powerful cephalometric technique. Shea contributes a thoughtful discussion of ontogenic scaling with its implications for adaptive growth, functional cranial analysis, heterochrony, genetics, taxonomy, and evolutionary transformation.

Although most of the book is concerned with scaling of morphological variables, two chapters deal with mating behavior, sexual dimorphism, and body size. Clutton-Brock reviews the changing views concerning why polygynous species tend to have greater sexual dimorphism in body size than monogamous species. Leutenegger and Cheverud find that the variance in an absolute measure of body size dimorphism is explained primarily by the variance due to body weight of the species and only slightly by mating system, diet, habitat, or activity rhythm. Their quantitative genetic analysis reveals that sexual dimorphism can evolve most readily if there is dimorphism in genetic variance rather than dimorphism in selection.

The book contains many controversial views and even some mistakes in analysis and logic. Contradictions from one chapter to the next are common, for example, concerning the appropriateness of the reduced major axis. Some of the mistaken "allometricks" that W. A. Calder III warns against in *Size, Function, and Life History* are repeated. On the whole, however, the book is an excellent addition to the literature on size and its consequences among primates.

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Quantum Chemistry

The Quantum Theory of Unimolecular Reactions. H. O. PRITCHARD. Cambridge University Press, New York, 1984. xvi, 175 pp., illus. $49.50.

Intramolecular rate processes are in some sense the simplest molecular transformations, but the detailed theory of these processes involves many conceptual intricacies. The theory of gas-phase unimolecular processes has been under active development since the pre–quantum-mechanical 1920's, but it has recently taken on a new excitement due to the stimulation provided by new laser spectroscopic investigations of intramolecular vibrational relaxation and the search for mode-selective chemistry. The RRKM theory of unimolecular processes (named for Rice, Ramsperger, Kassel, and Marcus) has become widely accepted as an essentially correct framework. This theory treats the phenomenological rate constant as arising from a twofold competition in each microcanonical ensemble of energetically activated molecules between reactive events treated by transition state theory and deactivation processes treated by a strong (or modified strong) collision approximation. This conventional theory and the new insights obtained by the current explosion of interest in the nonlinear mechanics of intramolecular vibrational relaxation are not described in detail in this book, but they inevitably form a background against which many readers will judge it.

Pritchard describes a very attractive alternative to RRKM theory, namely a master equation approach. In this approach one deals in principle with state-to-state processes rather than microcanonical ensembles, although in practice coarse-graining approximations may be used to recover the microcanonical level of description. The basic entity of the master equation approach is the matrix of state-to-state rate constants. Pritchard shows clearly how the phenomenological rate constant is related to an eigenvalue of the rate matrix, and he shows how simple approximations to the reaction rates and energy transfer rates may be used to calculate the basic physical observables on which he concentrates, which are the rate constants for thermal reactions in small molecules and their temperature and pressure dependences.

What are the advantages of the master equation approach? It is a self-contained and general theory formulated in terms of transition rates between discrete states that may consistently be labeled with the most fine-grained information that is available concerning the quantal state. Any approach that tries to deal with mode selectivity will eventually gravitate to something very similar to what Pritchard has described here. State-to-state rate constants provide a more detailed picture of "what is really happening" than do microcanonical rate constants.

What are the disadvantages of the approach? Although we often want to allow for more mode specificity, we know that under most circumstances it is hard to observe, which supports the economical assumption that there is complete statistical mixing in each microcanonical ensemble. The master equation approach allows for the introduction of an almost unlimited number of parameters in the state-to-state rate constants; there is usually not enough information available to pin down all these rate constants. There are several possible responses to this difficulty, including reverting to the terser RRKM prescription or reverting to the simplest possible coarse-grained rate-matrix parametrizations for practical applications to most systems and giving a high priority to research aimed at obtaining the missing information for detailed treatments.

Pritchard makes about as strong a case as is possible for the second response; he has organized the material logically and has succeeded in making the presentation both more coherent and more elegant than the presentations in the original literature. In addition to making a strong case for the second response, he seems to reject the first response as unacceptable. He appears to have two primary reasons. First, he considers the idea of a transition state to be "a crutch" that often leads to "a considerable overelaboration of experimental results" and to which we should "resort" only if there is no other approach available. Second, he considers RRKM theory to suffer from fatal disabilities in that it sometimes predicts volumes of activation smaller than dissociative volume changes at high pressure. Many others, dating back to Wigner, consider a transition state to be a phase space hypersurface upon which one can build a well-defined economical description rather than an overelaborate one, although it is hard to use in a quantum mechanical world. I do not find Pritchard's references to volumes of activation to be an adequate reason to abandon RRKM theory. First of all, the volume of activation refers to a transition state species that is missing one degree of freedom, and it is very dangerous to compare it to real volume changes. Second, recent work aimed at incorporating internal frictional effects into the transition state theory of high-pressure reactions shows promise as a way to extend that kind of theory beyond its original validity limits.

Another problem with Pritchard's arguments against the idea of a transition state is that he errs in assuming that vibrational periods are independent of quantum number, which is true only for harmonic oscillators. On the basis of an argument that involves this error, Pritchard seems to conclude that the potential surface in the vicinity of the reactant's equilibrium geometry is more important than that in the vicinity of the transition state. Here again I disagree.

Of course, one doesn't have to be convinced that the first response is unacceptable in order to appreciate a clear and balanced treatment of the second one. Many of us are willing to use both

RRKM and master equation approaches, or even a combination, depending on the application.

