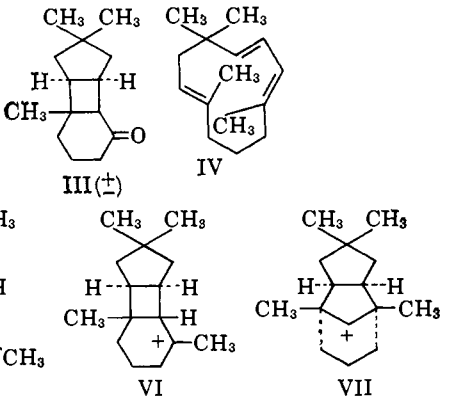
40% aqueous sulfuric acid at 0 to −5° for 15 min., and further at 25° for 2 hr., gave synthetic α-caryophyllene alcohol (approximately 50% yield), m.p. 118–118.5°, undepressed upon admixture with authentic material.[8] *Anal.* Found: C, 81.14; H, 11.77. The n.m.r. and infrared spectra of the synthetic and naturally derived α-caryophyllene alcohol were identical. The former showed peaks due to methyl groups at 0.82 p.p.m. (two CH_3), 0.90 p.p.m. (one CH_3), and 1.03 p.p.m. (one CH_3).

An especially simple mechanistic explanation for the formation of II from humulene by an acid-catalyzed process involves prototropic rearrangement of humulene to the isomeric conjugated triene IV and protonation of IV with subsequent formation of the carbonium ions V, VI, and VII. On the basis of this hypothesis, it is to be expected that the tertiary alcohol obtained by methylation of the ketone III would give rise to α-



caryophyllene alcohol under acidic conditions, as is indeed the case.[9]

(8) We are indebted to Drs. A. Nickon and J. B. DiGiorgio for providing an authentic sample of naturally derived α-caryophyllene alcohol.

(9) This work was supported by the National Science Foundation, Grant GP-221.

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BOOK REVIEWS

Techniques in Protein Chemistry. By J. LEGGETT BAILEY. American Elsevier Publishing Company, Inc., 52 Vanderbilt Ave., New York, N. Y. 1963. 310 pp. 21.5 × 14 cm. Price, $11.66.

A volume of this type seems primarily designed as a textbook for students and research workers concerned with modern techniques for the analysis of protein composition and purity. It covers most of the standard techniques such as paper and column chromatography, electrophoresis, and ion exchange for amino acids and peptides. Techniques such as dialysis and gel filtration, column chromatography, and zone electrophoresis of proteins are also described. Dr. Leggett Bailey includes extensive dicussions of reactions used to study the composition of proteins. There are sections dealing with disulfide bonds and selective cleavages of peptides in a framework of sequence determinations. The over-all subject matter is extremely well presented.

I do have some criticism regarding the scope and organization of the book. It is somewhat distressing that a chapter on thin layer chromatography is absent. In addition, since the author stresses techniques in a rather random fashion, it is difficult to follow a logical sequence from the isolation through the analysis of a given protein. Lastly, the title of the work seems too broad. Certainly, ultracentrifugation, X-ray diffraction, light scattering, rotatory dispersion, and salt precipitation are important techniques in protein chemistry which are not included. Perhaps the book should have been called "Chromatography and Sequence Determination in Protein Chemistry." Within these two general areas the book should prove to be a valuable source since it describes the techniques from an experimental point of view.

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Polyanions et Polycations. By P. SOUCHAY, Professeur a la Faculte des Sciences de Paris. Gauthier-Villars, 55 quai des Grands-Augustins, Paris (VI^e), France. 1963. 247 pp. 16.5 × 25 cm. Price, 42 F.

Interest in the constitution and behavior of the polyions is in no sense a recent development. The interaction of phosphates with molybdates was indeed observed by Berzelius as early as 1826. It remained, however, for chemists of the modern era to demonstrate the great generality of the phenomenon of condensation in solution brought about by acidification. The nature of the condensed ionic species in solution is sometimes very difficult to establish with certainty, as the conversion of one form to another may be so slow that true equilibrium is rare even at high temperatures. The newer techniques developed for the study of complex ion equilibria have nonetheless been brought to bear on the problem with fruitful results. Together with X-ray analysis, they have been able to elucidate the structures of many of these remarkably complex inorganic compounds.

