

In Figure 1A are shown the results for a solution containing $1.0 \times 10^{-5} M$ AO and $2.3 \times 10^{-2} M$ PGA. The measured birefringence is the sum of that due to the polymer (large and positive) and that due to the dye (variable). The dispersion curve of the dye is easily seen superimposed on the separately determined dispersion curve of the polymer (dotted line). These curves can be smoothed out by removing the $1/n\lambda$ dependence as shown in the plot in Figure 1B.

The main feature of the dispersion curve is a relatively intense positive curve centered around 5000 Å. No assignment can be made at present for the dispersion in the region of dimer absorption (*ca.* 4700 Å). More than one transition is probably involved and the experimental data need refinement. Although the center of the strong anomalous dispersion is shifted somewhat to the red relative to the absorption maximum at 4900 Å, this same shift is found in both the optical rotatory dispersion⁴ and circular dichroism⁵ spectra. The shift is not due to electrical dichroism as none could be observed at 5000 Å. The reason for this shift is unknown and under active investigation.

Some conclusions can now be drawn concerning the structure of the complex. From this positive dispersion, the transition moment for the long wavelength absorption can be assigned as roughly parallel to the dipole moment in the complex responsible for the orientation in the electrostatic field. The dipole moment in the polymer is very large and directed along the long axis of the helix. The transition moment in

the free dye is long-axis oriented⁹ and, therefore, the long axis of the bound dye must be approximately parallel to the polymer axis. The direction(s) of the transition moment(s) for the aggregate absorption cannot be identified as yet. It is likely, though, that both perpendicular and parallel polarized transitions are present since the optical rotatory dispersion⁴ is normal while a complex circular dichroism is found.⁵ The dye is probably bound to the polymer in the form of a left-handed helix as previously suggested;⁴ the known tendency of acridine orange to aggregate supports this view. The specification of the orientation of the long axis of the dye molecule as parallel to the polymer axis by this direct measurement corroborates the previous assignment inferred from circular dichroism measurements on partially oriented solutions.⁵

Kerr constant dispersion is in principle a most versatile tool since the Kerr effect is common to all matter and the system need not be asymmetric. Even in systems which are amenable to examination by other techniques, much information of a complementary nature can be obtained. We are currently studying Kerr-effect dispersion in a variety of macromolecular systems.

(9) H. Jakobi and H. Kuhn, *Z. Elektrochem.*, **66**, 46 (1962).

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Book Reviews

The Solid-State Chemistry of Binary Metal Hydrides. By GEORGE G. LIBOWITZ, Kennecott Copper Corporation, Ledgemont Laboratory. W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1965. xi + 139 pp. 15.5 × 23.5 cm. \$7.50.

Here is a short book surveying the solid binary hydrides from a physical-chemical viewpoint, with a bare minimum of descriptive material. Although its brevity makes it vulnerable to criticism for what it leaves out, it also permits a beginner in the field to grasp the fundamentals efficiently. The book has six crisp chapters on classification and bonding, preparation and chemical properties, crystal structures and phase relationships, thermodynamics, electrical and magnetic properties, and nonstoichiometry. The review on hydrides by Gibb (1962) should have been mentioned by more than a reference or two, and the classic work by Smith ("Hydrogen in Metals," 1948) deserved more than a footnote.

Many references, some quite important, to work on hydrides were not mentioned at all. Some of these are: the early work by Pietsch (1933) and the later work by Siegel and others (1960-1964) using atomic hydrogen; Mikheeva and Kost's review of the rare earth hydrides (1960); Goon's paper on lanthanum hydride (1959); the magnetic structures of TbD₂ and HoD₂ by Cox, *et al.* (1963); and Beck's discussion of the Zr-H system (1962). The data on EuH₂ and YbH₂ are presented, but no references. Only a few papers from the vast literature on the Pd-H system are covered. No mention was made of the interaction of certain hydrides with mercury. Except for a brief discussion of the Ni-H system, the author avoided, perhaps wisely, the hotly disputed and controversial hydrides of Fe, Co, and Ni. The proposed structure for BeH₂ (Figure 3-13) could be improved to indicate tetrahedral Be atoms. Most recent work on the tender compound, copper hydride, was ignored, and the structure for it given in Figure 3-12 is incorrect. There are a half a

dozen or so errors of the typographical kind, and activation energy is used instead of enthalpy on page 119.

