

BOOK REVIEWS

Anorganische und Allgemeine Chemie in Einzeldarstellungen. Band V. Die Kernmagnetische Resonanz und Ihre Anwendung in der Anorganischen Chemie. By EKKEHARD FLUCK. Springer-Verlag, Abteilung VI., 1 Berlin 31 (Wilmersdorf), Heidelberger Platz 3, West Berlin, Germany. 1963. 16 × 24 cm. 290 pp. Ganzleinen DM 48.

The author of this book explains in his foreword that it was his intention to summarize the scattered literature on the applications of n.m.r. to inorganic chemistry in order to illustrate the areas in which it has been used and to suggest further possibilities. The book begins with a brief qualitative introduction (75 pages) to the phenomena of high resolution n.m.r. This introduction is designed to prepare the nonmathematically inclined chemist to evaluate and interpret simple spectra, and to apply this method to his own problems. The remainder of the book is devoted to chapters dealing separately with studies of nuclear resonance of protons, boron, carbon, nitrogen, oxygen, fluorine, aluminum, silicon, phosphorus, tin, mercury, lead, and "other elements." Appended are extensive tables of chemical shifts and coupling constants for boron, fluorine, and phosphorus compounds. The book as a whole is intended to familiarize the preparative inorganic chemist and the theoretical chemist with a physical aid to the solution of their problems.

Unfortunately, in this reviewer's opinion, the book fails in its primary purpose. In the attempt to keep the theoretical introduction short and qualitative, oversimplifications and inaccuracies have inevitably crept in, and the logic of many conclusions will not be apparent to the student. In addition, numerous undefined terms which are likely to be unfamiliar to the uninitiated reader (e.g. Larmor frequency, p. 4) are introduced, and must certainly cause difficulty for the beginner. More serious, however, are the errors of omission and commission which could lead to misunderstanding on the part of the reader and eventually to misuse of the n.m.r. method. These are sprinkled thickly through the introductory section. To give an example, in the section dealing with analysis of ABX spectra: (1) it is stated that the two lines at $\nu_x + D_+ + D_-$ and at $\nu_x - D_+ - D_-$ are seldom observed because they are so weak; (2) it is stated that combination transitions involve two nuclei; (3) it is stated that the outer lines of the X part of the spectrum (not counting the lines at $\nu_x + D_+ + D_-$ and $\nu_x - D_+ - D_-$) are separated by $J_{AX} + J_{BX}$; (4) no attention is called to the fact that it is always possible to find two sets of parameters which will give an exact fit for the positions of all lines and the intensities of the AB part (and sometimes the intensities of the X part within experimental error); (5) in connection with the signs of the coupling constants, it is stated only that the absolute values cannot be determined. Similarly, in the section dealing with AB_2 spectra, it is stated that the spectrum is unchanged when the coupling constants between nuclei A and B become unequal, and that the spectrum may then be calculated as an AB_2 spectrum with J_{AB} equal to the average of the two coupling constants.

There are areas, important to present day application, which receive little or no attention: the matter of relative signs of coupling constants and their determination is essentially ignored; the determination of spin densities in paramagnetic complexes is not mentioned. A section on sample preparation, suitable solvents, the effect of dissolved oxygen or other paramagnetic impurities, and similar topics would certainly have been useful for the beginner.

The sections dealing with applications of the magnetic resonance of different nuclei are of varying degrees of completeness and usefulness. The most exhaustive is that covering phosphorus (60 pages), and this section may be sufficiently valuable for those interested in phosphorus chemistry to justify the purchase of the book. The sections on hydrogen (25 pages), fluorine (25 pages), and boron (18 pages) are less complete. The supplementary tables on boron, fluorine, and phosphorus form a handy compilation of useful data.

The book is well printed, and contains no more than the average number of typographical errors. Its cost is reasonable. It would have met a real need. It is regrettable that it cannot be recommended.

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Nouveau Traité de Chimie Minérale. Tome IX. Titane, Zirconium, Hafnium, Thorium. PAUL PASCAL Editor. Masson & Cie Editeurs, Libraires de L'Académie de Médecine, 120 Boulevard Saint-Germain, Paris, VIe, France. 1963. 25.5 × 17 cm. 1211 pp. Price, Broche 200 F; Cartonne Toile 212 F.

Nouveau Traité de Chimie Minérale. Tome VIII. Germanium, Etain, Plomb. PAUL PASCAL, Editor. Masson & Cie Editeurs, Libraires de L'Académie de Médecine, 120 Boulevard Saint-Germain, Paris VIe, France. 1963. 25.5 × 17 cm. 815 pp. Price, Broche 136 F; Cartonne Toile 148 F.

These two volumes continue the massive revision that Paul Pascal has undertaken of his treatise on inorganic chemistry. In addition to making considerable abbreviation of the treatment of industrial chemical operations, the present work concentrates more than its 25-year old predecessor on the descriptive and theoretical study of physical-chemical properties. The intent has been to expand the interpretation of systematic properties in terms of structure and bonding, but the extent to which this has been realized depends greatly on the identity of the particular author contributing a specific section.

In Volume VIII, the material on germanium by A. Tchakirian, P. Bévilard, and A. Godfrin is very good. It comprises 284 pages and its scope extends from a wry comment on the origin of the name of the element germanium *vs.* that of gallium to a clear phenomenological interpretation of the operation of *p-n* junctions. The descriptive material on the compounds is quite complete and includes not only the classical reactions but also thermodynamic and structural crystallographic data where available. There is almost no discussion of bonding, even in the extensive section (over 100 pages) devoted to organo-germanium derivatives. As everywhere in the treatise, there are copious references to the original literature—easily located because of the praiseworthy system of noting on the bottom of each page the location of the next set of bibliographical references. The part on tin (180 pages) is by Bernard Lemanceau. Well-documented, it also is encyclopedic. Interpretative speculation is completely absent. René Faivre and Raymond Weiss contribute 330 pages on lead, which seem to be the broadest in scope of Volume VIII and the most likely to receive special reference. The data on the lead ternary compounds that have interesting dielectric properties are particularly well summarized, as are the data on the binary chalcogenides which are of electrical interest.

Volume IX has 210 pages on titanium by A. Chrétien and W. Freundlich, 555 pages on zirconium by P. Lehr, Ph. Albert, L. Renucci, and J.-P. Langeron, 231 pages on hafnium by P. Albert, and 200 pages on thorium by J. Flahaut. There is considerable reference to commercially important processes and, particularly in the section on titanium, there are also numerous sketches of apparatus that are of special usefulness. The coverage on perovskites and related systems is surprisingly brief as is that on the effect of deviation from stoichiometry on the properties of TiO_2 . However, phase diagrams are liberally represented, especially for the binary systems. Zirconium is well and systematically treated but lacks much of the interesting aqueous solution behavior. Methods of separating hafnium and zirconium, particularly solvent extraction and ion exchange, are satisfactorily discussed with special remarks directed to the French research. The aqueous chemistry of hafnium and thorium are both adequately presented though not so well as the high temperature and nuclear properties.

Both volumes are efficiently indexed, and, in fact, the indexes represent a happy compromise between the notoriously under-indexed British works and the over-indexed German compendia. It is always impressive to read summary volumes such as these, since the staggering expansion of chemical research is made clearly evident. There is no doubt that Volumes VIII and IX will be useful reference for any inorganic chemist working with the titanium or germanium subgroup elements. The fact that these subgroups contain several elements particularly attractive to the materials research people will make these volumes especially valuable.

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