In the nine chapters of this book, Professor Souchay has summarized the present knowledge on the structure, behavior, and uses of substances consisting of polycations, isopolyanions, or heteropolyanions. He writes with authority, as one who has contributed to the development of the subject and has observed the work of others with the discernment and perspective that are indispensable to a useful assessment of its value.

In the introductory chapter, the different kinds of polycations and polyanions and the methods by which they are formed are described. Reactions initiated by acidification, dehydration, deammoniation, and solvolysis are likewise discussed. The isopolyanions formed by polymerization of simple chromates, phosphates, vanadates, silicates, and tungstates are perhaps most familiar to the reader. Chapter 2 is devoted to a discussion of these systems together with the corresponding acids. A brief but rewarding description of the composition of borate solutions is included. A separate chapter, Chapter 7, deals in detail with the polyanions of phosphorus.

Chapter 3 is devoted to heteropolyanions, especially those containing tungsten and molybdenum, which are among the most important and typical of this class. Chapters 4 and 5 describe in some detail the methods that have been used for the study of polyanions in solution and in the solid phase. These include spectrophotometry, polarography, kinetics, cryoscopy, potentiometry, differential thermal analysis, and X-ray methods. Compounds related to the polyanions, for example, peracids and persalts and derivatives containing sulfur and fluorine, are described in Chapter 6.

As polyanions are often formed by the action of a strong mineral acid on certain anions, similarly polycations are formed by the action of hydroxide ion on certain simple cations. The methods of studying these condensed cations, described in Chapter 8, are analogous to those used in the investigation of polyanions. The application of sedimentation and light scattering methods is dis-

cussed, as are potentiometric methods, including the special advantages of the concept of the "potentiometric surface." The mechanism of the condensation process is also examined. The final chapter is devoted to the constitution of basic salts in the solid state. Hydrolytic mechanisms are considered briefly as is the role of basic salts in industrial operations such as chrome tanning.

The bibliography of 299 citations appears to touch upon the most important general references of recent date. Its usefulness suffers, however, from a curiously random arrangement of references. The list is neither alphabetical nor chronological, and there is, moreover, no relationship to the order in which the references first appear in the book. For example, a mention (p. 6) of work on tungstate ions by Jander (1933) leads the reader to discover, after a lengthy search, that the only paper cited of which Jander was the sole author (item 9) was published in 1940. He finally settles on item 23, five papers by Jander, Witzmann, Banthien, and Exner, of which two were published in 1933. His decision is supported by observing that the only two prior citations in the book were to items 21 and 22. A few minutes in the library, however, revealed that each of the five papers cited in item 23 carried the names of Jander and one of the other three; the authors of the two papers published in 1933 were Jander and Witzmann.

In the reviewer's opinion a specialized monograph of this type should be a good source of literature references which can be depended upon to lead the reader quickly and with a minimum of effort to the most relevant of the original publications. This is not to say that Professor Souchay has failed to compile an adequate bibliography, but rather to deplore an arrangement poorly suited to the convenience of the reader. Fortunately, this defect does not seriously impair the usefulness of this welcome and authoritative contribution to the specialized literature.

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Chemical Analysis. Complexation in Analytical Chemistry. By ANDERS RINGBOM, Department of Chemistry, Abo Akademi, Abo, Finland. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. x + 395 pp. 15.5 × 23.5 cm. Price, $15.00.

This is Volume 16 of "Chemical Analysis," a series of monographs (by various authors) on analytical chemistry and its applications. Its purpose is to serve as a guide for the critical selection of analytical methods based on complexation reactions. The author has extended the treatment of Schwarzenbach as given in the latter's excellent monograph on complexometric titrations. His aim was to show: "how to compare, without involved calculations, existing methods to determine their relative accuracy; how to choose the most favorable experimental conditions for each analysis; how to calculate and eliminate the interference of various side reactions"; and finally, "how to develop new methods for solving special analytical problems."

There are nine chapters in the book; they cover the following topics: complex reactions, complex equilibria, masking, complexometric titrations, acid–base titrations, complexation in ion-exchange analysis, complexation in metal extraction analysis, complexation in electrochemical analysis, and complexation in photometric analysis.

