BOOK REVIEWS

The Statistical Approach to X-Ray Structure Analysis. By VLADIMIR VAND and RAY PEPINSKY. X-Ray and Crystal Analysis Laboratory, Department of Physics, The Pennsylvania State University, State College, Pennsylvania. 1953. xvi + 98 pp. 21.5 × 28 cm. Price, $1.50.

This little volume is primarily devoted to a critical examination of the method recently proposed by H. Hauptmann and J. Karle for a direct mathematical solution of the phase problem in crystallography. The procedure involves application of the statistical random walk problem to structure factor equations to determine the probability of a given sign assignment. In view of the far reaching consequence of such a general solution, this critique will be of considerable interest to X-ray analysts. Its contents are presented in a concise manner, appropriately written for those familiar with the various techniques used in solution of the structure problem from X-ray data.

While the authors emphasize that the Hauptmann–Karle approach is of considerable value and has given new insight to the phase problem, they present evidence to show that the statistical approach is not reliable except in special cases and disagree strongly with the claim that it gives a general solution for all centrosymmetric space groups, provided the number of observed structure factors is sufficiently great.

The formulas given by Hauptmann and Karle are transformed "into a form more suitable for practical computation." Alternate methods of derivation of the probability distribution functions are presented which point up the relation of these equations to Patterson and Harker functions and provide a better basis for understanding the meaning and limitations of the statistical relations. The statistical treatment is interpreted as corresponding to a "probability sharpening" of Patterson peaks with the origin removed; this leads to convergence of the structure to that of the highest peaks of a Patterson and hence gives the correct answer only if the Patterson function resembles the actual structure. A hypothetical structure with four atoms in the unit cell, space group $P\bar{1}$, in which the statistical method does not give the correct result is discussed in some detail. An analysis of the success of the statistical method in deriving the naphthalene structure is presented.

Extension of the statistical treatment has led authors to new functions which give better representations of the structure of naphthalene than the conventional projections. They suggest that further study will be necessary to show whether these functions will be generally useful in the determination of more complex structures. In their view, however, the statistical approach in its present form cannot be relied upon to furnish a correct solution of the phase problem.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON N. W. GREGORY
SEATTLE 5, WASHINGTON

Advances in Enzymology and Related Subjects of Biochemistry. Volume 14. Edited by F. F. NORD, Fordham University, New York, N. Y. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1953. x + 470 pp. 16.5 × 23.5 cm. Price, $9.25.

Contributions in this volume from the United States, Germany, France, Austria and the Argentine continue to make the "Advances" an international journal. Bücher surveys the difficult problem of energy transport in the living cell. Several theories and models are considered and critically evaluated. A clear style and good organization make this a very readable chapter. Snell and Brown deal with pantethine and related forms in the lactobacillus bulgaricus factor (LBF). The related forms are mixed disulfides of pantethine. Preparation of LBF from culture filtrates, identification and synthesis are described. Pantethine is formed from coenzyme A by the action of intestinal phosphatase. Lerner's article on phenylalanine and tyrosine metabolism brings home the fact that in spite of much work the conversion of tyrosine to melamine in the mammalian skin is still incompletely understood. The review deals with a great variety of subjects, such as the chemical reactions involved in homogentisic acid, thyroxine and adrenalin formation as well as the question of hormonal control of melanin formation and the loss of certain enzymes in men with abnormalities of metabolism of tyrosine and phenylalanine. Sizer deals with a related subject, the action of tyrosinase and peroxidase on proteins. A number of hormones and enzymes are inactivated by tyrosinase while others are not, though in the latter case there is evidence that they too are oxidized. Langenbeck discusses the covalent intermediaries which have been shown to be formed between catalyst (or coenzyme) and substrate in certain non-enzymatic or enzymatic reactions. It is believed that the enzyme protein (apoenzyme) activates the coenzyme and determines the specificity of the reaction. Leloir's article on isomerases, mutases and related enzymes is an excellent resumé of a field to which he has contributed so much by the discovery of the coenzymes glucose-1,6-diphosphate and uridine diphosphate glucose.

Hoffmann-Ostenhof in a long article has again attempted the impossible, a systematic nomenclature of enzymes. The classification and names of the enzymes are based on the reactions catalyzed by them. Trouble arises when mechanisms are assumed in disregard of experimental evidence, *i.e.*, the starch phosphorylases are lumped with sucrose phosphorylase and called amylose-transglucosidases. Hexokinase would have to be renamed ATP → hexose (rather than glucose) transphosphatase. The author writes for this enzyme a freely reversible reaction, as he also does for *Q*-enzyme, renamed amylose → amylopectin transglucosidase. In the reviewer's opinion our knowledge of enzyme mechanisms is still so incomplete that it is best to desist from classifications as they are here attempted.

