

$A_p > A_m$ (20, 13 and 7 c.p.s.) while the H-F coupling constants are $A_o > A_m > A_p$ (8.5, 6.5 and 2.2 c.p.s.).⁸ Further experimental and theo-

(8) C. H. Holm, "Structural Applications of Radiofrequency Spectroscopy," Ph.D. Thesis, University of Illinois, 1955; to be published.

retical studies of the H-H, H-F, and F-F coupling constants are in progress.

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BOOK REVIEWS

Principles and Problems in Energetics. By J. N. BRØNSTED. Translated from the Danish by R. P. Bell, Balliol College, Oxford University. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y., 1955. vii + 119 pp. 15.5 × 23.5 cm. Price, \$3.50.

In this book the author criticizes the classical presentation and some of the concepts of classical thermodynamics, gives a number of quotations from a great variety of authors to show that the concepts of heat, work and entropy are unsatisfactorily developed and presents an alternate development with special prominence to a generalization of the concept of work. In this generalization, the classical work done and the capacity of the system to do work are combined, so that, in a reversible process, Brønsted's "loss of work," $\Sigma \delta A_1 = 0$.

Brønsted develops the concept of entropy rather differently from what he calls the classical development, stressing in particular the entropy production in an irreversible process. In addition to his generalization of the concept of work, he now writes $T\delta S = \delta Q$ (p. 56) in which δS is the entropy production in the irreversible process, and δQ is a new quantity which Brønsted defines as the "energetic heat evolution." With these radical redefinitions of work and heat, Brønsted obtains the at first sight startling conclusion that the conversion of heat into work, as in the heat engine, is impossible. Work is undeniably obtained, but since he has lumped classical work and the capacity to do work in his "work," and a system of two reservoirs at T_1 and T_2 , respectively, can be made to do work, this system obviously possesses the capacity to do work, and the work actually done plus the remaining capacity to do work is unchanged in a reversible process.

The general development of his concepts, along with criticisms of the "classical" viewpoints, and those of Carathéodory and Born, as shown by carefully selected quotations, occupy the first two-thirds of the book; the last third is devoted to applying these concepts to a number of specific cases, of which the greater part, the consideration of the bimetallic thermolement and of the electrochemical cell with the electrodes at different temperatures, involves the assumption that the irreversible heat flow does not produce thermodynamically unpredictable disturbances.

Because of the reputation of the author, I commenced reading this monograph with anticipation of great pleasure and satisfaction, but ended it with a feeling of disappointment. To justify the presentation of a viewpoint different from that of classical thermodynamics, Brønsted quotes from a great variety of authors, including Mach and Planck, indicating that the concepts of heat and work are vague and unsatisfactory. Some of the sources quoted seem too unimportant to make his points, and it seems surprising that he makes no reference to Lewis' viewpoints,¹ particularly since his development of entropy is somewhat similar to that of Lewis, and the vagueness that he complains of in the use of heat and work is absent from Lewis' developments, where a gain of energy by means of thermal conduction or radiation is called heat absorbed, and a loss of energy by *other methods* is called work done. It is only energy *changes* during a *process* which deserve such dis-

(1) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

tinctions; the energy of a mole of a chosen gas at 25° and 1 atmosphere is the same whether it attained this state by contact with a thermostat at 25°, by reversible compression from a lower temperature and pressure, or by any other process, reversible or irreversible, and it does not appear profitable to apportion this energy into "heat" and "work." In Brønsted's scheme, the interdiffusion of one mole of helium and one of neon (both here assumed perfect) at constant temperature would involve a "loss of work" equal to $2RT \ln 2$, and a like "energetic heat evolution," although no work in the ordinary sense has been done, and no energy, thermal or otherwise, has been exchanged with the surroundings, nor has the kinetic energy distribution amongst the molecules been altered.

