BOOK REVIEWS

Polyolefins. By A. V. TOPCHIEV and B. A. KRENTSEL,' U.S.S.R. Academy of Sciences. Translated from the Russian by A. D. NORRIS, M.A., D.Phil.(Oxon), F.R.I.C., F.I.L. (Lecturer in Physical Chemistry, Hull University). Pergamon Press Ltd., Headington Hill Hall, Oxford, England. 1962. xi + 92 pp. 14.5 × 22 cm. Price, $3.50.

This short book is a translation into English by A. D. Norris, of Hull University, of the Russian edition published in 1959. Thus, only information known prior to that year is reported; therefore, the wide knowledge acquired in the field of polyolefins during the last few years is lacking. The authors, who have personally carried out research in this field, refer to some results and interpretations obtained from research carried out in the Soviet Union, but the complete bibliography of work done either in Russia or in Europe and in the United States is lacking, *e.g.*, references to journals and year of publication are not given. The translator, an expert in the topics dealt with, has slightly modified the original text and used different symbols or signs for some formulas in an effort to make them more intelligible to readers who are used to conventions adopted by European and American Chemists.

In the *Introduction*, the low-molecular-weight ethylene polymers obtained since 1884 by Russian chemists are mentioned as well as the far more important high polymers of ethylene, obtained at either high, low or medium pressure. The very important polypropylenes are also treated.

Chapter I describes raw materials derived from petroleum from various sources and in particular gives the average composition of cracking gases, and of some Russian natural gases which are more suitable than others for the production of ethylene and propylene by dehydrogenation because of their high content in C_2-C_5 fractions (30–70%).

Chapter II deals with the production of polyethylene by high-pressure processes and discusses its structure and its physical and chemical properties.

Chapter III deals with the production of polyethylene by the low-pressure Ziegler methods, and by the methods used by Ziegler for the production of organometallic compounds of lithium and of aluminum. In comparing the properties of polyethylenes obtained at high and at low pressure, the authors refer to average products, but do not consider the remarkable variations in properties of both the high-pressure polyethylenes, whose properties (*e.g.*, crystallinity) markedly vary with the degrees of polymerization or with molecular weight and branching, and of the low-pressure polyethylenes whose properties also vary considerably with the content of methyl groups (from about 0.3% for polymers obtained with most typical Ziegler-type catalysts to less than 0.1 for those obtained with the aid of catalysts with a crystalline component), which cause remarkable variations in crystallinity, and in the melting temperature (from 130 to 138°).

Chapter IV describes the processes using moderate pressures developed by Philips and by ESSO Standard Oil of Indiana for the production of high-molecular-weight polyethylene with the use of catalysts based on oxides and containing chromium and molybdenum compounds, respectively.

Chapter V deals with the variations of properties of polyethylene treated with high-energy radiations. On page 53, it is stated that the melting temperature of irradiated polyethylene can exceed 200°. Actually, this is either the softening or the viscous flow temperature, because the real melting temperature which corresponds to the complete disappearance of crystalline regions does not exceed 138° for any polyethylene; this value corresponds to the more linear ones, and it is reduced and not increased by the effect of radiations, which reduce the crystallinity.

Chapter VI deals with sulfo-chlorinated polyethylene, its preparation and its properties. The term "Gipalon" used to indicate the product made in the USA is the Russian transliteration of "Hypalon," the correct name.

Chapter VII describes the industrial and domestic applications of polyethylenes. Products obtained at high and at low pressure are compared as to their use for the production of fibers.

Chapter VIII deals with the preparation, properties and practical applications of the new polymers of propylene and describes results and steric configurations of the products, and the influence of these on the properties, mainly referring to results published by Italian authors. Among the applications of polypropylene, a brief description of fibers (compared with those of Nylon) and of films (compared with those of polyethylene) is included.

Finally, the translator has included a short addendum on the mechanism of polymerization processes. Considering that the translation was done in 1961, the addendum is rather incomplete, particularly with regard to chain transfer processes and to interpretations of sterospecificity.

This book is written clearly and can be easily read; thus it may be useful to students or non-specialized chemists who wish general information on the new polyolefins which are acquiring great importance in macromolecular chemistry.

