

To condense this information within the confines even of this fairly bulky volume was indeed an ambitious undertaking; that many important facets of zirconium metallurgy are, as a result, inadequately reflected is of less consequence than the author's achievement of a critical and valuable collation of the data in several areas.

After two short introductory chapters devoted to occurrence and use of zirconium, the author discusses extraction from the ore and processes proposed for separation of zirconium and hafnium. It is unfortunate that the book was apparently sent to press late in 1956 and that hence the declassification of information on the Zr-Hf separation processes early in 1957 did not permit concentration on description of the processes commercially in use. The following three chapters admirably and critically review the reduction and refinement processes for metallic zirconium with respect to early developments in this field, present practice, and processes showing promise for future development. No better review of the present status of this subject can be recommended to the reader.

The physical properties of metallic zirconium are reviewed in a subsequent chapter which consists primarily of a listing of available data. The reader will find this section useful for reference but will gain from it an inadequate appreciation of the interesting physical metallurgy behavior of zirconium and its alloys.

The book continues with two lengthy but not very critical chapters on mechanical properties of zirconium and of zirconium alloys. The author, apparently by oversight, chose to include exactly the same curve (Figs. 76 and 92) in each chapter, and that curve of somewhat questionable significance in the first place. Little or no discrimination or emphasis is employed in discussion of the properties so that the reader not previously informed on this subject would have difficulty in separating information of value for application from that included merely for the sake of completeness. The effect of heat treatment on properties of zirconium is often more profound than that of the amount or nature of the alloying addition. In most cases the treatment prior to determination of properties is not specified so that only doubtful interpretation and use of the data are possible.

The following two chapters are devoted to the chemical properties of zirconium. Here again one gains the impression that the author has aimed at inclusiveness rather than discrimination and emphasis. For example there appears to be little value, in a book dated 1957, in devoting space to Fig. 123 showing pressure changes on heating zirconium powder in nitrogen without specification of particle size, heating rate, etc., particularly when data are available permitting quantitative calculation.

It was expected that the chapter on alloying behavior of zirconium would exhibit the high quality which one has come to expect of discussions of this topic in British metallurgical texts. In general the chapter confirmed these expectations. It is, however, incomplete in that the author, probably again by oversight, omitted mention of several systems on which information is readily available. For example, the systems of zirconium with indium, zinc, and cadmium are omitted even though each can be of considerable technological and metallurgical importance. A further point of criticism is the concealment of information on explosions noted during pickling of zirconium-uranium alloys, which has been a major subject of concern in the discussion of the zirconium-uranium binary system, with no index reference to it that the reviewer was able to find.

The chapter on melting practices impressed the reviewer as being complete, critical, and authoritative, and is again recommended to the reader as the best exposition available in this field. On the other hand, even though zirconium production has expanded ten-fold during the past four years and its fabrication has, during this period, made the transition from largely government-operated facilities to commercial fabrication, the author chose to devote no more space to this subject than he did in his first edition. In fact, the subsequent chapter on powder metallurgy of zirconium occupies almost as much space as that devoted to all other fabrication, joining, and surface finishing practices even though no significant quantity of material is presently fabricated by the former technique. The reader is cautioned therefore that the state of the art as of 1957 is by no means adequately represented in the fabrication chapter. The author concludes with an interesting discussion of

zirconium compounds and an appendix on metallography of zirconium. The reviewer believes that the discussion of metallography could have been considerably improved by including suitable micrographs, and was surprised to note that the entire text was issued without a single illustration of a typical microstructure.

The particular interests of the author in metal reduction and melting undoubtedly account for the high quality of the sections devoted to these topics; it is regrettable that the reviewer cannot equally commend his coverage of other fields. It was well known in 1957 that practically all the commercial production of zirconium was devoted to nuclear applications, particularly those involving exposure to high temperature water. Yet, the author appears reluctant to associate his subject with nuclear energy. This is exemplified in his discussion of uses of zirconium in which he devotes almost as much space to neurosurgical applications, which will furnish an outlet for a few ounces of zirconium per year, as to nuclear applications, and far less than is devoted to electronic applications utilizing pounds rather than tons of zirconium. This attitude has a much more serious effect with respect to the author's discussion of radiation effects on zirconium. Here he confines his discussion to four references, one of which can be seriously misleading to the reader unless properly interpreted. Even these references were improperly abstracted in that the flux exposure was quoted in terms of thermal flux, which probably has little or no pertinence to property changes, rather than in terms of fast flux. This lack of appreciation of the problems arising during application appears to have led, for example, to complete omission of information on the technologically highly important fatigue properties; to omission of data on hydrogen pickup during processing and operation, and on control of hydrogen content; to an inadequate discussion of the mechanical property effects of hydrogen; to no consideration of the hazards and problems in use of zirconium in hot water systems; to lack of mention of the principal application of zirconium in fuel elements, much less of fabrication techniques such as roll bonding; to scattered and incomplete reference to the major commercial alloy of zirconium, Zircaloy-2, and no reference to its modifications; to failure to discuss the problems of surface finishing and pickling which are of such commercial concern and the effects of melting practice on weldability, corrosion resistance, etc. Many additional omissions could be added to this list.