Admitting that one can operate without logical contradictions with Brønsted's quantities (although with what seems unnecessarily roundabout bookkeeping of energy quantities), I strongly object to his appropriating the words *work* and *heat* for them. Too frequently scientists have "generalized" some older term until it became useless. A prime example is *air* in which case we were finally rescued by the invention of the word *gas*. If a new concept is developed, it should be given a new and distinctive name.

In spite of my disagreement with Brønsted's general thesis, I recommend the book to all serious students of thermodynamics and especially to teachers of the subject, for even if they reject his point of view they will be stimulated to re-examine and logically justify their own.

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Advances in Carbohydrate Chemistry. Volume 10. By MELVILLE L. WOLFROM, Editor, and R. STUART TIPSON, Assistant Editor. Academic Press, Inc., Publishers, 125 East 23rd Street, New York 10, N. Y., 1955. xx + 437 pp. 15.5 × 23 cm. Price \$10.50.

With the advent of Volume 10, the utility of this well-established series to the practicing carbohydrate chemist is significantly enhanced. The present volume continues the exemplary tradition of its predecessors in providing an array of well-written, thorough and timely surveys on topics of interest to carbohydrate chemists in particular and to organic chemists in general.

The present eight chapters cover a broad range of interests. In "The Stereochemistry of Cyclic Derivatives of Carbohydrates" J. A. Mills summarizes and applies concepts of conformational analysis to the stability and chemistry of a number of carbohydrate derivatives. W. W. Binkley's survey of "Column Chromatography of Sugars and Their Derivatives" provides for the practitioner a useful complement to the treatment of paper chromatography which appeared in the previous volume. The preparation, properties, reactions and uses of several important classes of carbohydrate derivatives are delineated in chapters on "Glycosylamines" (G. P. Ellis and J. Honeyman) and "The Glycosyl Halides and Their Derivatives" (L. J. Haynes). The scope, mechanism and details of "The Amadori Rearrangement" are summarized by J. E. Hodge, and extensive Tables on "The Methyl Ethers of the Aldopentoses

and of Rhamnose and Fucose" and "The Methyl Ethers of D-Galactose," provided by G. G. Maher, bring previous surveys of these carbohydrate classes up to date. "Polysaccharides Associated with Wood Cellulose" by W. J. Polglase provides information on the carbohydrates associated with wood and wood cellulose preparations, and "The Chemistry of Heparin" by A. B. Foster and A. J. Huggard describes the history, isolation, purification, structural data and the chemical and physiological properties of this important anticoagulant.

Several desirable practices, instituted earlier in the series, are continued in the present volume. Extensive Tables of Physical Properties of pertinent derivatives are given at the ends of the several chapters where this is appropriate. A complete list of the topics covered in previous volumes is appended after the extensive index, and frequent references to these earlier chapters prevent undue duplication when certain of the material under discussion has already been surveyed. Another salutary policy is continued by E. L. Hirst and A. G. Ross, who provide a biographical sketch of the late Professor E. G. V. Percival, whose untimely death in 1951 deprived carbohydrate science of one of its most productive investigators.

The present volume meets fully the standards of excellence which have come to be expected of the series, and most assuredly belongs on the carbohydrate chemist's bookshelf beside its predecessors.

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Kinetic Theory of Liquids. BY J. FRENKEL. Dover Publications, Inc., 920 Broadway, New York 10, N. Y. 1955. xi + 488 pp. 13.5 × 20.5 cm. Price, \$3.95 cloth, \$1.95 paper.

This book is very interesting reading and provides a great deal of food for thought. It was first published in 1946 by the Oxford Press and Dover deserves a great deal of credit for having reprinted it to sell for a modest price.

