

catalysts, simple and mixed oxides, gels). Scholder's section on Hydroxo-Salts is essentially a review of the preparative aspects of his own researches. The material on Iso- and Heteropoly Acids by the late G. Jander and one of his students, Gruettner, goes beyond the vanadium, molybdenum, and tungsten iso- and heteropoly derivatives to mention the polysulfates, -chromates, -arsenates, -tungstates, and -niobates, but neglects entirely any discussion of the polyphosphates and polymetaphosphates. The section by Seel on carbonyls and nitrosyls is devoted almost entirely to the preparative accomplishments of the Hieber school. The fifth and final section on alloys and intermetallic compounds by Brauer represents an excellent compilation on high temperature experimental methodology, with illustrative procedures for preparation of silicides, borides, and amalgams.

Professor Brauer is to be commended for his efforts in editing (and himself contributing to) this very excellent treatise on preparative inorganic chemistry. Its scheduled appearance in English will enhance its value to American chemists.

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**Zone Electrophoresis in Blocks and Columns.** By H. BLOEMENDAL, Department of Biochemistry, Antoni van Leeuwenhoekhuis, The Netherlands Cancer Institute, Amsterdam (The Netherlands). American Elsevier Publishing Company, Inc., 52 Vanderbilt Avenue, New York 17, N. Y. 1963. viii + 219 pp. 13.5 × 19.5 cm. Price, \$6.50.

This is a good book. It is for the user of electrophoresis—the migration of solute with respect to solvent in a d.-c. field. "Zone" refers to the arrangement in which the space occupied by the initial sample is narrow compared to the distance available for electrical migration. Omitting only paper and agar gel subtypes, the author covers block, gel (starch, silica, and polyacrylamide), continuous, column, and density gradient techniques. These are each deftly treated in categories of apparatus, electrodes, preparation of supporting medium, introduction of sample, the run itself, influence of temperature and electroosmosis, location of the resolved zones, recovery, evaluation, and applications.

The 444 references appear to be complete through 1961 with a few from 1962. They are especially well cross-indexed and described appropriately.

It might have been better to indicate in the title that this is a practical book, for there is no theory to speak of, except as it pertains to engineering design. Often the theory as listed is so sketchy as to be misleading. For example, in the review of droplet sedimentation the explanation given on page 160 is reversed. Sucrose diffuses into the sample zone faster than protein diffuses out. The tendency to an inverted density gradient because of the additional sucrose leads to a stream of droplets originating from the lower boundary.

Nevertheless, the practicality of the text is superb. Not only are there many pictures and diagrams of commercial equipment and its operation, but there are excellent descriptions of simple, inexpensive apparatus made from ordinary items found in any laboratory. There are many tables giving working conditions for numerous chemical and biological substances and for the various supporting media; yet the book is small and compact.

The monograph fills a vacancy left by other publications and can be recommended as practical reference in a physical biochemistry course and as a laboratory manual for those using electrophoresis.

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**Thermodynamics of Small Systems, Part I.** By TERRELL L. HILL. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1963. 171 pp. 16 × 24 cm. Price, \$4.95 paper, \$9.00 cloth.

The fundamental importance of classical thermodynamics to the physical chemistry of matter in bulk is that it places ex-

perimental measurement within the context of a comprehensive deductive scheme, whose assumptions are clearly stated. To an increasing extent, quantitative research activity has become directed toward matter in states of greater subdivision (*e.g.*, colloids, powdered absorbents, dilute macromolecules) than was the case during the early years of thermodynamics. Professor Hill has anticipated the resulting need for extension and generalization of the usual thermodynamic concepts to include description of small systems. This book is the first half of an exposition of that extension.

The dominant feature of small system thermodynamics is that quantities such as energy and entropy, which are extensive in character for macroscopic systems, will exhibit nontrivial size variations for small systems. In this manner, system size itself becomes an interesting thermodynamic variable (even though it may only indirectly be subject to change, for example, by examining a sequence of colloidal suspensions with varying size distributions). Accordingly, considerable emphasis is given in this text to isolating these nonextensive deviations, and to deriving those thermodynamic identities that are important for small systems, but which are either lacking in the usual macroscopic formalism, or which reduce to trivialities in that limit.

The author devotes a good deal of effort toward distinguishing the operational differences between the various "environments" in which the small systems are immersed, and by which one may control particle and energy interchanges with the small systems, and exert stresses. Although it is pointed out that the thermodynamic relations may be derived once and for all without any reference to particular environmental variables, it was deemed important to handle each case separately, since the magnitudes of various thermodynamic properties are not the same in each case (though the small system thermodynamic relations remain invariant), and since the quantities have differing experimental significances when they are fixed or can fluctuate. Of the six chapters included in this first installment, four are devoted to specific environments.

The major fraction of the examples given by the author have come not from experiment, but from statistical mechanical theory, where it is relatively easy to construct model small system partition functions, and to effect at least approximate evaluations of the thermodynamic quantities, with results that explicitly show size dependence. Lattice gases and model polypeptides undergoing simplified helix-coil transitions are called upon repeatedly as illustrations. Indeed, it seems fair to say that this development of small system thermodynamics was largely motivated by recent statistical mechanical theory, in a way historically that classical thermodynamics could not have been comparably motivated.

Two particularly interesting applications of small system thermodynamics covered are chemical and phase equilibria (Chapter 5). In the case of the latter, the author remarks that even though phase change in its ordinary interpretation (discontinuities in certain thermodynamic functions) cannot exist here, extrapolation procedures can identify vestigial "phase change," and lead to novel "equal-areas" constructions. Some model calculations are included by way of estimating rate of convergence to macroscopic first-order transition behavior with increasing size.

Assuming that the soon-to-be-available second part of this exposition resembles the first in stress and style (as is indicated by the reprinted paper, included at the end of this volume, from which both parts stem), the result will amount to a systematized handbook of available knowledge on small system thermodynamics. It is thus not a source of scintillating light reading for graduate students or mature scientists with casual interest. Workers in the fields of colloid and protein chemistry, as well as those concerned with surface films (systems small in at least one dimension), however, should give the subject of this book a serious perusal, since it may harbor potentially useful tools. Assuming that aggressive exploitation of small system thermodynamics by both theoreticians and experimentalists develops, it seems reasonable to look forward to a combined second edition of "Thermodynamics of Small Systems" with new quantitative examples taken directly from experiments on real systems.

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