In summary, then, Dr. Miller is considered to have made a substantial contribution to the literature on reduction and refining of zirconium metal and its subsequent melting; those interested in the physical metallurgy, fabrication, and subsequent application of zirconium will find this book interesting and helpful, but will find it advisable to supplement the information by extensive reference to other literature.

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Free Radicals in Solution. CHEVES WALLING, Professor of Chemistry, Columbia University. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1957. xii + 631 pp. 15.5 × 23.5 cm. Price, \$14.50.

After reading this book I was compelled to look again at two earlier works on Free Radical Chemistry, namely, "The Aliphatic Free Radicals" by F. O. Rice and K. K. Rice, and "The Chemistry of Free Radicals" by W. A. Waters. Doing this gave one the proper perspective against which to assess the present volume. It also brought home very forcibly how tremendous have been the advances in the chemistry of free radicals in the past few decades. That Professor Walling has been able to give such a very lucid, learned, and detailed account of this enormous branch of chemistry is nothing short of amazing.

Professor Walling introduces his subject with a chapter on The Structure and Physical Properties of Free Radicals. In this he discusses the evidence for the existence of free radicals and includes a brief account of the recent paramagnetic resonance work. This chapter is followed by a very good one in the Chemical Reactions of Radicals in which the various types of free radical reactions are discussed. The latter part of this chapter is taken up with an excellent account of Bond Dissociation Energies. Then Professor

Walling goes on to discuss Free Radical Polymerizations in the next three chapters which are called, respectively, Free Radical Polymerizations; The Kinetics of Radical Chain Processes (Chapter 3); Copolymerization, Chain Transfer, and Inhibition in Polymerization (Chapter 4); Some Further Characteristics of Radical Polymerizations (Chapter 5). These are superb accounts of the whole field of free radical polymerizations. The treatment is very detailed, but most lucid. All the important work in this vast field is summarized succinctly and the reference coverage is remarkable for its inclusiveness. There are excellent compilations of data in tabular form. Here great care has obviously been taken in selecting reliable information and in assembling it in a manner as to make it easily accessible. Here again I felt compelled to compare Professor Walling's account with that given in a standard work, namely, "The Mechanism of Polymer Reactions" by G. M. Burnett, and this certainly indicates just how thorough and up-to-date is the account of this field which Professor Walling has given.

After this very excellent and complete account of free radical polymerizations, Professor Walling proceeds to discuss in turn Radical Addition Reactions Yielding Small Molecules (Chapter 6); Radical Addition Reactions Involving Atoms Other than Carbon (Chapter 7); and Halogen Substitution Reactions (Chapter 8). In these the same high standard is maintained and important stereochemical aspects of free radical reactions are stressed throughout. Kinetic details of the various reactions are also carefully and critically discussed.

The book then continues with a really outstandingly well-written and complete account of Autoxidations (Chapter 9). In the reviewer's opinion, this is by far the best review of the chemistry of autoxidation which has appeared in the literature. The literature coverage is excellent and the subject matter most judiciously selected. There then follow two very good chapters on Radical Formation by Thermal Cleavage of Covalent Bonds (Chapter 10) and Radical Production by Photochemical, High-Energy Radiation, and Oxidation-Reduction Processes.

Throughout the book the literature seems to be very completely covered right up to about the middle of 1956. It is also pleasing to note that Professor Walling has included a large number of references to important relevant Russian work. The book has two good indexes, and it is interesting to note that the Author Index is twice as large as the Subject Index; this is an indication of how extensively the literature has been covered.