Frenkel, who died quite recently, was one of the greatest theoretical physicists of our generation. His books on electricity and magnetism and quantum mechanics are classics. He had a great deal of experience in the study of the structure and properties of crystals. At various times he worked on the optical, magnetic and electrical phenomena in crystals; the theory of fusion; order-disorder phenomena; lattice defects and their migrations; etc. Much of his theory of crystalline phenomena is included in the present book. He thought of a liquid as being essentially a crystal with long range disorder and used much of his knowledge of crystals to explain the parallel phenomena in liquids. This viewpoint is in sharp contrast to that of so many of the people who are currently working on the theory of liquids and regard a liquid as a very dense gas. Since a liquid is intermediate between a gas and a crystal, there will always be this conflict of viewpoints and the contrast is very stimulating.

I am amazed at the breadth of topics considered in this book.

Chapter I, Real Crystals at Elevated Temperatures: Evaporation; hole formation; dissociation; lattice distortions; diffusion of impurities; electrical conductivity and optical properties.

Chapter II, Perturbations in Mixed and Molecular Crystals: Order-disorder; distant and local alteration order; extension of Bragg-Williams theory; thermodynamical theory of order phenomena; order in dipole crystals.

Chapter III, Theory of Liquids and Mechanism of Fusion: Relation between solid and liquid states; mechanism of melting; local order in liquids; Kirkwood's free volume

theory; temperature dependence of the rigidity of a crystal; relative stability of solids and liquids.

Chapter IV, Heat Motion in Liquids: Various theories of viscosity and rigidity of liquids; propagation of ultrasonic waves through liquids; the equations of hydrodynamics.

Chapter V, Orientation and Rotational Motion of Molecules in Liquids: Various theories of rotational Brownian movement with and without electric fields; flow by refraction; scattering of light; cybotaxis.

Chapter VI, Surface Phenomena: Mono- and poly-molecular films; cohesion between molecules; orientation of molecules in the surface layer; dependence of surface tension on temperature.

Chapter VII, Kinetics of Phase Transitions: Vapor liquid equilibria; nucleation; crystal growth.

Chapter VIII, Properties of High Polymers: External and internal bonds; self-dissociation of dissolved substances; solutions of high polymers; statistics and kinetics of configuration of long chain polymers in solution; the mechanical and thermodynamical properties of rubber-like substances.

Each of these topics is discussed in a simple and yet deeply penetrating fashion. You may disagree with Frenkel, but it is not wise to disregard him. I believe this book should be particularly useful to a wide variety of chemists. The ideas which Frenkel has expressed will serve as seeds for a great many basic and applied developments in chemistry.

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Methoden der Organischen Chemie. (Houben-Weyl). **Physikalische Methoden.** Band III, Teil 1. By EUGEN MÜLLER (Editor). Georg Thieme Verlag, (14a) Stuttgart, Herdweg 63, Germany. 1955. xxix + 954 pp. 18 × 26 cm. Price, DM 162, —.

The old "Houben-Weyl" contained in the first of its four volumes a number of sections dealing with the determination of physical properties of organic molecules. With the appearance of the volume under review, the new "Houben-Weyl" completes its treatment of the same theme, to which two entire volumes are devoted, impressive testimony to the increased availability and popularity of physical tools for the organic chemist.

The volume begins with two sections of greatest importance for the chemist inclined toward theoretical considerations: thermodynamic methods and kinetic measurements. These chapters are followed by discussions of the determination of the usual physical properties: density, solubility, vapor pressure, molecular weights, surface tension, and calorimetric data. A very useful and praiseworthy addition following these discussions is the introduction to statistics of errors, fiduciary limits, averaging of values, etc.

The rest of the volume is devoted to microscopy, study of liquid crystals, mass spectrometry and use of isotopes.

Whereas an American reader will have no difficulty in finding discussions of comparable excellence and, because of references to locally available apparatus, possibly greater usefulness, in the indigenous literature, he may find the volume under review unique in possessing a chapter by G. Briegleb devoted to the "Study of molecular shape with the aid of space models and to-scale atom models." Perusal of the material presented by one of the originators of the Stuart-Briegleb models is likely to enable the reader to make more intelligent and more fruitful use of his set of models.

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