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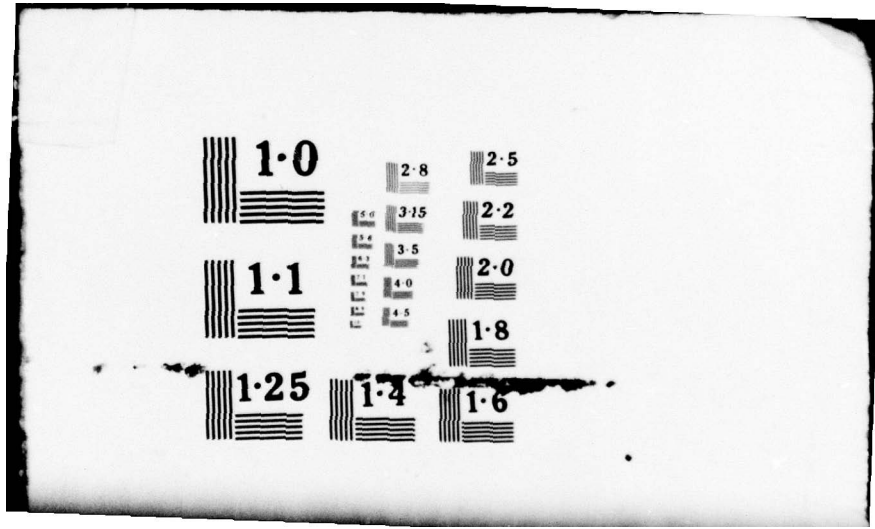
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ANNUAL SUMMARY REPORT, 1 August 1978 - 31 July 1979

High Temperature Gas Energy Transfer

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This report covers the period 1 August 78 - 31 July 79

I. Complete listing of technical reports:

1. Technical Report TR01, 7 January 1976.
Vibrational Energy Transfer in Reaction Systems at Elevated Temperatures
by B. S. Rabinovitch, D. G. Keil, J. F. Burkhalter and G. B. Skinner.

In this report a theoretical analysis was given of shock tube data for high temperature gas reactions. The data were analysed to show that collisional energy transfer efficiency appears to decrease at high temperatures.
2. Technical Report TR02, 20 April 1976
Temperature Dependence of the Arrhenius Activation Energy. High Temperature Limit by J. F. Burkhalter and B. S. Rabinovitch.

In this report a conventional approximation to the high temperature vibrational partition function is shown to be defective, and the usual high temperature expression for the Arrhenius activation is in error. The variation of the activation energy for unimolecular reactions as a function of temperature is calculated for various representative systems.
3. Technical Report TR03, 15 October 1976
Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems
by D. C. Tardy and B. S. Rabinovitch.

This report gives a comprehensive and detailed survey and analysis of energy transfer in thermal gaseous systems. The present status of the field is delineated and future areas of work indicated.
4. Technical Report TR04, 15 April 1977
On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations by S. E. Stein and B. S. Rabinovitch

This report describes an algorithm for accurate state sum and density calculations and refutes an error in the literature.
5. Technical Report TR05, 15 August 1977
Vibrational Translational Energy Transfer in Atom-Polyatomic Molecule Collisions in Thermal Reaction Systems by I. Oref and B. S. Rabinovitch.

In this report a simple theoretical model describing energy transfer probabilities is given. Conservation of angular momentum was imposed. The importance of completeness and detailed balance conditions and correction of an earlier model in the literature are illustrated. The model is applied to experimental data.

6. Technical Report TR06, 1 September 1977
Problems of Diffusion in a Low Pressure Gas Stream as Related to the Polanyi Diffusion Flame (Cloud) Method by D. G. Keil, J. F. Burkhalter and B. S. Rabinovitch.

A theoretical and experimental study was made of flow and diffusion of a reactant in a low pressure gas stream. Connection is made with earlier theoretical analysis.

The following were submitted in the period covered by the present report:

7. Technical Report TR07, 10 October 1978
Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically?
by I. Oref and B. S. Rabinovitch.

The literature is surveyed and analysed. A variety of excitation techniques including crossed molecular beam, laser, chemical activation, photochemical and thermal are considered. The answer to the title question is "yes." The relationship to the present work on intermolecular transfer is the following: multiphoton laser experiments frequently involve collisional heating of the gas. In order to understand the results, one must have a good basis for interpretation of data. In this survey, some suggested models for energy relaxation by molecular collisions are criticized and data reinterpreted in light of results obtained in this laboratory.

8. Technical Report TR08, 1 November 1978
Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane. by E. Kamaratos, J. D. Burkhalter, D. G. Keil and B. S. Rabinovitch

A study of vibrational energy transfer by the Diffusion Cloud Method has been made at temperatures from 975 K to 1175 K in the cyclopropane isomerization system. H_2 , He, N_2 and CO_2 were studied as inert bath gases. Their relative efficiencies increase in that order. Values of $\langle \Delta E \rangle$ vary from 150 cm^{-1} to 1100 cm^{-1} at 975 K. It was shown that these values decline, and the collisional efficiencies, β_c , decrease markedly with rise of temperature to 1175 K. This is only the second measurement of such a phenomenon.

9. Technical Report TR09, 15 March 1979
Collisional Relaxation of Non-Equilibrium Vibrational Energy Distributions in a Thermal Unimolecular System. Surface Collisions. by D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch

A novel, simple technique, the Variable Encounter Method, is described for obtaining information on energy transfer efficiency between a gas and a solid

in the transient region, and as a function of temperature. The method is as powerful as it is simple. Results for cyclopropane are described. Decrease in collisional efficiency $\langle \Delta E \rangle$ with rise of temperature is confirmed, and the form of the transfer probability matrix P is discovered. This method and these results are considered to be some of the most innovative and important that have ever been made in this field.