There are several subjects about which Pritchard holds unconventional views, and a strength of his book is the stimulating and clear way in which he presents these issues. An example is the importance of long-range interactions for intramolecular vibrational relaxation even in low-pressure systems. It is very useful to see a detailed exposition of what we can and cannot infer about intramolecular vibrational relaxation from completely thermal rate measurements, although many readers (and perhaps the author) will not be satisfied with the eventual invocation of a phenomenological "stirring" process. I also disagree with Pritchard's view, which is apparently still quite conventional, that tunneling contributions to chemical reactions are only rarely important. I would say they are probably important at room temperature whenever a reaction has an intrinsic barrier of more than a few kilocalories per mole and a significant hydrogenic component in the reaction coordinate. Pritchard seems too willing to accept a simple expression (his eq. 4.9) that makes the microcanonical rate constant vanish at a threshold equal to the high-pressure activation energy, especially since this is obtained by the notoriously ill-conditioned inversion of a thermal rate expression.

I hope many potential readers will not pass this book by because it doesn't include their most hallowed references reporting work that takes other approaches to unimolecular reactions. If they do, they will miss a clearly written, although idiosyncratic, account of a subject long overdue for a cohesive treatment in monograph form.

The master equation approach treats a rate process in terms of coupled kinetic equations for the time-dependent concentrations of molecules in individual quantum states. These coupled equations can always be solved by numerical integration and can sometimes be solved by eigenvalue-eigenvector methods or analytically. The associated numerical problems, once considered a serious impediment to the use of this approach, have been greatly ameliorated in the last few years by the general availability of convenient high-speed computers. For this reason, and because of very recent work extending the eigenvalue approach to non–first-order processes, I think we can expect a great increase in attention to master equation approaches in the coming years.

The two most widely cited books on the transition state approach to unimolecular reactions are by Robinson and Holbrook (*Unimolecular Reactions*, Wiley-Interscience, 1972) and Forst (*Theory of Unimolecular Reactions*, Academic Press, 1973). Despite their age both books are far from outmoded. It is a shame that Wiley let the former go out of print several years ago. The present book promises to be an instant classic, and I hope Cambridge University Press will keep it available for decades at least.

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The Liquid State

Theory of Molecular Fluids. Vol. 1, Fundamentals. C. G. GRAY and K. E. GUBBINS. Clarendon (Oxford University Press), New York, 1984. xiv, 626 pp., illus. $79. The International Series of Monographs on Chemistry, 9.

In the 1960's and '70's, methods of computer simulation joined with theory and experiment as invaluable tools in the study of the liquid state. With an attack on the subject on these three fronts, progress has been very rapid. The considerable advances up to the mid-1970's were put into context in the superb monograph *Theory of Simple Liquids* by Jean Pierre Hansen and Ian R. McDonald (Academic Press, 1976). But as that monograph went to press, developments beyond the realm of simple atomic fluids were already making incomplete the story it told. In particular, the ideas about packing effects, perturbation theory, and fluctuating forces, so useful in attaining an understanding of the structure and dynamics of simple liquids like argon, were beginning to be successfully applied to the more complex polyatomic molecular fluids. Until now, however, no monograph has appeared that describes the advances that have been made in our understanding of this aspect of the subject. Volume 1 of *Theory of Molecular Fluids* attempts to fill this gap. In an apparently tireless effort, the authors have compiled thousands of citations to the literature, with historical perspectives and pithy quotations from many of the classic papers in the field.

To judge the value of the book, it is helpful to consider the physical issues that distinguish molecular fluids from atomic noble-gas liquids. In particular, the constraints imposed by the chemical bonding of atoms in molecules introduce a variety of length scales incommensurate with the van der Waals distances characterizing intermolecular interactions. Further, the absence of spherical symmetry in molecules implies the presence of permanent electrostatic moments. These features can conspire to produce cooperative macroscopic phenomena such as dielectric effects and also phase transformations involving interesting changes in symmetries. Liquid crystallinity is one of a variety of examples. At the microscopic level, these features can produce short-ranged order or intermolecular liquid structure that is far more intricate than that encountered with simple fluids, the latter being characterized by only one length scale, the van der Waals diameter of an atom.

Ultimately, the precise description of these phenomena requires formulations of intermolecular potential models and methods for analyzing the spontaneous fluctuations as influenced or prescribed by the interactions. At present, there is no consensus concerning the best approach to this formulation, and the "best" way may be system-specific. One popular approach, however, is the one that provides the theme of Gray and Gubbins's book. It is based upon the semi-invariant analysis of intermolecular interactions and structure. At its simplest level, this approach expresses the deviations from spherical or radial symmetry in pair interactions and correlations in terms of expansions in spherical harmonic functions or the Wigner rotation functions. It is a particularly powerful perspective when dielectric effects driven by long-ranged dipolar interactions are under consideration. It is also very useful in the parameterization of thermodynamic perturbation theories for the equations of state of molecular liquids and liquid mixtures. Unfortunately, the semi-invariant approach has proven less satisfactory in treating the nature of short-ranged order (that is, the local relative arrangements of atoms) in fluids. The reason is rather obvious: molecules are composed of atoms bound together and forming highly nonspherical objects. Descriptions of local structures in dense materials must account for these shapes, and it is impossible to describe molecular shapes with a small number of terms in the multipole expansions of the semi-invariant analyses.

Theories in which molecules are treated as collections of atoms have been successfully formulated and applied to many systems. In addition to providing a framework for discussing local intermolecular structures, this atomistic approach to molecular fluids leads natural-