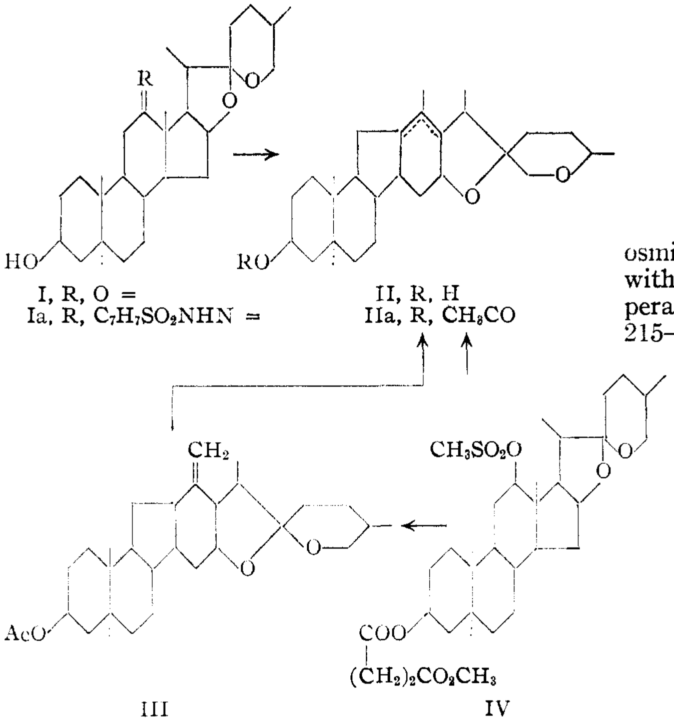
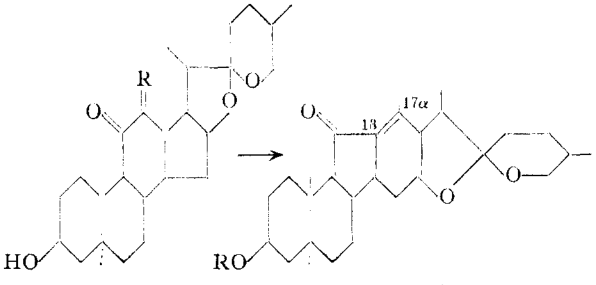


I, R, O =
Ia, R, $C_7H_7SO_2NHN$ =

II, R, H
IIa, R, CH_3CO

III

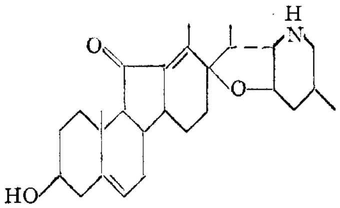
IV



V, R, O =
Va, R, $C_7H_7SO_2NHN$ =

VI, R, H
VIa, R, CH_3CO

exhibited no absorption in the double bond region of the infrared and was smoothly converted with



VII

osmium tetroxide to a triol which on treatment with acetic anhydride in pyridine at room temperature gave only a monoacetate derivative m.p. 215–18°; $[\alpha]^{25}\text{D}$ −39.3° ($CHCl_3$). Found: C, 71.00; H, 9.45.

In a similar manner 11-ketohecogenin (V)[3] was converted to its toluene *p*-sulfonylhydrazone derivative (Va), m.p. 156–158° (dec.); $\lambda\lambda_{\text{max.}}^{\text{CH}_3\text{OH}}$ 228 mμ (3.90), 275 mμ (3.82). Found: N, 4.84. The latter rearranged on treatment with potassium hydroxide in refluxing ethylene glycol to give the 11-keto-$\Delta^{13(17a)}$-C-*nor*/D-*homo*-sapogenin (VI) m.p. 190–192°; $[\alpha]^{24}\text{D}$ −78.4° ($CHCl_3$); $\lambda\lambda_{\text{max.}}^{\text{CH}_3\text{OH}}$ ultraviolet 255 mμ (4.17), 350 mμ (2.88); $\lambda\lambda_{\text{max.}}^{\text{CHCl}_3}$ infrared 5.85 μ, 6.1 μ (more intense). Found: C, 75.54; H, 9.62. *Acetate:* (VIa) m.p. 178.5–179.5°; $[\alpha]^{24}\text{D}$ −80.7° ($CHCl_3$); $\lambda\lambda_{\text{max.}}^{\text{CH}_3\text{OH}}$ 225 mμ (4.18), 350 mμ (2.87). Found: C, 73.74; H, 8.92.