The last three articles deal with related subjects. Desnuelle discusses techniques used in the elucidation of protein structure, Zittle deals with adsorption of proteins on a variety of substances and the methods of elution. Many examples of successful chromatographic separation of proteins are collected. Schwimmer and Pardee deal with methods of isolation of enzymes; they state that 72 enzymes have been obtained in the crystalline state.

The volume contains a cumulative index for Volumes I–XIV.

DEPARTMENT OF BIOLOGICAL CHEMISTRY
WASHINGTON UNIVERSITY GERTY T. CORI
ST. LOUIS, MISSOURI

The Chemical Structure of Proteins. A Ciba Foundation Symposium held 1st to 3rd December, 1952. Edited by G. E. W. WOLSTENHOLME, O.B.E., M.S., M.B., B.Ch. and MARGARET P. CAMERON, M.A., A.B.L.S. Little, Brown and Company, Boston, Massachusetts. 1954. x + 222 pp. 21 × 14.5 cm. Price, $6.00.

This book comprises the papers and informal general discussions given at the Ciba Foundation's symposium on "The Chemical Structure of Proteins." The methods discussed herein have mainly been developed within the last few years. The critical discussion of the usefulness and specificity of these methods in protein chemistry adds greatly to the value of this book.

The first three chapters deal with the purification of proteins, in particular by the methods of column and partition chromatography. Many chapters are devoted to a critical survey of C and N end-group analyses, both by chemical and enzymatic means. The problems of the partial hydrolysis of proteins and the subsequent separation of the resultant peptides are also considered. The book ends with a discussion of chemical and electron microscope studies on the structure of collagen.

These papers are all written by authorities in their fields, and they therefore provide excellent introductions to the

potentialities of these various chemical and enzymatic tools in the elucidation of protein structure. This reviewer finds the discussions which follow the lectures as valuable as the lectures themselves, for here the various problems in the interpretation of the results are thrashed out—viewpoints it is difficult to find in more formal publications. The references at the end of each paper are remarkably comprehensive, and this book should be of great interest and value both to the general reader and to the worker in the field.

DEPARTMENT OF BIOPHYSICAL CHEMISTRY
HARVARD UNIVERSITY MARGARET J. HUNTER
BOSTON, MASSACHUSETTS

Crystal Data. By J. D. H. DONNAY, The Johns Hopkins University, Baltimore, Md., and WERNER NOWACKI, University of Berne, Switzerland, with the collaboration of GABRIELLE DONNAY, U. S. Geological Survey, Washington, D. C., and many assistants. The Geological Society of America, 419 W. 117 Street, New York 27, N. Y. 1954. ix + 719 pp. 17.5 × 25.5 cm. Price, $5.00.

This book is really two separate, related works bound together in one volume. Part I, by Professor Nowacki, is entitled "Systematic Tables—Classification of Crystalline Substances by Space Groups"; Part II, by Professor Donnay, is entitled "Determinative Tables—Identification of Crystalline Substances from Cell Dimensions."

Part I presents the distribution of about 3800 crystalline substances among the 219 space groups that are distinguishable without a knowledge of the right or left handedness of the crystal structure. Under each space group, the substances are divided into seven categories, as follows: I, Elements and alloys; II, Sulfides and related bodies; III, Oxides and hydroxides; IV, Halides and oxyhalides; V, Salts of oxygen acids containing covalently bound oxygen; VI, Salts of other oxygen acids; VII, Organic compounds. Subsidiary tables set forth the numbers of substances in each category that belong to each space group, each crystal system, each crystal class, each space lattice, etc. In addition, the percentage distribution of substances in each of these ways is tabulated.

Even a casual perusal of the tables in Part I confronts one with some remarkable statistics. There are 41 space groups in which no substance is known to crystallize, according to the literature available to Prof. Nowacki in mid-1948, and there are 32 for which only one example is known; thus, there are only 146 space groups in which more than one substance crystallizes, *i.e.*, only two-thirds of the possible space groups are used by nature to an appreciable extent. Furthermore, almost half of all crystalline species belong to one or another of only ten space groups. Indeed, 9% of all substances (including 22% of all organic substances) crystallize in the monoclinic space group C_{2h}^{5}-$P2_1/c$. The tendency of molecules and ions to arrange themselves in certain selected symmetrical patterns, which is indicated by these figures, is certainly interesting and may become significant in the future. Of course, many more detailed correlations between chemical nature and symmetrical arrangement are presented, or can be discovered, in the tables of Part I; it is a painstaking and thorough piece of work, probably providing the data for many coming investigations.