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Introduction to Thermodynamics of Irreversible Processes. Second, Revised Edition. By I. PRIGOGINE, University of Brussels, Brussels, Belgium. Interscience Division, John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1961. xi + 119 pp. 14.5 × 22 cm. Price, $5.00.

Professor Prigogine is justly renowned for his contributions to the theory of irreversible processes. Therefore it was with high anticipation that I opened my copy of the "Second, Revised Edition" of "Thermodynamics of Irreversible Processes." However, upon turning to the Preface, I was disappointed to discover that "since the appearance of the first edition of this book in 1955, no fundamental progress has been achieved in the thermodynamics of irreversible processes. For this reason, the only modifications introduced herein are the addition of paragraph 6 to Chapter V dealing with "continuous["] systems, and the replacement of the appendix in the first edition by Chapter VII, which deals with non-linear problems." In other words, the second edition is the same as the first except for some rather minor alterations. Since the first edition is too widely known to be reviewed again, I shall focus my attention principally upon the few changes which have been made and upon some which, in my opinion, should have been made.

The new paragraph 6 of Chapter V demonstrates by a formal Fourier expansion procedure that continuous systems can in a certain sense be treated like discontinuous ones. No practical application is made of the result and its physical importance remains concealed in the formalism. The first two sections of the fifteen page Chapter VII are similar to those of the old Appendix. The remaining four sections are concerned mostly with a brief but intriguing account of some academic non-linear reaction rate problems treated from the point of view of entropy production.

The pagination and the corresponding page listings in the Index and in the List of Symbols have been changed to conform with the additions to the text. However, these changes are the only outward signs of care taken by the publisher. A relatively large number of careless editorial errors suggests that the book was constructed hastily. On p. 32, we are referred to reference 9c which has been deleted. On p. 68, a misspelling of the word "proportional" is retained from the first edition. On p. 82, reference is made to the now nonexistent Appendix. In the list of references, number 13, *Thermodynamics* by E. A. Guggenheim, has been twice revised since the 1949 edition which is listed. Number 63, an article by Glansdorff and Prigogine "to appear *Physica*, 1954," presumably has been published. These are but minor irritations. More important is the absence of a systematic revision by the author of the entire list of references. In the first edition, sixty three references were cited. They

are retained without change except for the completion of the data for reference 33 and the aforementioned dropping of reference 9c (which was, significantly, the projected third volume of the treatise by Prigogine and Defay). Seven new references are cited in the second edition. They all appear, however, in connection with Chapter VII. Thus the author has ignored the entire recent literature on the subject matter of the first six chapters. In my mind, the most important single omission is a reference to the encyclopedic article by Meixner and Reik which appeared in 1959 in the *Handbuch der Physik*. I would have liked comments on the pertinent papers by Coleman and Truesdell (*J. Chem. Phys.*, **33**, 28 (1960)) and Koenig, Horne and Mohilner (*J. Am. Chem. Soc.*, **83**, 1029 (1961)) but probably these appeared too late to be mentioned.

In brief, the second edition of "*Thermodynamics of Irreversible Processes*" is essentially the same concise, readable introduction as the first edition. It still captures remarkably well the essence of the theory without dwelling on details and subleties. I therefore recommend it to the beginner on the condition that he remember that the book offers no clues to most of the literature which has appeared since 1954. For these, he must turn to the other important textbooks and treatises which are now available.

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Nonequilibrium Thermodynamics. A Phenomenological Theory of Irreversible Processes in Fluid Systems. By DONALD D. FITTS, Department of Chemistry, University of Pennsylvania. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1962. xviii + 173 pp. 16 × 23.5 cm. Price, $7.95.

This book is intended as a sequel to the recent thermodynamics text by Kirkwood and Oppenheim, and is being billed by the publisher as "the first textbook in the field of nonequilibrium thermodynamics." What makes it a textbook rather than a monograph is presumably the inclusion of a small number of problems at the end of certain chapters. In other respects, the book resembles deGroot's work on the same subject, although the range of material covered is considerably narrower. The author has confined his attention to transport processes occurring in fluids, and his treatment is rigorously postulational in character. Thus, for example, the Onsager theory leading to the reciprocal relations is discussed only in an appendix, and rather inadequately at that.