The nonmathematical description of rates of hydride formation in Chapter 2 is uncommonly complete, and helps one retain a large body of observations. The pithy discussion in Chapter 3 of volume changes which occur when metals react with hydrogen is especially lucid. Rare earth hydrides are covered well, although the ionic conductivity of lanthanum hydride (Chapter 5) was not related to the diffusion of hydrogen in the solid as revealed by nmr studies (Chapter 6). When discussing the magnetic properties of lanthanum hydride, unpaired electrons are mentioned; the reader wonders what unpaired electrons. In Chapter 3, the lighter rare earth trihydrides are said to have the bismuth trifluoride-type structure; actually BiF₃ is orthorhombic, not cubic. In the section on actinide hydrides, the mobility of hydrogen in UH₃ was missed (Bigelsen and Kant, 1954), americium hydride was not included (Westrum, *et al.*, 1951), and the reference to PaH₃ was not given. The various sections on those frightful hydrides of V, Nb, and Ta are the best correlating summaries available.

The chapter on thermodynamics of hydrides goes far to compensate for some of the omissions noted above. The comparison of hydrides and deuterides and their relative dissociation pressures is brief but cogent. The treatment of partial molal quantities is especially clear. On observing that $-\Delta H_{form}$ for MgH₂ is lower than is the case for other alkaline earth hydrides, the author concludes that this illustrates its partly covalent nature. Yet if this criterion is applied to LiH and CsH, one would conclude that CsH is more covalent, whereas the opposite is true. The section on hysteresis competently summarizes current theories.

Except for some quaint nomenclature, the chapter on nonstoichiometry gives a satisfying account of the energetics of defect solids. The treatment of large deviations from stoichiometric

compositions is especially skillful. Martin and Rees' interpretation (1954) of the solubility of hydrogen in zirconium might have been included, as well as Takeuchi and Suzuki's discussion (1962) of the plutonium-hydrogen system.

In summary, this succinct volume may be recommended to researchers in the chemistry of metal hydrides, along with a word of caution on its omissions.

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The Alkaloids. Chemistry and Physiology. Volume VIII. The Indole Alkaloids. Edited by R. H. F. MANSKE, Dominion Rubber Research Laboratory, Guelph, Ontario, Canada. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. xv + 861 pp. 16 × 23.5 cm. \$32.00.

This book constitutes the eighth volume of a long-standing, well-known series of treatises on alkaloids and encompasses twenty-two chapters written by twelve knowledgeable authors. While the book covers only the subject of indole alkaloids, its large size and the apparent need for a repeated survey of this field only 5 years after the appearance of an extensive chapter thereon in the seventh volume of "The Alkaloids" bespeak the extraordinary, recent growth of this area of the chemistry of organic natural products.

Since the majority of the chapters are well composed and many reflect the personal research efforts of the authors, the subject matter comes strongly alive. Indole alkaloids represent some of the structurally most complex, monomeric organic compounds. Hence watching the unravelling of the mystery of their molecular labyrinths, the unfolding of the chemistry of their multiple, proximate, functional groups, the chemical resurrection of their bizarre molecular architectures, and the exact retracing of the pathways of their natural births are intellectually stimulating and rewarding experiences. Reading the alkaloid book yields such satisfaction. Furthermore, it creates vistas *inter alia* for new organochemical research program and for tortures of graduate students on new examination questions.

The book contains only a minimal number of mistakes (e.g., CXIX on p 721) and appears to yield exhaustive coverage of the chosen topics. Thus, for example, one of the earliest communications revealing the gross structures of rotundifoline and mitragynol [*Proc. Chem. Soc.*, 206 (1963)] is cited while having been overlooked in a previous review [*Ann. Rept. Progr. Chem.* (Chem. Soc. London), 60, 408 (1963)]. Whereas predictably some discussions have been rendered obsolete already by new research data, the book in general is surprisingly up to date. There is a heavy dose of mass spectrometry, the new plaything of the structure analysis enthusiasts, permeating the book. It can be expected to recede into the background in future volumes of "The Alkaloids" series, as this new research tool is acceptable as commonplace and takes its position alongside all other plebeian methods of instrumental analysis.

The greatest weakness of the book lies in its general organization. There is an extraordinary amount of duplication of discussion by the various authors. (Suffice it to illustrate just one case of wasted effort, Chapter 18; its subject matter is covered largely in Chapter 14.) This problem will only worsen in future volumes unless traditional lines of organization are abandoned. Since the same or structurally closely related alkaloids are constituents of a great variety of plant species, any division of discussion along taxonomic lines must prove to be awkward. Since the book purports to speak mostly to the organic chemist, classification by structure types may be the most efficient method of presentation. A separate listing (perhaps in form of a chapter) of all botanical species to be discussed and their alkaloidal contents could be included.

