

BOOK REVIEWS

Mecanismes Electroniques en Chimie Organique. Augmented 2nd Edition. By MARC JULIA, Faculty of Science, Paris. Gauthier-Villars, 55 quai des Grands-Augustins, Paris (VIe), France. 1963. 113 pp. 16 × 24 cm. Price, 16 NF.

This small paper-back (102 pp.) was prepared as a guide and stimulus to studies of electronic mechanisms in organic chemistry. The hope was stated in the preface that the book may serve to help diminish organic chemistry's reputation as "an assembly of kitchen recipes."

Most aspects of the theory of organic chemistry are considered concisely and with clarity but, unfortunately, in much too uncritical and doctrinal a manner. Except for broad reference to the well known but now out-dated works by Dewar, Alexander, and Ingold and a French publication by Mathieu and Allais in 1957, the text is without documentation.

The book may well contribute to a promotion of already obsolete ideas or inadequate interpretations. The following specific comments should adequately illustrate the basis for this judgment. On p. 15, much stress is placed on the significance of the "resonance energy" of butadiene, a concept which only recently was strongly challenged by Dewar (see *J. Am. Chem. Soc.*, **85** 837 (1963)). Hyperconjugation rationalized through no-bond resonance is used on p. 18 to explain the decreasing heats of hydrogenation observed as ethylene is progressively substituted by methyl groups. Such one-parameter explanations are often useful rough approximations when concerned with very large effects. However, in this case, a difference of only 6.2 kcal. separates the heats of hydrogenation of ethylene and tetramethylethylene. In order to illustrate as objectively as possible the disservice rendered to beginning students by such flippant rationalizations, the reviewer approached separately three physical organic chemists for explanations of this hydrogenation data. One considered that hyperconjugation, whatever the term really means, may be of importance. All believed the relative strengths of the kinds of C-H bonds made would contribute to the observed heats to an important degree. One felt that differences in the strengths of the double bonds may be important but would attribute the differences to changes in hybridization rather than to "hyperconjugation." None felt that the data could be profitably rationalized at this time. The statements on p. 19 that charge distribution in the ground state of a conjugated system favors reaction at certain localities obscures the all important fact that reactions proceed by way of the most favorable transition states. The great pedagogical value of energy-reaction coordinate diagrams in the rationalization of the energetics of reactions is not employed with some serious consequences. The catalysis provided by aluminum chloride in the chlorination of benzene is used (p. 84) to prove that the substitution is electrophilic rather than to exemplify the resistance displayed by benzene to electrophilic attack. Thus, although the book is admirably concise, self-consistent, and undoubtedly of considerable intellectual appeal to a beginning student, the lack of critical evaluation together with the largely outdated approach renders the effort of doubtful value.

A "budding" chemist would be well advised to consult a better documented text where the prevailing theory of organic chemistry is presented more rigorously and with much more respect for the complexity of the subject.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA

R. U. LEMIEUX

Boron Hydrides. By WILLIAM N. LIPSCOMB, Professor of Chemistry, Harvard University. The Physical Inorganic Chemistry Series, W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1963. ix + 275 pp. 16 × 23.5 cm. Price, \$14.00.

An appropriate alternative title for this book might have been "Lipscombology"; and then for anyone having recent contact with the lore of polyboranes and related substances, such a title would be a complete and adequate review of the book. However, for chemists not so closely in touch with the subject, let it be said

that the major part of our present knowledge of the structural patterns of the polyboranes came directly from X-ray studies by Lipscomb and his immediate colleagues, and that the very useful electronic and topological rationale of these structures also was primarily his work. Accordingly, no boron chemist need be surprised to find here a book which elaborates in considerable detail the rules of connectivity and basis for predicting the stability of boron networks; but many of us might not have been aware of the large amount of closely reasoned computation underlying these relatively simple ideas and rules.

After the first chapter has described the known structural patterns and the second chapter has elaborated the topology of such structures by use of the group theory of symmetry and the styx numerology, the third chapter elaborates the methods of developing the molecular orbitals for such frames. At this point we find great respect for the electronic computer, whose cooperation the author seems to have requested with utmost courtesy, and whose high ability to deal with extremely multiplex systems of secular equations is honored by elaborate tables of numerical results. For estimation of charge distributions in polyboranes and in the corresponding polyboranide anions or carboranes, three different methods of simplification were used, and careful arguments are given for choosing among the somewhat conflicting results of nonfinal theories. Chapter 4, on interpretation of nuclear magnetic resonance results, has bearing here.