The spectral characteristics of VI are essentially the same as those of jervine (VII).[4] Of particular note is the unique reversal in intensity of the C=O and C=C bands in the infrared spectra of both VI and jervine.

[3] C. Djerassi, H. Ringold and G. Rosenkranz, *ibid.*, **73**, 1513 (1951).

[4] J. Fried, O. Wintersteiner, M. Moore, B. M. Iselin and A. Klingsberg, *ibid.*, **73**, 2970 (1951).

RESEARCH LABORATORIES
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BOOK REVIEWS

Computing Methods and the Phase Problem in X-Ray Crystal Analysis. Report of a Conference Held at The Pennsylvania State College, April 6–8, 1950. By RAY PEPINSKY (Editor). The X-Ray Crystal Analysis Laboratory, Department of Physics, The Pennsylvania State College, State College, Pa. 1952. xvii + 390 pp. 21.5 × 27.5 cm. Price, $7.50.

The conference report presented in this volume is the result of a meeting of about fifty specialists in the field of crystal structure determination from X-ray diffraction data, which was organized by Professor Ray Pepinsky at the Pennsylvania State College under the joint sponsorship of the Rockefeller Foundation and the Office of Naval Research. It was the intent of the conference and the resulting report to review the current status of the problem posed by the lack of experimental information on the phases of the X-ray beams scattered by a given crystal and also of the progress in computing methods applicable to crystal structure determination. This intent has been very successfully fulfilled, and this collected review is a basic contribution to the literature of that field.

The report consists essentially of four parts. The first is a group of ten papers dealing with the basic mathematical problems involved in the application of Fourier transformations in the analysis of the experimental intensity data. Following an introduction by R. Pepinsky and a general statement of the problem by J. M. Bijvoet, papers by C. A. Beevers and A. L. Patterson discuss the structural information which can be obtained from the "Patterson" synthesis using $|F|^2$ coefficients. M. J. Buerger then presents another installment of his discussions on the transformation of the Patterson map to an electron density map with the aid of image theory. The remaining papers in this group deal directly with the problem of the phase relations and include a group of three by C. H. MacGillavry, by J. A. Goedkoop and by B. Friedman, which consider the limitations imposed on the structure factor by the requirement that the electron density be everywhere positive and distributed among chemical atoms; a paper by J. M. Bijvoet describing his method of phase determination by isomorphous substitution and his special trick in the non-centrosymmetric case of Na Rb tartrate whereby he distinguishes the optical isomers; and a paper by M. S. Ahmed describing in a special case the analysis of diffuse scattering as a means of recognizing neighboring reciprocal lattice points showing small phase differences. An omission in the present volume is the general treatment by Karle and Hauptmann of the consequences of the criterion of positiveness in the electron density function; while their treatment is formidable mathematically, it shows promise of being reduced to manageable proportions, as described in the publication of this discussion elsewhere.

The second part deals with the problem of analogue computers applied to the calculation and representation of both structure factors and electron density projections. This part includes papers by J. M. Robertson; C. W. Bunn, A W. Hanson, C. A. Taylor and H. Lipson; C. A. Beevers and J. M. Robertson; and I. W. Ramsay and H. Lipson.

The third part concerns the use of digital computers in crystal structure problems and comprises two papers by E. G. Cox and by E. W. Hughes on the use of punched card methods and a paper by F. Ordway concerning the applicability of the high speed automatic computer at the National Bureau of Standards to crystallographic computations.

The fourth part contains a detailed description of the development and application of the electronic analog computers devised by Ray Pepinsky. The power of a computer constructed for a specific application is well illustrated in X-RAC which specializes in ease of phase permutation and the instantaneous presentation of the two-dimensional synthesis in contour lines on the screen of an oscilloscope. This synthesizer stands in a class by itself and is described very fully here in a paper by Pepinsky including 28 pages of text and 88 pages of drawings and photographs followed by nine appendices of 106 pages prepared by Pepinsky and his collaborators.

The impression given by this volume is one of great strides made since the war in the systematic attack on the problems of crystal structure determination from X-ray diffraction data through a clarification of the mathematical problems involved and the development of well-adapted computational aids. Further rapid progress seems inevitable in view of the activity reported by the contributors to this excellent review.

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Hydrazine. By CHARLES C. CLARK, Ph.D. Mathieson Chemical Corporation, Baltimore, Maryland. 1953. ix + 133 pp. 16 × 23 cm. Price, $3.00.

