

Ga[GaBr₄] are better than GaCl₂ and GaBr₂; the SbCl₂F₃ may be a mixture of SbCl₃ and SbF₃; on page 879 the correct formula is Cs₃[Tl₂Cl₉] rather than Cs[Tl₂Cl₉]. G. S. Forbes and H. H. Anderson published the paper on Si(NCO)₄ present as a reference on page 623.

Volume I clearly belongs in the library of every establishment involved in inorganic research.

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Encyclopedia of Physics. Volume III/2. Principles of Thermodynamics and Statistics. Edited by S. FLÜGGE. Springer-Verlag, Heidelberg Platz 3, Berlin-Wilmersdorf, Germany. 1959. vii + 678 pp. 18 × 25.5 cm. Price, DM. 160.—; Subskriptionspreis, DM. 128.—.

As the title indicates, the object of this volume is to give a survey of the fundamental principles of classical and irreversible thermodynamics, statistical mechanics and other topics in statistical physics. This is accomplished in five articles; (1) Thermodynamics, Classical and Statistical, by E. A. Guggenheim, (2) Axiomatik der Thermodynamik, by G. Falk and H. Jung, (3) Prinzipien der Statistischen Mechanik, by A. Münster, (4) Thermodynamik der Irreversiblen Prozesse, by J. Meixner and H. G. Reik, and (5) Probability and Stochastic Processes by A. Ramakrishnan.

The applications of these principles are left for later volumes of the encyclopedia, and only a few illustrations are to be found in this volume. The value of having these subjects presented in a single volume certainly cannot be based on any claim of continuity or uniformity of presentation, for each author not only uses his own style but also his own individual notation. The pertinent question, however, is whether or not the volume as a whole is thorough and exhaustive in its coverage of the field. In this respect, it is rather successful, with the possible exceptions of its presentations of chemical thermodynamics and stochastic processes. The kinetic theory of gases, which one might hope to see included in such a treatise, has been omitted completely and is scheduled to be published in an article by H. Grad in Volume XII. Aside from these general comments, the book can best be reviewed by considering each chapter independently and comparing it with other current publications on the same subject.

The initial chapter, written by Edward A. Guggenheim, covers classical chemical thermodynamics and the statistical thermodynamics of ideal gases and crystals. The manner in which it is written is in sharp contrast to the other chapters (which tend to be very mathematical). Mathematical derivations and details are kept to a minimum and much use is made of physically plausible arguments in developing the basic equations. The presentation is almost in outline form and often too many details are omitted.

The section on thermodynamics is very brief and has little to offer when compared with many of the standard texts on this subject, including Professor Guggenheim's own book ("Thermodynamics," E. A. Guggenheim, Interscience Publishers Inc., New York, N.Y., 1957.) The statistical thermodynamics in this chapter is limited to the study of independent particles. (A more general treatment is given in the article by A. Münster.) In addition to this limitation, only the simplest cases (*e.g.*, all interactions between rotational and internal vibrational degrees of freedom are neglected) are considered. Most of the material considered here can be found in all the older and well known treatises on statistical thermodynamics and often in greater detail. Only the section on Fermi-Dirac and Bose-Einstein statistics contains any recent developments. The serious student or worker in this field may be interested in the presentation of the Fowler-Darwin method, where the use of generating functions for the combinatorial expressions is given a very lucid presentation, but on the whole he will be disappointed with the superficial and limited treatment of most of the topics. On the other hand, for the chemist who is not at home in statistical mechanics and who seeks an authoritative and accurate presentation of many of the common statistical formulae for thermodynamic properties of ideal gas molecules, this chapter can be highly recommended. The summary of the calculation of symmetry factors due to different nuclear spin states and isotopic composition could be particularly useful. The

reader will also find a good summary of the properties of degenerate Fermi-Dirac and Bose-Einstein ideal gases and a very brief treatment of radiation and external fields.

The second chapter by G. Falk and H. Jung, entitled Axiomatik der Thermodynamik, is a highly abstract development which is claimed to be a generalization of Caratheodory's formulation. The axioms are developed in terms of set theory in which the possible states of a thermodynamic system are regarded as an abstract set. The authors then proceed to define relationships over these sets which, in turn, are used to define the various state functions. This chapter will probably be of interest only to those readers concerned with the purely formal mathematical aspect of thermodynamics. The developments presented are to a large extent original, and the reviewer knows of no other publication which can be compared to this article. Although most of the workers in thermodynamics will have little interest in the formalism presented by Falk and Jung, they will find in the appendix to this chapter a very lucid presentation of the Caratheodory theory. This presentation is strongly recommended to those who wish to have a better understanding of this famous formulation of thermodynamic principles.

