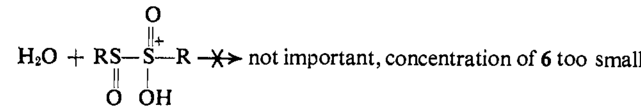
We suggest that the reason such an acid-catalyzed mechanism can make a contribution to the hydrolysis rate of **2a** but not to that of **1** is because sufinyl groups are so much more basic than sulfone groups.[12] Thus, at a given acidity, the equilibrium concentration of **5** is orders of magnitude larger than the equilibrium concentration of sulfonyl-protonated **1** (**6**). As a result, the acid-catalyzed reaction in eq 4 can compete with the uncatalyzed hydrolysis of **2a**, but this is not possible with **1** because of the extremely minute equilibrium concentration of **6**.

The important general mechanistic significance of

The value observed is in the range considered[11] typical for an A2-type process of the sort shown in eq 4.

(11) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83,** 3207 (1961); J. G. Pritchard and F. A. Long, *ibid.*, **78,** 6008 (1956); **80,** 4162 (1958).

(12) See ref 3a for a discussion of this point.



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this result is that it suggests that the function of acid catalysis in these and related substitutions at sulfinyl sulfur is *protonation of the leaving group*, and *not* protonation of the sulfinyl group at which substitution is to occur. Otherwise there would be no reason for the different behavior exhibited by **1** and **2**.

The chemistry of sulfinic anhydrides and their possible interconversion with sulfinyl sulfones is currently under intensive study.

John L. Kice, Katsuyata Ikura

Department of Chemistry, Oregon State University
Corvallis, Oregon 97331

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Book Reviews

Theory of Energy Transfers and Conversions. By FEDERICO GRABIEL, Space Systems Division, Hughes Aircraft Co., Culver City, and Loyola University, Los Angeles, Calif. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1967. xii + 217 pp. 16 × 24 cm. $10.95.

In this small volume, Federico Grabiel has provided a novel linear theory of energy transfers and conversions, which includes, as special cases, the second and third laws of thermodynamics. The development is axiomatic, with definitions and postulates induced from experience, and theorems deduced with the aid of elementary set theory and calculus. The chapter headings convey the flavor of the book: 1, Introduction; 2, Mathematical Preliminaries; 3, The Fundamental Theorems on Functions of State; 4, The Second Law of Energy Transfers and the General Gradient Law; 5, The Convertibility Equation. The Increment of the Associated Extensive Parameter or Coparameter, Its First Two Properties: Additivity and Extensiveness; 6, Interpretation of the Coparameter Increment; 7, Evaluation of the Irreversible Production of the Coparameter: Parasitic Conversions. Frictional Dissipation; 8, Evaluation of the Irreversible Production of the Coparameter: Internal Gradients; 9, The Finite Propagation Hypothesis and the Law of Degradation; 10, Third Fundamental Property of the Coparameter: Function of State; 11, Irreversible Production of the Coparameter: Internal Gradients—General Case; 12, Criteria for Equilibrium; 13, The Physicochemical Potentials; 14, The Fundamental Physicochemical Equation; 15, General Conditions for Equilibrium; 16, Processes in the Neighborhood of Absolute Zero Value of an Intensive Parameter; 17, The Process Velocity and the Affinity Function. The Direction of Time; 18, Systems Far from Equilibrium. Negative Absolute Values of the Intensive Parameter.

The contents are highly original, and Grabiel obviously has keen insight into his subject matter. It is, therefore, rather unfortunate that he chose to minimize the number of examples, omit exercises, and select his few concrete illustrations from phenomena other than heat. The net result is a succinct, fairly abstract text, faintly reminiscent of the difficult writings of Gibbs, in that the meaning is sometimes difficult to decipher. For example, on p 45 we find: "The symbol A_0^p, called the *absolute zero value of the parameter p*, represents the lowest *p*-value that can be *conceptually predicated* of the whole universe $U = \mathcal{S} \cup \mathcal{E}$." The four appendixes, however, were written in a more leisurely style, and the reviewer found considerable pleasure in reading them.