Recent developments in the field of hydrazine chemistry will more than justify the appearance of this newest addition to the technical literature dealing with this versatile chemical. The organic chemistry of hydrazine is given major emphasis and in this respect the book constitutes a much needed companion volume to the Audrieth–Ogg treatment of the inorganic chemistry of hydrazine ("The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N.Y., 1951). "Scientific and technical personnel in various branches of chemical activity are now provided with basic reference sources, readily available and reasonably complete." In addition to the descriptive chemistry which constitutes the larger part of the book, information is also presented on handling, toxicological data and analytical procedures, together with an interesting and stimulating chapter covering the uses and applications of hydrazine and its derivatives.

The author, Dr. Charles C. Clark, is to be commended for his missionary effort in making available a very useful compilation covering both the open literature as well as new information based upon researches conducted in the laboratories of the Mathieson Chemical Corporation under whose sponsorship this book was written.

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Ion Exchangers in Analytical Chemistry. By OLOF SAMUELSON, Professor of Engineering Chemistry, Chalmers Institute of Technology, Göteborg, Sweden. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1953. xviii + 291 pp. 15.5 × 23.5 cm. Price, $6.50.

The development of the chemistry of ion exchange resins is typical of that for many industrial products or processes, in that a highly developed and specialized technology (water treatment) preceded more specialized uses (separations and analytical procedures), which in turn were followed by fundamental studies on the systems *per se*. Prof. Samuelson's excellent book on the uses of ion exchange resins in analytical chemistry represents the second phase of development of this field.

The book itself is divided into three sections. The first (30 pp.) reviews the fundamental properties of ion exchange systems briefly, with stress placed upon their selectivity coefficients toward various ions. The next section (70 pp.) describes the various parameters that obtain in column operation, such as particle size, flow rate, solution concentration, etc., and gives detailed information on choice of resins, their conditioning and the techniques of operating a column. The remainder of the book (160 pp.) is devoted to a discussion of specific applications. Detailed procedures are given where available.

The sections are as follows:

1. *Total Cations or Total Anions.*—All salts present are converted to the corresponding acids or bases and titrated as such.
2. *Removal of Interfering Ions in Inorganic Analysis.*—Interfering ions of opposite sign to the one being determined are exchanged for non-interfering ions. An example is the determination of sulfur in pyrites, where all of the iron and other interfering cations present are exchanged for hydrogen ions.
3. *Applications to Solutions Containing Inorganic Colloids and Polyelectrolytes.*—The preparation of salt-free sols as well as the uptake and determination of ionic species in the presence of colloids are described.
4. *Isolation of Trace Constituents.*—The resin absorbs the trace species from its dilute solution; it is then concentrated in a small volume of eluting solution.
5. *Inorganic Separations by Column Elution.*—Here separations such as those of the rare earth metals are described; these are followed by classical analytical methods.
6. *Isolation of Low Molecular Weight Organic Acids and Bases by Elution Separations.*—In addition to carboxylic acids, separations of aliphatic and heterocyclic bases, amino acids, vitamins, alkaloids and antibiotics are described.
7. *Isolation of Aldehydes, Ketones and Sugars.*—Non-ionic substances such as aldehydes and ketones which form bisulfite addition products are salts of strong acids; as such, they can be absorbed and separated using anion exchange resins. The same is true of sugars and polyhydric alcohols which form complex ions with bisulfite or borate.
8. *High Molecular Weight Organic Electrolytes.*—Low molecular weight polymers can be separated from those of higher molecular weight because, due to steric hindrance, the latter cannot penetrate the resin gels. For the uptake of proteins, very loosely cross-linked resins can be used. The method has been applied to enzymes and also to viruses.
9. *Study of Complex Salts.*—Here the resin acts as an "electrode" for an ionic species, in that when its distribution coefficient and the amount present in the resin phase is known, the ion concentration in the equilibrating solution phase can be calculated. For example, the calcium ion concentration can be determined in the presence, in solution, of anionic complexes with citrate; formation constants can be calculated therefrom.

The reader is impressed at once with the excellence and the simplicity of the ion exchange procedures. A large number are the result of Prof. Samuelson's pioneering work in this field; this book makes them more available to American chemists. Many of the procedures were developed for the control of industrial processes, where the ion exchange method is sure to find wider application.