The chapter by A. Münster, Prinzipien der Statistischen Mechanik, is by far the most outstanding article in this volume of the encyclopedia. The article first of all presents the principles of classical statistical mechanics with the emphasis being placed on the Gibbs theory and the mathematical development of the ergodic problem. While most treatises give at most a brief word description or outline of these topics, Professor Münster, in a very lucid presentation, carefully gives enough detail to enable the reader to obtain a thorough understanding of the subject. The principal theorems are proved in detail, and sufficient references are given for all the supplementary mathematical points.

It is natural to try to compare this chapter with Tolman's well known work ("The Principles of Statistical Mechanics," by Richard C. Tolman, Oxford University Press, London, 1950). Although Münster has not attempted to give the detailed background on classical mechanics and quantum mechanics found in Tolman's book, he has given a much broader coverage of the fundamental principles, since he has emphasized several accepted basic approaches to the theory. In the reviewer's opinion, the discussion of these principles given by Professor Münster can only be matched by his own book, ("Statistische Thermodynamik," by A. Münster, Springer-Verlag, Berlin, 1956). The encyclopedia article does, however, assume a rather sophisticated background in classical, quantum and statistical mechanics.

Aside from the clarity of presentation, the feature that makes this chapter so outstanding is its coverage of modern developments. Professor Münster has included discussions of the most important developments of the past two decades. These include the Kirkwood theory of transport phenomena and derivation of the Boltzmann transport equation, the low temperature expansion and the Feynman formulation of the quantum mechanical density matrix, the modern theory of generalized ensembles; and the Yang and Lee formulation of the theory of phase transitions. Consistent with the purpose of this volume, very few applications are discussed. The Bose-Einstein condensation for an ideal gas is used as a model of a phase transition and discussed in some detail. In addition, the thermodynamic properties of a one-dimensional system are calculated as an illustration since this special case is amenable to an analytical treatment.

In the fourth article, Thermodynamik der Irreversiblen Prozesse, J. Meixner and H. F. Reik give an excellent discussion of the subject, emphasizing the point of view of hydrodynamics. Their presentation departs radically from that found in many current publications (*e.g.*, "Introduction to Thermodynamics of Irreversible Processes," by I. Prigogine, Thomas, Springfield, Ill., 1955; and "Thermodynamics of Irreversible Processes," by S. R. DeGroot, Interscience Publishers, Inc., New York, N.Y., 1951). The authors omit entirely the treatment of discontinuous systems and also omit any introductory examples, starting the presentation with the development of the entropy production equation and the linear phenomenological laws in all their generality for continuous fluid systems. The derivation of these equations is given in a very compact

but readable manner. One of the outstanding features is an excellent summary of the linear flux-force relations for all types of forces (scalar, vector and tensorial in character) with a good discussion of the application of Curie's law to reactive multicomponent fluid systems. The general equations are then simplified for various special systems and applications. This discussion is also carried out in a formal manner, again being directed toward those readers familiar with hydrodynamics.

One of the unique and interesting features of this article is a discussion of the role of internal variables (which are usually used to describe molecular relaxation processes) in the irreversible thermodynamics and the frequency dependence of the thermodynamic variables in a medium with sonic and ultrasonic waves. There is also a section devoted to the relativistic theory. The article not only develops the thermodynamic principles but also includes a discussion of the statistical and molecular basis of these laws. Most of the emphasis is placed on the development of the Onsager-Casimir reciprocal relations.

The last article, Probability and Stochastic Processes, by Alladi Ramakrishnan, is a presentation of some of the results of the mathematical theory of stochastic processes in a physical language without the use of measure-theory concepts. The author uses Bartlett's recent book ("Stochastic Processes," by M. S. Bartlett, Cambridge University Press, Cambridge, 1955) as a guide and refers to this chapter as a sequel to Professor Bartlett's book.

The parts of probability theory basic to the subject of stochastic processes are covered in a conventional and adequate manner. The treatment of the principles of stochastic theory, however, is too often in the form of an inadequate summary. Many topics are mentioned as a passing reference, giving the reader only the vaguest impression. Most of the discussion is directed toward stochastic problems in astrophysics. The sections relating the theory to statistical mechanics and quantum mechanics will seem almost trivial to readers acquainted with these fields. In line with this, the treatment of Markov processes is outstanding and worth reading, while the subject of power spectra and correlation functions is given a very superficial treatment. The article does contain brief outlines of many applications of the theory, but the chemist will be disappointed to find no mention of recent applications to the theory of chemical kinetics.