Thus, one criticism of the book is that it is too tightly constructed. Another criticism, common to all formal treatments of physical subjects, is that statements obvious to the author are not necessarily self-evident to others. By the way of illustration, let us consider the important Definition 4-1: "A δ_p-*set* (or δ_p-*cell*) is the smallest subsystem (or subset) of $\mathcal{S}$ at which property p is measurable." It is not clear to the reviewer that such a smallest subsystem is always well defined. He also wonders whether it is possible to formulate properly the definition without extended consideration of the meaning of the term "property" and of the role of experimental uncertainties.

In summation, the "Theory of Energy Transfers and Conversions," as developed by Grabiel, merits serious study by scholarly students of thermodynamics. However, the reviewer fears that, because of its unfamiliar format and closely knit structure, it will suffer the temporary fate of Gibbs' treatise on statistical mechanics, which was said by Poincare to be a "little book, little read, because it is a little hard."

Richard J. Bearman

Department of Chemistry, University of Kansas
Lawrence, Kansas 66044

Statistical Mechanical Theories of Transport Processes. By ROBERT M. MAZO. Pergamon Press Inc., 44-01 21st St., Long Island City, N.Y. 1967. xiii + 166 pp. 15.5 × 23 cm. $9.50.

The kinetic theory of dilute gases was brought to a theoretical high point by the studies of Enskog and of Chapman in the first quarter of this century. This work, which assumed the validity of the Boltzmann equation, developed algorithms for the calculation of the thermal conductivity, viscosity, and other transport coefficients in terms of the properties of the intermolecular pair potential. In the period 1920–1946 little of fundamental significance was added to the theoretical structure, and, aside from an isolated study by Enskog in 1922 and the model activated state theories of Eyring, little attention was devoted to transport phenomena in dense fluids. Interest in the theory of transport phenomena was stimulated by the publication, in 1946, of a paper by Kirkwood on the general theory of irreversible processes. Since that time, many investigators have made contributions that have greatly deepened our understanding of the nature of irreversible phenomena, have provided formalisms for the calculation of transport coefficients as general as the partition function formalism for the calculation of the free energy, and have provided models of varying degrees of sophistication (usually solved approximately) which describe with moderate accuracy the steady-state transport coefficients in a dense fluid. The monograph by Mazo touches on most of these subjects. Throughout the treatment is clear and clean, with the approximations made stated openly and their meaning discussed. The first three chapters deal with macroscopic relations, general dynamical theorems (including a good but brief discussion of the Poincaré recurrences of dynamics), and the definition and equations of evolution of the hierarchy of distribution functions defining the state of a fluid. Both the classical and quantum mechanical cases are considered in these chapters. In Chapter 4 Mazo shows how the Boltzmann equation, descriptive of transport in a dilute gas, may be derived by use of the classical "balance in phase space" argument. The chapter also includes a brief description of the Chapman–Enskog procedure for solving the Boltzmann equation. Chapter 5 probes more deeply the meaning of the Boltzmann equation and the conditions sufficient to derive it. The Kirkwood derivation (using time coarse graining) is given as an example of a derivation from the hierarchy equations of statistical mechanics, but the work of other investigators is also discussed. In Chapter 6 the Enskog theory of the dense hard sphere gas and the Uhlenbeck development of the Bogoliubov theory of the same system are discussed. The author was able to add, in proof, a brief description of the divergence of the density expansions of the transport coefficients, a recent discovery of much theoretical interest. Chapter 7 develops the theory of Brownian motion as a preparatory step to the description of the available theories of transport in a dense fluid (liquid). Chapter 8 describes the general relationships between fluid structure and the stress tensor, heat flux, etc., and Chapter 9 describes the calculation of transport coefficients for liquids. Finally, Chapter 10 considers the correlation function representation of transport coefficients, due largely to Green and Kubo, and Chapter 11 covers the general theories of Prigogine and coworkers and of Zwanzig.

It is my opinion that Mazo's book is one of the best elementary presentations of this field of statistical mechanics. All those who take the trouble to study it will be rewarded with a greater understanding of the nature of irreversible processes as well as with considerable physical insight into the molecular dynamics characteristic of dense fluids.

Stuart A. Rice
The James Franck Institute
The University of Chicago, Chicago, Illinois