This then is a major work of scholarship and it will obviously be the standard monograph on the Chemistry of Free Radicals in Solution for some considerable time. It will appeal to all chemists, and no physical or physical-organic chemist who wishes to keep informed of the advances in free radical chemistry can afford to be without a copy.

In closing, one might note that the book is dedicated to Morris S. Kharasch and Frank R. Mayo, pioneers of free radical chemistry, who first aroused and then maintained Professor Walling's interest in the subject. Regrettably, Professor Kharasch died recently. This book would be a fitting memorial to this great chemist who laid the foundations of much of the work described in its pages.

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Ion-Exchange Resins. By J. A. KITCHENER, University Reader in Physical Chemistry, Imperial College of Science and Technology, University of London. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. vii + 109 pp. 11 × 17 cm. Price, \$2.00.

Although the ion-exchange process was discovered more than a hundred years ago, synthetic organic ion-exchange materials were not invented until 1935. As a matter of fact, the currently popular sulfonated styrene-divinylbenzene cation-exchange copolymers did not make an appearance until 1944 and the strongly basic quaternary ammonium type anion-exchange resins were unknown until 1948. With the advent of stable, high capacity ion-exchangers which possessed a single functional group, it became possible to understand the behavior and properties of ion-exchange media. Many thorough investigations of ion-exchange

equilibria have cast light on the mechanisms involved and have expedited the exploitation of sorption and elution processes by industry. Uses of ion-exchange resins are becoming so numerous and in some instances are so elegant that it behooves the chemist and chemical engineer to acquaint himself with the fundamental principles involved in ion-exchange processes.

Kitchener has not tried to justify all the theories concerning ion exchange, but instead has attempted to sift out the main, well established principles from those which are controversial in a formidable amount of original literature. Considering the versatility and complexity of the process, he has done an excellent job of organizing and condensing the pertinent details into a minimum number of pages.

The book is interesting and written in such a manner that anyone with a rudimentary knowledge of physical chemistry can understand its contents. It appears that the information contained would be valuable supplementary material for a standard course in physical chemistry and should by all means be included in the course on unit processes offered to chemical engineers.

Only one discrepancy is apparent in the entire book. It occurs in the elution sequence for divalent ions on page 29. The appearance of Ba^{++} as the first and last member of the sequence will cause some consternation among those who read the book.

The author has covered the important applications of ion exchange rather well, in general, except that he has apparently not kept up with the most recent developments in the separation of rare earths by this method. The most recent reference cited on this subject is more than ten years old and citric acid is not the complexing agent used for the commercial production of pure rare earths. Citric acid has been replaced by the more efficient chelating agents such as ethylenediaminetetraacetic acid and N-hydroxyethylthylenediaminetriacetic acid.

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The Physical Chemistry of Electrolytic Solutions. Third Edition. ACS Monograph No. 137. By HERBERT S. HARNED, Professor of Chemistry, Yale University Emeritus, and BENTON B. OWEN, Professor of Chemistry, Yale University. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, New York, 1958. xxxiii + 803 pp. 16.5 × 23.5 cm. Price, \$20.00.

Although not truly "a drastic revision," the Third Edition of Harned and Owen's "The Physical Chemistry of Electrolytic Solutions" is much bigger and better than the earlier editions. This book has grown from 643 pages in 1943 and 681 in 1950 to 836 pages in 1958.

The numerical values in Chapter V and in the equations throughout the book are now up-to-date except that 1.858 instead of 1.860 persists for the freezing point constant of water. Of course the authors have not revised all the experimental results which depend upon these values because they are mortal and have only two lives to give to their science. Otherwise the first edition is reprinted almost unchanged except that the material in the 37 pages of Appendix B of the second edition and much new material is incorporated at the ends of the appropriate sections or as new sections at the ends of the appropriate chapters. The first five theoretical chapters have been increased by 60 pages, and the experimental chapters and appendix by 120 pages.

The important additions are discussions of "Irreversible Thermodynamics" (25 pages), of the Fuoss-Onsager treatment of the conductance of moderately concentrated solutions (25 pages), of the Onsager-Kim treatment of the Wien effect, the effect of high field strengths on conductance (10 pages), of the Mayer treatment of chemical potentials (3 pages), of the Glueckauf-McKay cross-differentiation methods (10 pages), and the presentation of new experimental material (about 100 pages). The authors have made a noble effort to give clear discussions, but the nature of the material necessarily makes the reading of the first four chapters even more difficult than before, and pushes the first presentation of an experimental result back to page 197.