In summarizing this third volume of the encyclopedia, one can say that it will be a valuable reference in the field of statistical mechanics and a good source of material on the irreversible thermodynamics of fluids. One could also use it as a reference for elementary statistical thermodynamics and as an introduction to the theory of stochastic processes, but it is not outstanding in these subjects.

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Instability Constants of Complex Compounds. By K. B. YATSIMIRSKII and V. P. VASIL'EV. Translated from the Russian by D. A. Paterson. Translation Editor: R. H. Prince, Ph.D., University Demonstrator in Chemistry, University of Cambridge. Pergamon Press Ltd., 4 and 5 Fitzroy Square, London, W. 1, England. 1960. viii + 218 pp. 14.5 × 22 cm. Price 42s. net.

During the past two decades the emphasis in studies on metal complexes has changed from the earlier preparative and qualitative approach toward more quantitative physico-chemical measurements. This has been particularly true with regard to the collection of thermodynamic data on the solution chemistry of these systems. In recent years thousands of papers have been published on many different methods of determining the stabilities of metal complexes in solution and the application of these to the determination of numerous stability constants. More recently current chemical bonding theories for such species have been applied in an attempt to explain the observed trends in their stabilities.

The authors of this book are to be congratulated for having done a good job of bringing together in a condensed form much of the information on the stabilities of metal complexes. This includes tables which give the instability constants of 1,381 complex compounds, from data published

up to 1954, and in some cases up to 1955-1956. There are 99 tables listed according to ligands, 24 of which are inorganic ligands and the remainder are organic. No attempt is made to report all of the available data on a given system, instead the authors choose the literature values that appear to them to be most reliable. For example the system $\text{Cu}^{2+}\text{-NH}_3$ has perhaps been investigated by more different investigators and by more different methods than any other, yet only the results of Professor J. Bjerrum are given along with two other supplementary references.

One other feature of the book that is very good, particularly for the uninitiated, is the summary of the experimental approaches, methods of calculation and theoretical discussions. In most cases the experimental methods and the mathematical treatment of the data collected are given in sufficient detail to be directly useful. Specific references are always provided where more information is required. The chapter on the factors determining the stability of complex compounds in solution is especially good. It makes good use of the current chemical bonding theories for these systems.

This book can certainly be recommended to research workers who wish thermodynamic data and a better understanding of the solution chemistry of metal ions. However, one must call attention to the much more complete literature coverage that is given by the volumes "Stability Constants," compiled by J. Bjerrum, G. Schwarzenbach and L. G. Sillén under the auspices of IUPAC and published by the Chemical Society of London.

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Progress in Semiconductors. Vol. 4. ALAN F. GIBSON, B.Sc., Ph.D., General Editor, Prof. R. E. BURGESS, Vancouver, B.C., American Editor, and Dr. F. A. KRÖGER, Salfords, European Editor. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N.Y. 1960. vii + 291 pp. 16 × 23.5 cm. Price \$10.50.

This volume is the fourth in an annual series covering areas of current interest in the semiconductor field. The editor continues the previous format. Since the field is large and growing rapidly, only a very limited number of the multitude of possible topics are covered.

Volume 4 contains eight well-written papers by authors from the United States, Germany, Japan, the Soviet Union, Great Britain and Holland. The subjects are generally concerned with physics, although "Oxidation Phenomena on Germanium Surfaces" is certainly chemistry.

The first paper, "Negative Effective Masses in Semiconductors" by H. Krömer, describes the physical origin of effective mass and the general conditions under which it may be negative. Germanium is treated in considerable detail. A possible practical way to apply negative mass to achieve amplification is discussed.

"Oxidation Phenomena on Germanium Surfaces" by M. Green presents an excellent review of techniques for obtaining "clean" surfaces and the effects of oxidation and surface treatments on properties like surface conductance, work function, and surface recombination velocity.

"Theory of Avalanche Multiplication in Non-polar Semiconductors" by J. Yamashita contains extensive and complex mathematical treatments of hot electrons and electron multiplication. Avalanche breakdown on *p-n* junctions is depicted in terms of McKay's simplified model, and the limitations of this model are portrayed. Impact ionization and the effects of magnetic fields and crystal orientation on breakdown also are treated.

Various possible mechanisms of "Internal Field Emission" are treated by A. G. Chynoweth. The concept of quantum mechanical tunneling of carriers, which has recently led to a new family of practical solid state devices with promising futures, is treated.

D. Sautter discusses the various sources of "Noise in Semiconductors," describing experimental results and physical mechanisms. Generation-recombination noise is treated most extensively.

In "Effects of Dislocations in Semiconductors," W. Bardsley describes the types of dislocations generated in the diamond structure during growth or by bending, twisting, compression and indentation, and tensile deformation.