The author pleads for more experimental-chemical results which might relate fairly directly to the theoretically derived charge distributions. There is indeed room for much further pertinent work on chemical reactions, but one might hope for more good, hard thought about the theoretical meaning of chemical facts already known, than one author could be expected to accomplish in a summary such as Chapter 5. Here the chemical facts of the subject are presented in large measure by tables, often with little judgment of validity or relative importance, but with a major attempt to see relations to theory. It is abundantly apparent that the author regards this fact-theory correlation as incomplete, for we find at many points strong hints for further thought and more experimentation.

In sum, then, this book is required *study* for anyone who hopes to understand the polyboranes—and we still do not have to consign all of the fun to the computer. The bibliography of 339 references offers ample assistance for finding the more detailed knowledge upon which a thorough study must depend.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES, CALIFORNIA 90007

ANTON B. BURG

Radionuclide. Zweite, völlig neubearbeitete Auflage von Radioaktive Isotope. By Dr. KURT SCHMEISER, Knapsack-Griesheim AG., Werk Knapsack Bei Köln. Springer-Verlag, Heidelberg-berger Platz 3, Berlin-Wilmersdorf (West), Germany. 1963. 282 pp. 25.5 × 17 cm. Price, DM 59.

The stated goal of this relatively small book is to be a guide for the practical use of radioactivity in research and development in a variety of fields. The author uses about one-fourth of the space for a simple treatment of nuclear structure, the production of radionuclides, the laws of radioactive decay, the statistical limitations of measurement, and the interactions of radiation with matter. These sections are by no means incisive, but they serve to give an adequate background for the more detailed treatment of instrumentation and techniques that form the main part of the book.

About one-half of the book deals with the common instruments for the detection of radioactivity and with the techniques for using them with various radionuclide sources. Scintillation counting is treated quite completely from its uses for γ -ray spectrometry through the techniques for the assay of radioactive samples in liquid scintillator systems. The author brings up all of the many practical problems lying between the collection of raw measurements and the calculation of quantitative measures of relative or absolute activity, giving (generally graphically)

solutions for the problems for typical instrumentation. A good applied radiochemist is a man who can achieve this same success with the particular nuclides and counting equipment required for his special problems. He would have to dig some, but the author has shown him the general problems and numerous examples of how they have been solved in typical cases.

The remaining quarter of the book deals with a wide-ranging selection of typical applications of radioactivity, going from chemistry to medicine and industry. Radioautography of thin slices is treated in some detail, but for biology alone; radiography, in similar detail for metallurgy. There is a small section on radiation protection problems and German legal requirements.

The book has 234 figures, a large fraction being plots with quantitative data for practical situations, although a few seem to be too highly specialized for the needs of the text. The literature references are fairly numerous and about one-half to the American literature, but they are not always to the most recent authoritative sources. On the whole, the book seems to be a good one for a general view of the very many ways radioactivity can be used as a tool in modern science and technology, and a useful one to encourage a new worker to broaden his techniques and to increase his abilities to use radioactivity effectively.

DEPARTMENT OF CHEMISTRY AND CHARLES D. CORYELL
LABORATORY FOR NUCLEAR SCIENCE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

Noble-Gas Compounds. Edited with Introduction by HERBERT H. HYMAN. The University of Chicago Press, 5750 Ellis Ave., Chicago, Ill. 1963. xiii + 404 pp. 16 × 24 cm. Price, \$12.50.

The book is, in the main, a collection of research papers by many authors on the novel and relatively new noble-gas compounds. The papers are an "up-to-the-minute" report on work done between the time of the publication of Bartlett's work on Xe + PtF₆, June, 1962, and April 22, 1963, the opening day of the conference on noble-gas compounds held at the Argonne National Laboratory. This book is an out-growth of that meeting. The amount of research described in the book is indeed impressive, since less than 1 year elapsed from the preparation of the first xenon tetrafluoride to the completion of the manuscripts for the book.

The first section contains a presentation of four papers which are concerned with a chronological account of some noble-gas chemistry up to and including the preparation of XeF₄. The first paper by E. N. Hiebert of the University of Wisconsin on the discovery of argon is very well done and is exceedingly appropriate for this book because his theme emphasizes the painstaking care that Ramsay and Rayleigh gave to their experiments and the reluctance of their contemporaries, particularly Dewar, to accept the fact that there could be an element or elements that did not exhibit chemical properties.

The second paper by D. M. Yost of the California Institute of Technology describes his experimentation on xenon with chlorine and fluorine in 1933 but without success. Yost's new generation experimenters were led by Bartlett and Jha at the University of British Columbia with their experiments on Xe and PtF₆. They were quickly followed by Claassen, Malm, and Selig at the Argonne National Laboratory with their preparation of XeF₄.

