

Theoretical Studies in Chemical Kinetics
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The research performed under this contract can best be summarized under several headings.

(a) Alkali-Halide, Alkali-Halide (MX, M'X') Exchange Reactions.

This project is being continued. A careful study of certain parameters obtained from alkali-halide crystals and used in the first surface for the KCl, NaBr were not valid. Consequently, a new method of determining these parameters from diatomic molecule data had to be developed. This has now been done and the revised surface is being compared with the original surface. The differences appear not to be very large, but some may alter the details of the reactive collisions.

Using the new method it has been possible to generate surfaces for all of the alkali halide dimers. These appear to give good agreement with the available data on dissociation energies, equilibrium bond lengths, and vibrational frequencies.¹ The calculations suggest that additional experiments to examine more systems would be worthwhile.

(b) Inversion Problem.

The method for phase determinations developed previously for particle scattering has now been extended to the scattering of electromagnetic waves.² This makes possible a novel approach to a very basic problem, namely the determination of phases from the observed crystal intensities

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in x-ray diffraction. Some previously used formulae have been derived and the new method is now being tested on model problems. Its potential utility looks highly promising.

(c) Quantum Mechanics of Scattering Processes.

The work on the H, H_2 system is continuing. Since we are in the middle of the calculation, there are no significant results to report. However, it now appears that all of the problems remaining at the beginning of the year have been solved, so that quantum reactive cross sections for comparison with the classical results should be calculated during the next year. Many persons are eagerly waiting for this comparison, which should give the first real information concerning quantum effects in reactive scattering.

(d) Transition State Analysis of Classical Trajectories.

The method for comparing the transition-state theory results with those from accurate trajectory calculations developed previously has been applied to $H+H_2 \rightarrow H_2+H$, $H+HBr \rightleftharpoons H_2+Br$, and some model systems within the linear approximation.³ It has been found that the first reaction gives good agreement for a wide range of energies, but that the other reactions yield significant deviations. A detailed analysis of these deviations shows that they arise from two types of violations of transition-state theory. For some cases (e.g., $H_2+Br \rightarrow HBr+H$) the transition-state population deviates from the equilibrium form, while for other cases (e.g., $HBr+H \rightarrow H_2+Br$), the transmission coefficient is significantly less than unity. These comparisons provide the first real quantitative test of transition-state theory, in spite of the fact that it has been used for almost forty years.

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Preliminary results for a complete three-dimensional study have also been obtained. Again important deviations from transition-state theory are found.⁴

(e) Differential Cross Sections from Classical Trajectories.

A recent crossed beam study by Fite and coworkers of the $D+H_2$ reaction has provided the first apparently reliable measure of the differential cross section and final velocity distribution for an example of the fundamental $H+H_2$ exchange reaction. Their results, if valid, thus provide a significant increase in our knowledge and permit an additional check to be made of our theoretical approach to the problem. With center-of-mass trajectory results for $D+H_2$, the conversion to the laboratory cross sections is being carried out. Preliminary comparisons show that there is excellent agreement between theory and experiment.⁴ However, an examination of the sensitivity of the laboratory results to the center-of-mass parameters has yet to be made.

(f) Other Studies.

A variety of other studies has been completed, written up for publication, and/or published. The list of papers follows.⁶⁻¹⁴

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