Previous instances of halogen rearrangements in radical systems were reported by Demole,[3] Swartz,[4] Urry and Eiszner,[5] and Nesmeyanov, *et al.*[6]

The details of this rearrangement are being investigated further. Since these same bromoalkyl radicals are also produced in the peroxide-induced additions of hydrogen bromide to olefins these halogenation studies also offer the promise of elucidating the details of hydrogen bromide additions.

(3) E. Demole, *Ber.*, **11**, 315, 1302 (1878).

(4) F. Swartz, *Inst. intern. chim. Solvay*, 5eme Conseil de Chemie, 79 (1934).

(5) W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc.*, **74**, 5822 (1952).

(6) A. N. Nesmeyanov, R. Kh. Freidlina and V. N. Kost, *Tetrahedron*, 241 (1957).

(7) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)-457.

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE UNIV.
UNIVERSITY PARK, PENNA.

PHILIP S. SKELL[7]
RICHARD G. ALLEN
NILES D. GILMOUR

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BOOK REVIEWS

Nouveau Traité de Chimie Minérale. Tome VII. Scandium, Yttrium. Éléments des Terres Rares. Actinium. (2 Fascicules). Edited by PAUL PASCAL. Masson et Cie., 120, Boulevard Saint-Germain, Paris 6, France. 1959. xxxix + 1473 pp. 17.5 × 26 cm. Price, brochés, 180 NF; cartonnés toile, 200 NF.

Some 27 years ago the original "Traité de Chimie Minérale," published under the direction of Professor Paul Pascal, treated the chemistry of those rare earth elements known at that time as completely as possible.

Obviously during the interim between that publication and the present an extensive amount of research on these elements has been done. The next development was to collect the data and ideas and compile them into one compact source. Such has been done in Volume VII of the Nouveau Traité. So great has been the amount of research that this volume has had to be published in two parts.

The form is similar to the old Traité but far more extensive: Part 1 (706 pages) begins with general statements regarding the rare earth elements scandium and yttrium and then deals with the history of these elements, which is most complete and well authenticated. This part is unusually well done. The remainder of this part of Volume VII is given over to the treatment of the various ores and the separation of the elements themselves plus the physical properties of the metals. Several such methods are given. Many specific separations are outlined. Limitations are pointed out in the various methods of separating the salts in a mixture. These separations range from the divalent state of the ions to complex ions. Even industrial separations are outlined. Schematic drawings of the processes are given.

The last section of this part of Volume VII, dealing with the physical properties of the metals themselves, is particularly well done and most inclusive. Several pages are given over to these properties of each rare earth in its elemental state. On reading this volume one will be surprised to find many useful thermodynamic data available, from specific heats to the Gibbs function. Important electrical properties are also discussed.

Part 2 (740 pages) deals with the chemical properties of the metals and their salts, including methods of analysis for the cations. Much is also done with the alloys of the rare earths with other metals. This part of the book contains many two-component melting point diagrams. One ternary diagram, Fe–Al–Ce, is included.

Nuclear properties of the radioactive isotopes of the lanthanides along with their uses in the domains of physical chemistry, biology and medicine are fairly thoroughly treated.

The section devoted to detection of and analysis for the cations of the rare earths is outstandingly well done and highly specific. Pitfalls are pointed out in the various analytical procedures. Both chemical and physical analytical methods are treated. Fairly complete data on absorption spectra and flame spectra for these lanthanides are given.

This volume, all in all, is very well done, and is probably the most comprehensive work on scandium, yttrium and the lanthanides yet printed.

DEPARTMENT OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA

FREDERIC C. SCHMIDT

Handbuch der Präparativen Anorganischen Chemie Zweite umgearbeitete Auflage. Erster Band. Edited by GEORG BRAUER, o. Professor für anorganische Chemie an der Univ. Freiburg i, Br. Ferdinand Enke Verlag, Hasenbergsteige 3, Stuttgart W. Germany. 1960. xiii + 884 pp. 16.5 × 24.5 cm. Price, Geheftet DM., 118.00; Ganzleinen DM. 124.00.

Chapter I contains one hundred and twelve useful pages on preparative methods, with ninety-one diagrams and sixteen tables. Authors Schenk and Brauer cover the topics glass, ceramic materials, metals, purification of mercury, electric furnaces, temperatures, high vacuum techniques, gases and purification of compounds.

Chapter II, in eighteen sections with seven hundred and sixty-six pages and one hundred and eighty-nine diagrams total, describes more than seven hundred and fifty detailed preparations of compounds and elements and indicates preparative methods for almost twelve hundred compounds and elements. The coverage includes hydrogen and all the elements of the seven regular groups in the Periodic Table except francium, radium, polonium and astatine. These authors include silver(I) fluoride as a derivative of fluorine. Much credit is due the thirteen authors of individual sections: Baudler, Becher, Dönges, Ehrlich, Fehér, Glemser, Hofmann, Klement, Kwasnik, Rüdorff, Schenk, Schmeisser and von Wartenberg. This reviewer selects the following as twenty typical preparations: AgF_2, $AlCl_3{\cdot}SO_2$, BiF_5, $CaCN_2$, CF_3I, DBr, EuF_2, F_2O, GeH_4, $HICl_4{\cdot}4H_2O$, InCl, $KIBr_2$, KSO_2F, $LiAl(CN)_4$, NH_4PF_6, $(PNCl_2)_n$, $Pb(C_2H_5)_4$, SO_2ClF, Si_2OCl_6 and TlOCOH.

In the foreword Editor Brauer considers the experimental descriptions reliable because of information from the laboratories of the authors or from other laboratories. An eight page formula index is at the end of Volume I. A future Volume II on the transitional elements will complete the book.

Some minor weaknesses are always inevitable. Careful fractional distillation receives little attention in either chapter. Preparation of tetrafluorosilane should employ either fluorosilicic and concentrated sulfuric acids, as in the book, or the heating of barium fluorosilicate. Page 291 could mention that a mixture of perchloric and concentrated sulfuric acids oxidizes moderate amounts of organic matter smoothly. Also, phosphorus and iodine (in the ratio one to five atoms, respectively) react with water to yield hydrogen iodide quite satisfactorily, with adequate drying by passage over a long tube of phosphorus pentoxide. Formulas are subject to slight improvement sometimes: $Ga[GaCl_4]$ and

$Ga[GaBr_4]$ are better than $GaCl_2$ and $GaBr_2$; the $SbCl_2F_3$ may be a mixture of $SbCl_5$ and SbF_5; on page 879 the correct formula is $Cs_3[Tl_2Cl_9]$ rather than $Cs[Tl_2Cl_9]$. 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.

CHEMISTRY DEPARTMENT
DREXEL INSTITUTE OF TECHNOLOGY
PHILADELPHIA 4, PA. HERBERT H. ANDERSON

Encyclopedia of Physics. Volume III/2. Principles of Thermodynamics and Statistics. Edited by S. FLÜGGE. Springer-Verlag, Heidelberger 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 Axiomatic der Thermodynamik, is a highly abstract development which is claimed to be a generalization of Carotheodory'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, ("Statistiche 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