While the subtitle of "The Alkaloids" implies coverage of both chemistry and physiology, only the first subject has been done full justice in Volume VIII as well as in most previous volumes. Since the pharmacology of alkaloids should not be merely an afterthought of alkaloid chemistry and deserves its own place under the sun as a separate scientific discipline with its own adherents, serious consideration should be given to deletion of the small "physiology" sections in future volumes.

Although the price of the book will preclude its mass purchase by students, no practitioner of alkaloid chemistry can afford to be without a desk copy.

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Fluorine Chemistry. Edited by J. H. SIMONS, University of Florida, Gainesville, Fla. Volume IV. By HAROLD C. HODGE and FRANK A. SMITH, Department of Pharmacology and Radiation Biology and Biophysics, University of Rochester School of Medicine and Dentistry, Rochester, N. Y. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1965. xviii + 786 pp. 16 × 23.5 cm. \$28.00.

The Volume IV edition of the text entitled "Fluorine Chemistry" is a most misleading title. There is no discussion at all of the chemistry of fluorine. In fact, the authors very frequently misuse the proper nomenclature in not naming fluoride compounds with the most electronegative element last. After some perusal, one notes that Volume IV reflects a series of volumes, all under the same title. Volumes I and II concern themselves with fluorine chemistry *per se*, Volume III with the biological effects of the organic fluorides, and Volume V to new information of fluorine chemistry. It appears that a subtitle to each generic title would have been most useful for explaining the exact contents of each volume.

Volume IV is particularly confusing in the design and use of the tables. One notes that Table 8, for example, is on page 192, while Tables 7 and 9 are on pages 20 and 39, respectively. Capitulation shows that Tables 8, 12, 21, 22, 25, 34, and 56 are at the end of the first chapter and not appropriately placed following the subject matter.

One is confused in correlating the figures with the body of the material. For example, on page 34, the authors refer to Figure 5 in their discussion of fluoride absorption and excretion. Figure 5 appears on page 422 and has nothing to do with either plasma fluoride or urinary fluoride.

The dedication of this volume is to the memory of Kaj Roholm, a most appropriate choice since, as the authors mention, his concepts which were introduced more than 30 years ago now have been substantiated by current research. While this gesture is much deserved, warmly prepared, and stated with much humility, it does seem inappropriate in some ways, since the authors themselves pioneered the basic research in fluorine chemistry along with such notable investigators as McClure at the National Institute of Public Health, Phillips at the University of Wisconsin, Armstrong at the University of Minnesota, and others too numerous to mention. These data, obtained by these latter workers, were not based upon speculation as stated by the authors in reference to the work of Roholm.

The text is divided into two chapters. Chapter 1 concerns itself with the biological properties of inorganic fluorides in both experimental animals and in man. Chapter 2 devotes itself to the effect of fluorides on the skeletal system and the dentition. Under the first chapter an extensive and thoroughly documented discussion is presented concerning both the acute and chronic effects of fluoride toxicity along with the inorganic metabolism of fluoride in the human and animal. The clinical effects of fluoride metabolism are discussed from both an industrial and nonindustrial environment. An appropriate discussion is presented on the biological effect of fluoride on both enzyme systems and in microorganisms.

Little new material is presented in Chapter 2. However, the completeness of the discussion provides the interested reader with a composite picture of previously unrelated facts. An exception to this is the newer concept of the effect of fluoride on the skeletal system with specific reference to the beneficial effect in osteoporosis.

The only serious drawback to this excellent text relates to the dental aspects of the effects of fluoride contained in Chapter 2. While an extensive literature review is presented in table form concerning the effect of many different fluorides attempted for use in the control of human dental caries, little discussion is presented by the authors to relate the advantages and disadvantages, limitations, and beneficial aspects of the variety of different human clinical studies presented. For example, the tables which present human clinical data may lead the noncritical reader to believe that the same results in reducing dental caries are produced by using concentrated fluorides as topical agents once a year, as occur from using stannous fluoride dentifrices three times a day, or a fluoridated water several times a day from birth throughout the first 8 years of life. The chapter on dental caries could have been improved considerably by discussing some of the known limitations of human dental caries studies and what the inexperienced reader should expect in interpreting tables of data listing results without such background information. The discussion on stannous fluoride dentifrices, for example, leads the reader to believe that the efficacy of the stannous fluoride-calcium pyrophosphate dentifrice is of recent vintage. The authors substantiate their feeling "that more data is needed"