditions for which this term is dominant, and find that when the molecule is large or the total energy is low or the rate of decomposition is small, our expression coincides with the phase space approach. We show that the separation of time scales (energy redistribution vs. decomposition) is large when the same conditions are met. Our analysis reduces to the Montroll-Shuler model for the decomposition of a diatomic molecule in a bath of inert atoms, in the appropriate limits. (130)

The treatment of the dynamics of many-body systems requires approximations and one of these which has been used in a number of applications is one of statistical reduction. One decides before-hand to treat a small number of degrees of freedom of the many-body system exactly and treat the remainder in a statistical fashion. Such approaches have been used in problems of spin relaxation, pressure broadening of line shapes, semi-classical theories of chemical processes and in laser processes. We have studied the problem of statistical reduction for strongly driven simple quantum systems (129).

We derive reduced equations of motion for simple quantum systems which are strongly driven by an external field and are modulated

stochastically by a coupling to a bath. In the derivation we make use of the cumulant expansion method of Kubo using two different time ordering prescriptions. We demonstrate how the choice of the ordering prescription is related to the statistical properties of the bath, once the cumulant expansion is truncated. Our equations of motion are valid for arbitrary time scale for the motions of the bath relative to those of the system and they change smoothly from the static to the Markov (motional narrowing) limit.

As examples we consider the problems of a randomly modulated and driven harmonic oscillator, and a modulated and damped 2-level system. In the Markovian limit both ordering prescription yield Bloch-type equations of motion; in general, however, the driving and modulation interfere and the different statistical properties of the bath, as determined by the two truncated ordering prescriptions, lead to different results.

We have made a suggestion on possible non-statistical behavior in laser induced chemistry (122). If the typical reaction time following laser excitation of a molecule is short compared to the time necessary for distribution of the excitation energy within a molecule then nonstatistical behavior may be expected, and this is well known. However, one may also obtain nonstatistical effects if the reaction time is much longer provided that the vibration-translation interchange

is slow. In that case the Trainor effect may become important and different vibrational modes of the molecule may have different effective vibrational temperatures. This is observed for relatively low vibrational excitation and the issue of whether this effect plays a role for high excitation necessary for chemical reaction is under discussion.

B. Irreversible Chemical Processes and Chemical Instabilities.

We have succeeded in formulating a thermodynamic and kinetic analysis of the stability and relative stability of multiple stationary states in chemical systems driven far from equilibrium (132). For given macroscopic kinetic equations we postulate that there exists an entropy state function which is maximum for the time-dependent solutions, that is concentrations of chemical species as a function of time of the kinetic equations. From that postulate we derive thermodynamic equations of motion which follow from a thermodynamic variational principle for the power dissipation and are consistent with the given kinetic equations. From the thermodynamic equations of motion we obtain necessary and sufficient conditions for stability, marginal stability, and relative stability of stationary states. The kinetic analysis is based on a stochastic approach in which we take fluctuations into account. We use the theory of mean first passage time (133) which gives a measure for the tendency of transition from

one stationary state to another. For one variable and effectively one-variable systems we can find analytic results which are in agreement with those of the thermodynamic analysis. We show that in the thermodynamic limit relative stability is determined only by the properties of the stationary states. We believe that substantial progress has been made in incorporating time-dependent behavior into classical thermodynamic formulations.

We have become interested in the important issue of the efficiency of rate processes. In our initial work on this subject we analyzed the power and efficiency of heat engines which operate subject to irreversible heat flow. The maximum efficiency of a heat engine operating between two heat reservoirs is given by equilibrium thermodynamics but is thus restricted to reversible processes and therefore to engines with zero power output. It takes infinite time to produce maximum work. Any engine that yields power operates while some natural irreversible processes take place.

First we consider a specific model, with a cycle for an ideal gas similar to that of a reversible Carnot engine ("isothermal cycle"), and find the maximum power, and efficiency at the point of maximum power (η_m), for given heat bath temperatures and compression ratio. We prove that the cycle chosen produces more power than any other conceivable cycle in the limit of large compression ratio; the derivation

is made for an ideal or van der Waals gas as a working fluid, but this is not restrictive in this limit. We use these results to obtain a general formulation, of upper bounds on power and η_m , valid for isothermal cycles to study the dependence of these quantities on the form of the law of irreversible heat conduction. We find that η_m depends only on the heat bath temperatures and the form of the irreversible rate process, but is independent of the material properties of the system. The dependence of η_m on the form of the rate process suggests the concept of "efficiency of rate processes."

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