Book Review

Comprehensive Chemical Kinetics. Volume 39. Unimolecular Kinetics, Part 1: The Reaction Step Edited by Nicholas J. B. Green (King's College London). Elsevier B. V.: Amsterdam. 2003. xiv + 248 pp. $155.00. ISBN 0-444-50893-7.

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Unimolecular reaction dynamics has long been an exciting and stimulating field of research. This book, with its well-chosen topics and extensive references, is an essential read for any researcher wishing to enter the field or for those working in related fields who wish to get up-to-date on all the current advances.

The book begins with a beautifully written introduction by Green that provides a historic overview of the field of reaction rate theory. This overview includes the Lindemann mechanism as well as the Rice−Ramsperger−Kassel, the Slater, the Rice−Ramsperger−Kassel−Marcus (RRKM), and the statistical adiabatic channel model (SACM) theories. The presentation is mathematically rigorous, and the implicit assumptions of each theory are clearly stated. Results from the various theories are compared to experiments to highlight the shortcomings and successes of each theory.

Although venerable, RRKM theory continues to be developed and improved. In the second chapter, Klippenstein reviews the current status of research on this theory. He begins the chapter by considering the classical dynamical expression for the rate constant and arrives at current research problems in short order. The author's initial focus is to illustrate how RRKM theory can be applied from an ab initio perspective. Here, all parameters used to describe the potential energy surface are calculated on the basis of electronic structure theory. Focusing on select chemical reactions, Klippenstein pays careful attention to the level of theory and size of basis sets that are required to obtain accurate parametrizations of the surface. Current advances in the theory itself are then presented. These include the treatment of multiple barriers, quantum tunneling at the barriers, and variational enhancements to RRKM theory. The treatment of traditional RRKM theory is concluded with a discussion of methods for determining the densities of states. The presentation takes us from the harmonic oscillator-rigid rotor descriptions of molecules to the inclusion of internal rotors and anharmonicities. The final section of the chapter includes a treatment of barrierless reactions where variational treatments become essential. Flexible RRKM theory is contrasted with a reaction path perspective to introduce the variable reaction coordinate approach to RRKM theory, an approach that combines advantages of both of the former treatments. The details of implementing these variational approaches are then described in detail, perhaps too much. Given the potential energy surface, the challenge here is the calculation of partition functions and the number of states.

Recent advances include novel methods of projection for reducing the dimensionality of the phase space integrals to be evaluated. The references, although they tend to emphasize the work of the Marcus school, are excellent.

Over the past decade there have been impressive experimental and theoretical advances that now allow researchers to calculate and elucidate the nature of unimolecular dissociation lifetimes at a state-to-state level. The validity of unimolecular theories can now be tested with great rigor. The third chapter, written by Yu, Grebenshchikov, Schinke, and Hase, introduces the reader to this field of modern quantum molecular dynamics. Scattering theory is presented and used to evaluate predissociative lifetimes of small molecules. These lifetimes are then compared to corresponding experimentally measured lifetimes. Both the experiments and the theories are carefully explained. In particular, there is a good balance between the description of one-dimensional models that illustrate resonances and the mathematical treatment of them, and the description of higher dimensional scattering treatments and the computational challenges of implementing them. Experimental and theoretical results are compared to those obtained using RRKM and SACM theories via the appropriate statistical averaging. The results for HCO, DCO, HNO, HOCl, NO_2, and H_2CO illustrate the role of mixing of states and the resulting distribution of lifetimes. The review of theory extends beyond exact quantum calculations and includes a section on the utility of random matrix theory for determining lifetime distributions and the use of scattering theory for calculating product state distributions. The discussion of lifetimes is concluded with a review of the evidence for the "steps" found in measured lifetimes at the threshold for dissociation. These observed steps, which have been heralded as proof of quantized transition states, are shown to be at odds with theoretical predictions because of the large calculated fluctuations in decay rates. At the end of the chapter, the authors return to the role of mixing of states by reviewing the use of classical mechanics for calculating rate constants. The role of phase-space structures and their implications for intrinsic RRKM behavior are reviewed. Given that quantum calculations are limited to small molecules, classical simulations remain an important tool for studying reactions dynamics, and it is appropriate that this review concludes with a summary of progress in investigating reaction rates with classical mechanics. As in the second chapter, the references are superb; they are up-to-date and broadly cover the field.

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