The first five chapters of the book are devoted to a development of general transport equations in a fluid with temperature, pressure and composition gradients. Three postulates are formally introduced along the way: the local equilibrium assumption, the linearity of the relations between fluxes and driving forces, and the Onsager reciprocal relations. Chapter 3 includes a discussion of the problem of defining a heat flux; two alternate definitions are given, which seems a rather unnecessary complication.

The remaining chapters are concerned with specific types of transport phenomena: heat flow, electrolytic conduction, ordinary diffusion, thermal diffusion and sedimentation. There is also a final chapter applying the reciprocal relations to chemical reactions near equilibrium. In addition to the appendix on the Onsager theory already mentioned, there are three other appendices, respectively covering tensors, stress–strain relations in viscoelastic media, and the effect of viscous stresses and inertial forces on the transport equations.

The general approach is probably too formal to appeal to most students, and concrete applications to particular systems are few in number, the principal one being a discussion of diffusion in the NaCl–KCl–water system. Even here, the only result is an experimental check on the validity of the Onsager relations when applied to cross-diffusion coefficients. The principle of minimum entropy production, surely one of the most interesting ideas to come out of irreversible thermodynamics, is not even mentioned. The student who has waded through the book (incidentally, he had better have taken a course in vector analysis beforehand) is likely to emerge wondering what all the complex manipulations and discussions of alternate definitions of transport coefficients have really accomplished. He will have been told, in considerable detail, how to set up a transport equation, but will have no idea of what to do with it from there on.

But beyond these criticisms lies the question of just how much time should be devoted to a presentation of irreversible thermodynamics in the already overcrowded curriculum facing the average physical chemistry graduate student. By writing a text on the subject, the author is suggesting a minimum of one quarter. In the opinion of this reviewer at least, to justify the expenditure of that much time, the scope of a course on irreversible processes would have to extend well beyond the contents of the present volume, to include not only the statistical foundations of the Onsager theory, but also some discussion of the molecular mechanisms by which transport phenomena occur, as well as a number of examples in which the transport equations are actually solved to give the position and time dependence of thermodynamic variables.

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Comprehensive Inorganic Chemistry. Volume Eight. Sulfur, Selenium, Tellurium, Polonium, and Oxygen. By ROBERT C. BRASTED, Professor of Chemistry, School of Chemistry, University of Minnesota. D. Van Nostrand Company, Inc., 120 Alexander Street, Princeton, N. J. 1961. ix + 306 pp. 16.5 × 23.5 cm. Price, $10.00.

This volume is the eighth that has been produced in a series that eventually will build up to a total of eleven. Its preface states that the volumes are presented as a reference work on the chemical elements and their compounds. The term comprehensive, which appears in the title, is used more in the sense of the fields covered than in any concept of encyclopedic treatment. Due to the brevity of treatment, coverage of the current literature is achieved by the author "exercising to an extreme degree, selectiveness in the material finally incorporated within a volume." A strong effort has been placed on including recent pertinent references. The volumes are intended for use by the advanced undergraduate, the graduate student, and the industrial and manufacturing chemist.

Volume VIII, which deals with the chemistry of sulfur, selenium, tellurium, polonium and oxygen, fulfills the aim as stated above. The selected material is well organized and is suitable for a rapid orientation to the general descriptive chemistry of these elements and their common compounds. It also presents considerable useful factual data on the more common aspects of the area. An abundance of literature references, mostly for the period 1945–1960, document the textual material and encourage more detailed search.

There is increasing and urgent need for up-to-date compilations of descriptive material to supplement the many new books which are devoted to general principles of inorganic chemistry but which are very light on factual information. The coverage and critical evaluation possible in this abbreviated treatment of course cannot compare with that available in the encyclopedic Gmelin Handbuch. But for the reader who wants a rapid over-all survey this volume fills a definite need and deserves a place on all scientific library shelves. Research workers and industrial chemists who are specializing in the chemistry of the sulfur group of elements should find the book a good addition to their personal reference shelves. The author has done chemistry a fine service by compiling this useful material.

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Hydroboration. By HERBERT C. BROWN, R. B. Wetherill Research Professor, Purdue University. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1962. xiii + 290 pp. 16 × 23.5 cm. Price, $10.00.

It is less than six years since Professor H. C. Brown first reported that olefins may be converted very simply to alkylboranes, a reaction conveniently termed hydroboration. The resulting organoboranes have proved to be of very great synthetic utility in organic chemistry; *e. g.*, oxidation with