Editor Hyman has logically divided the book into sections devoted to the particular type of research. These sections after the Introduction are: "Preparation and Some Properties of Noble-Gas Fluorides"; "Some Practical Considerations"; "Thermochemistry"; "Aqueous Chemistry of Noble-Gas Compounds"; "Diffraction Studies and the Structure of Xenon Compounds"; "Studies of Electron Spin Resonance, Nuclear Magnetic Resonance, Mössbauer, Infrared, and Raman Spectra and Related Experiments"; "Physiological Properties of Noble-Gas Compounds"; and "Theoretical Studies of Noble-Gas Compounds."

An outstanding feature of the papers in the book, other than their fascinating subject, is the detail given regardless of whether a paper is describing a preparative procedure, a physical measurement, or a molecular orbital calculation.

Editor Hyman has aptly remarked that in this assemblage of papers one can find a presentation that concerns almost every technique that modern chemistry, physics, and technology has made available. The relatively simple structured xenon com-

pounds seem to be good illustrations for the demonstration of these techniques in this area of preparative, physical, and theoretical chemistry.

There are 58 papers and 105 contributing authors, and the quality of the research represented by these papers is probably higher than that on any other group of related compounds. In some few cases, further experiments since the publication of the book have modified the interpretation of data, but by and large, the book is as authoritative today as it was in April, 1963.

The book is remarkably free of typographical errors, and the quality of the printing and binding is excellent. The 14 unnumbered pages of glossy prints add a lot to the appearance of the book, but the regular page stock could have been used to perhaps reduce the price of the book.

DEPARTMENT OF CHEMISTRY STANLEY M. WILLIAMSON
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720

Theorie und Praxis der Gravimetrischen Analyse. Band I. Theoretischer Teil. By Dr. LÁSZLÓ ERDEY, Professor an der Technischen Universität Budapest, Mitglied der Ungarischen Akademie der Wissenschaften. Akadémiai Kiadó, Alkotmány U. 21, Budapest V, Hungary. 1964. 382 pp. 17.5 × 24.5 cm. Price, \$9.00.

This is the first of three volumes on gravimetric analysis, which has the somewhat mysterious title of "Theoretical Part." Actually, most of the theory is covered in some 60 pages dealing with solubility and formation of precipitates and coprecipitation. This part is classical in nature, although the treatment is more extensive than in most introductory textbooks on analytical chemistry. However, in some respects it is not up-to-date; e.g., no differentiation is made between homo- and heteronucleation, surface tension data originally given by Dundon have not been replaced with some more accurate values, and much space is devoted to the outdated von Weimarn theory. The scope of the book is wider than might be expected from the title. Thus, in the 100-page section on separations, some 50 pages are devoted to immiscible solvent extraction, chromatography (especially ion exchange), and volatilization separation.

The book is of much greater value to the practicing analyst than to the more academic analytical chemist. Operations for dissolving samples, destruction of organic substances, performance of precipitation, filtration, washing, drying, and ignition of precipitates are presented in great detail.

Volume II will deal with gravimetric determination of metals, and Volume III, of anions. These will be of special importance to the analyst, because the author and his associates have tested all the methods and have determined the thermal stability of the precipitates by derivative and straight thermogravimetric procedures.

Once upon a time, gravimetric analysis was the major method of analysis. It is still of fundamental importance for highly accurate analyses and for calibration of other techniques. However, its practice is now greatly reduced as a result of the development of a score of modern techniques. The present treatise may revive some interest in this classical method of analysis.

DEPARTMENT OF CHEMISTRY I. M. KOLTHOFF
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA 55455

Ultrahigh Vacuum and Its Applications. By RICHARD W. ROBERTS, General Electric Research Laboratory, and THOMAS A. VANDERSLICE, Vacuum Products, General Electric. Prentice-Hall, Inc., Englewood Cliffs, N. J. 1963. 199 pp. 16 × 23.5 cm. Price, \$9.00.

Although ultrahigh vacuums were first obtained some 40 years ago by Langmuir, it is perhaps fair to say that pressures below 10⁻¹⁰ mm. are still regarded with awe by all but a relative handful of initiates. However, the actual and potential applications of ultrahigh vacuum techniques are increasing rapidly, and this small but very useful book is therefore highly welcome.

It concerns itself principally with the creation and measurement of ultrahigh vacuum and the relevant chapters—"Components" (pumps, gages, valves), "Materials" (glasses, ceramics, metals), "Ultrahigh Vacuum Systems"—are excellent, up-to-date, easily intelligible to the nonexpert, and rich in useful tabu-