Part II is of more immediate practical value than Part I. It presents the unit cell dimensions and, where possible, the space groups of about 5000 crystalline substances—all those for which data were available to Professor Donnay up to the end of 1951. These data are tabulated in order of increasing axial ratio a/b in the triclinic, monoclinic and orthorhombic crystal systems, axial ratio c/a in the tetragonal and hexagonal systems, and axial length a in the cubic system. (The rhombohedral system is included in the hexagonal.) A set of rules for choosing the proper unit cell and naming the axes correctly appears in the introduction to Part II; by the use of these rules each crystalline substance can be assigned an axial ratio which gives it a unique position in the tables. (A cubic crystal is uniquely placed by its axial length.) In addition to the main table, Part II is provided with two indexes in which each substance is listed alphabetically by formula or by name, with a reference to its position in the main table. Thus, from the data in Part II, the crystallographic constants of almost any known substance can be found, or, conversely, the chemical nature of almost any crystal.

The usual method for identifying unknown crystalline substances is by the use of the X-ray diffraction patterns of powdered specimens, because a library of powder patterns has existed for many years in the form of the well-known ASTM card file. This method, however, becomes extremely difficult to use on substances with large unit cells of low symmetry. Professor Donnay's tables in Part II of "Crystal Data" provide necessary means for making chemical analysis by X-ray diffraction a really efficient technique. All that is required is one tiny single crystal of an unknown substance and the ability to use a Weissenberg or Buerger Precession X-ray diffraction camera, or, even better, one of the new X-ray goniometers equipped with a Geiger–Müller counter; any of these devices allows rapid and accurate determinations of unit cell constants and space group from a single crystal which need not weigh even 100 micrograms. These data will allow a unique determination of the chemical nature of the unknown substance, provided they are listed in the table.

Part II also contains tables listing the criteria by which space groups can be determined by the use of systematic absences of "reflections" in X-ray diffraction patterns. These tables are arranged to allow space group deteminations (insofar as this is possible on the basis of absent reflections) no matter how the symmetry elements of the unit cell may turn out to be oriented, because of the formal orientation rules required by the main table. The inclusion of these tables makes Part II a complete handbook of single crystal data arranged for use in chemical analysis.

In the opinion of this reviewer, this book is one of the great additions to the reference literature of physical science. Not only crystallographers, but chemists, physicists and all others interested in useful data on chemical substances will soon find this work a necessity in the reference library. The scientific world is to be congratulated upon the existence of men like Professors Donnay and Nowacki who have been willing to spend years of painstaking, self-critical work, in order to provide us with this monumental book at no financial gain to themselves.

PROTEIN STRUCTURE PROJECT
POLYTECHNIC INSTITUTE OF BROOKLYN DAVID HARKER
BROOKLYN 1, NEW YORK

Metallurgy of the Rarer Metals. No. 2. Zirconium. By G. L. MILLER, Ph.D., B.Sc., A.R.I.C., M.I.Chem.E. Academic Press, Inc., Publishers, 125 East 23rd Street, New York 10, N. Y. 1954. xviii + 382 pp. 15 × 22.5 cm. $7.50.

This book is the result of a comprehensive inspection of the literature on zirconium. The author states that he has "examined" the assembled information critically in the light of his own experience and "as a result of knowledge gained during several visits to the U.S.A."

The first fifty pages cover the occurrence and preparation of zirconium compounds. In the next fifty pages the preparative processes of Van Arkel (thermal dissociation of the iodide) and Kroll (reduction of the chloride with magnesium) are described in some detail. The central portion of the book is devoted to the properties of the metal and its alloys while the last one hundred pages describe melting processes (either in use or being studied), fabrication of the metal, powder preparation and metallography.

The author has included extensive bibliographies at the conclusion of each chapter to indicate where further information may be found. The notations referring to books are incomplete. As an example, the reference cited on page 230 and found in the bibliography at the end of Chapter 14, page 273, "Smith, D. C., Hydrogen in Metals, Chicago, 1948" should include the publisher's name. The same applies to reference 1, page 116, "Barrett, C. S., Structure of Metals, New York, 1943," as well as to the other book references. Also, it would seem that the well known A.C.S. monograph by Venable, F. P., Zirconium and its Compounds, The Chemical Catalog Co., Inc., 1 Madison Ave., New York, N. Y., 1922, should be cited in the references at the end of Chapter 3.

A spot check of references to scientific articles in technical journals, however, disclosed only one incorrect in forty. Reference 12, page 60, should read, Hunter, M. A., The Reduction of Metal Chlorides by Sodium, *Trans. Electrochem. Soc.*, **44**, 23 (1923).