10. Technical Report TR10. 15 June 1979

Transients in Vibrational Relaxation of Polyatomic Molecules at High Temperatures by VEM. by M. C. Flowers, D. F. Kelley, F. C. Wolters, and B. S. Rabinovitch.

Extension of the VEM technique to cyclobutane is described. An exponential form of P is required to fit the data. The value of $\langle \Delta E \rangle$ declines with rise of temperature.

11. Listing of publications.

1. Vibrational Energy Transfer in Reaction Systems at Elevated Temperatures, Proceed. Tenth Internat. Shock Tube Sympos. ed. G. Kamimoto, Kyoto, 1976.
2. Intermolecular Vibrational Energy Transfer in Thermal Unimolecular Systems. D. C. Tardy and B. S. Rabinovitch, Chem. Revs., 77, 369 (1977).
3. On the Use of Exact Vibrational State Counting Methods in RRKM Rate Calculations by S. E. Stein and B. S. Rabinovitch, Chem. Phys. Lett., 49, 183 (1977).
4. Vibrational Translational Energy Transfer in Atom-Polyatomic Molecule Collisions in Thermal Reaction Systems, I. Oref and B. S. Rabinovitch, Chem. Phys., 26, 385 (1977).
5. Problems of Diffusion in a Low Pressure Gas Stream as Related to the Polanyi Diffusion Flame (Cloud) Method, D. G. Keil, J. F. Burkhalter and B. S. Rabinovitch, J. Phys. Chem., 82, 355 (1978).
6. Vibrational Energy Transfer in Thermal Unimolecular Systems by the Diffusion Cloud Method. Cyclopropane, E. Kamaratos, J. F. Burkhalter, D. G. Keil and B. S. Rabinovitch, J. Phys. Chem., 83, 984 (1979).
7. Do Highly Excited Reactive Polyatomic Molecules Behave Ergodically? I. Oref and B. S. Rabinovitch, Accts. Chem. Res., 12, 166 (1979).
8. Collisional Relaxation of Non-equilibrium Vibrational Energy Distributions in a Thermal System. Surface Collisions, D. F. Kelley, B. D. Barton, L. Zalotai, and B. S. Rabinovitch, J. Chem. Phys., 71, xxx (1979).
9. Transients in Vibrational Relaxation of Polyatomic Molecules at High Temperatures by Variable Encounter Method. M. C. Flowers, B. D. Barton, F. C. Wolters and B. S. Rabinovitch. Am. Soc. Mass. Spectrom. Proceedings, in press.

III. Current Work

The following work has been completed, but not reported, or is in progress.

1. Diffusion Cloud Method

Experiments have been completed at 975K with inert bath gases He and N₂ in the two-channel 1,1-cyclopropane-d₂ isomerization system. In this case, information on energy transfer is obtained both from the absolute rate of isomerization to propylene — as in the c-C₃H₅ system reported already (TRO8) — but independent measurements of the energy transfer amounts $\langle \Delta E \rangle$ to the bath gas is also deduced by deconvolution of the isotopic ratio, k_D/k_H . The values so obtained are in general agreement with each other and with the values reported earlier.

Work is continuing at high temperatures.

The theoretical analysis of reaction in laminar flow diffusion systems is also continuing. Some progress has been made. This work has been carried on by John Burkhalter.

2. Variable Encounter Method

Cyclopropane: a) In addition to the work reported in TRO9, additional measurements have been made on cyclopropane-d₂ by David Kelley on this system at two temperatures in an $m = 3$ reactor. The work in this reactor is now complete. A report is in preparation.

b) In another apparatus, Barrie Barton has made measurements on c-C₃H₆ in three different reactors, the results are in general agreement with the experiments of Kelley, giving slightly higher $\langle \Delta E \rangle$ values. A report is in preparation.

c) In the same apparatus as Barton, Fred Wolters and Dr. Michael Flowers have repeated Barton's pioneering work very carefully. They obtain agreement with Kelley, but on the low side. However, all the results are considered as very satisfactory confirmation of the general reproducibility of data. A report is in preparation.

These results show that a step ladder, or narrow gaussian, is not an appropriate model for the collisional transition distribution function, and that a poisson or "linear" exponential is best.

Additional theoretical analysis of VEM systems has been made and an "incubation" time is shown to be definable in terms of the fundamental quantity, the mean first passage time.

Cyclobutane. Analysis of the data reported in TR10 has continued. The down step sizes are smaller than for cyclopropane – a very interesting finding – and an exponential model fits the transition distribution well. A complete report is in preparation.

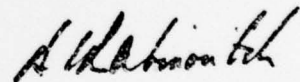
Cyclobutene. Work has started on this system which is characterized by a much smaller critical threshold than cyclobutane (~ 32 kcal vs 62 kcal).

Methylcyclopropane. Work will start soon on this species to discover the effect of variation of molecular properties on energy transfer efficiency relative to $c\text{-C}_3\text{H}_5$ and $c\text{-C}_4\text{H}_8$.

IV. Personnel

The following graduate students and fellows have been involved on this project in the period.

Barrie Barton
John Burkhalter
Dr. M. C. Flowers (Senior Lecturer, Southampton University, on leave)
David Keiley
Dr. Efsthios Kamaratos
Fred C. Wolters
Dr. Lajos Zalotai (Visiting Assist. Professor from Zeged, Hungary on U. N. Fellowship)



B. S. Rabinovitch
Principal Investigator