The theory is given in a simple form, but sufficiently correct to permit an analyst to calculate the accuracy attainable with a given method under widely varying experimental conditions. With the aid of diagrams, curves, and tables, speedy calculations may be made, correction coefficients being used to take into account the interference of side reactions. No laboratory procedures are given in the text, but there are many numerical examples to illustrate various types of problems. The methods of calculation are given in detail, many of the problems referring to original papers, thus showing "how empirical methods described in the literature can be improved and how their limitations can be expressed precisely." Indeed, by short calculations it may be proven that a given method is useless or even impossible, thus saving valuable laboratory time. "On the other hand, many new and unexpected solutions of analytical problems can be discovered by a brief critical study of equilibrium constants." At present the approach outline in the book suffers from the lack of values of equilibrium constants for many important compounds, and from the uncertainty of values given by various authors. Hope is expressed that the book will stimulate analytical chemists to determine equilibrium constants missing in the appendix, the selection admittedly being far from perfect. The author makes no attempt to review the extensive literature on the application of complexation reactions in analysis, and only a few select references are given. The book is directed to graduate students and to analytical chemists in research and industrial laboratories who should be capable of developing working procedures on the basis of a few fundamental principles. With the concepts set forth in this monograph, any advanced analytical chemist should be able to apply them in actual practice.

A useful feature of the book is an extensive appendix (82 pp.) which gives tables of values for the following: stability constants of acids, stability constants of metal complexes, solubility products of sparingly soluble metal salts, logarithmic values of $\alpha L(H)$ for ligands, logarithmic values of $\alpha M(L)$ for various metals and ligands, logarithmic conditional stability constants of metal–EDTA complexes, transition points of metal indicators, pH ranges of acid–base indicators, and extraction constants. The book concludes with author and subject indexes. Printing and paper and cloth binding are good.

Analytical chemists who are convinced that "increased application of theoretical principles to chemical analysis is indispensible" will find this monograph a useful and up-to-date treatment of complexation in analytical chemistry.

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Physics and Chemistry of the Organic Solid State. Volume 1. Edited by DAVID FOX, State University of New York, Stony Brook, N. Y.; MORTIMER M. LABES, The Franklin Institute Laboratories, Philadelphia, Pa.; and ARNOLD WEISSBERGER, Eastman Kodak Company, Rochester, N. Y. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. xvi + 823 pp. 15.5 × 23.5 cm. Price, $25.00.

This is the first of two planned volumes whose stated purpose has been to bring together the contributions in several disciplines of workers, who have been concerned with the properties of organic solids from a variety of aspects and approaches. To a solid-state physicist whose experience is largely limited to inorganic solids, as is that of this reviewer, the field of organic solids has seemed interesting but formidable in view of the relative complexity of the materials involved and their seemingly infinite diversity. A comprehensive survey of the field is an ambitious project, as this massive volume attests, but the book seems to be a fair compromise betweeen the dual goals of offering further enlightenment to readers, who are already experts in some phase of the field, and of giving nonexperts some idea of what the problems are and what the progress has been. There are thirteen articles in all. Each is most copiously referenced, but there are wide variations in the extent to which a didactic treatment is adopted, ranging from use of an almost self-contained textbook style to another extreme of a compact guidebook to an extensive bibliography. Examples of the former, especially welcome to a nonexpert, are: the treatment "Thermodynamics of Crystals" by E. F. Westrum, Jr., and J. P. McCullough, the several articles on crystal morphology and structure and on crystal growth, and the chapter on "Definition and Attainment of High Purity of Organic Compounds" by G. J. Sloan.

The complete contents are: (1) "Thermodynamics of Crystals" (Westrum and McCullough), (2) "Definition and Attainment of High Purity of Organic Compounds" (Sloan), (3) "Crystal Growth" (G. F. Reynolds), (4) "Thermal Reactions of Organic Solids" (H. Morawetz), (5) "Photochemistry of the Organic Solid State" (H. S. A. Gilmour), (6) "Crystal Form and Crystal Structure" (P. Hartman), (7) "Structure of Surfaces" (W. J. Dunning), (8) "Crystallization of Long-Chain Polymers" (H. D. Keith), (9) "Plastic Crystals" (J. G. Aston), (10) "Visible and Ultraviolet Absorption by Molecular Crystals" (D. P. Craig and S. H. Walmsley), (11) "Infrared Spectra of Molecular Crystals" (D. A. Dows), (12) "Dielectric Phenomena" (C. P. Smyth), and (13) "Electron Transfer across the Boundaries of Organic Solids" (L. E. Lyons).

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