This book is also to be recommended as an excellent introductory text on ion exchange chemistry. It is inevitable that it should have many deficiencies in this respect, due in large part to the fact that the applied aspects of the field have preceded the fundamental ones. For example, the body of published information on the organic and physical chemistry of these resins is treated rather superficially. The resin beds are referred to as "filters" which "breathe," *i.e.*, no attempt is made to treat these systems from the standpoint of the modern physical chemistry of electrolytic and polymer systems. The "how" of the analytical procedures are given, but not the "why." As a consequence, persons wishing to develop new procedures are limited by the empirical approach.

A few errors are found. The so-called "screening effect" where larger ions are prevented from being sorbed, presumably on a steric basis, has been shown to be due rather to differences in rates of sorption. Also, the separation of isotopes is described, although there is a serious question that this has been actually accomplished. In fact, most of the procedures, except those of the author, are described in a non-critical manner.

Literature references are given through 1951. The typography of the book is very good, and it is well indexed.

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Small Particle Statistics. An Account of Statistical Methods for the Investigation of Finely Divided Materials. By G. HERDAN, M.Sc., Ph.D., LL.D., Lecturer in Statistics, University of Bristol. With a Guide to the Experimental Design of Particle Size Determinations by M. L. SMITH, Atomic Research Establishment, Harwell. Elsevier Publishing Company, 402 Lovett Boulevard, Houston, Texas, 1953. xxiii + 520 pp. 16 × 23.5 cm. Price, $12.00.

"Small Particle Statistics" covers a wider field than the title would indicate. It is by far the most complete discussion of the science of small particles that has so far appeared, but the statistics of the small particle, while a major topic, is certainly not dominating. The presentation is logical; an elementary discussion of the range of particles to be considered followed by the statistics necessary for developing the subject. A discussion of statistical and experimental methods lays the groundwork for the section on the technological importance of particle size and its relation to other physical and chemical properties. After convincing the reader of the important effects of particle size, Herdan discusses means of attaining a desired particle size and homogeneity. One could wish that the actual practice of the methods that the author discusses were as straightforward as his presentation.

Part IV is partly a fireside talk about some of the current philosophies of experimentation from a statistician's point of view. It has often been difficult to convince statisticians of the value of classical experimentation, and scientists of the value of "experimental design"; Herdan's short discussion merits reading by both groups.

The presentation by M. L. Smith of "Experimental Design and Experimental Errors of Particle Size Determination" covers the field and provides the basis for a choice of methods for a particular problem on hand. Of necessity, original literature, to which references are given, would have to be consulted for detail.

No attempt has been made to give a complete bibliography (it would fill another book), but the references given are the important ones.

The most disruptive feature of the presentation which appears repeatedly and is entirely unnecessary is the dual definition of σ, N being given as divisor for large samples and $N - 1$ for small samples. This carries over into the definition of s ($\sqrt{N/N - 1}\ \sigma$). The more usual definitions of s as the square root of the variance and therefore the best estimate of σ, a parameter of the distribution, would simplify the discussion, remove the necessity for repeated explanations, and be in better conformity with other statistical texts.

In view of the discussion of experimental methods by M. L. Smith the parts in the main text on this subject that duplicate Smith's presentation could have been replaced by a reference to Smith. The index does not do the book justice and it is hoped that it will be expanded. The most glaring omission is that of σ, s, d_3 and other symbols that have definite meaning and are often referred to in small particle work. There perhaps is no serious objection to having "systematic" before "Svedberg" in the index but it is not in keeping with the general typographical excellence of the book.

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GENERAL ELECTRIC COMPANY
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H. G. PFEIFFER

Estimation of Organic Compounds. By F. WILD, M.A., Ph.D., F.R.I.C., Fellow and Senior Tutor of Downing College, and Research Chemist, Department of Medicine, University of Cambridge. Cambridge University Press, 32 East 57th Street, New York 22, N. Y. 1953. viii + 239 pp. 14.5 × 22.5 cm. Price, $5.00.

This book is a companion volume to the author's "Characterization of Organic Compounds" (1947); it presents methods for the quantitative estimation of the more important functional groups in organic compounds. The literature was reviewed through 1951 and all the important methods of analysis have been given in detail, as well as abstracts and references to other methods, and outlines for many special estimations. A critical evaluation has been made and a statement of the percentage accuracy is usually given for each procedure that is given in full. The equation is frequently given for the calculation of percentage of the constituent being determined. This adds to the convenience of the manual. Sources of error are mentioned and ways to eliminate them, or to reduce them to a minimum, are described. Procedures are given for the preparation and standardization (when required) of reagent solutions, as well as any special care that should be exercised in storing and handling them.

The book is divided into seven chapters as follows: Chapter I (40 pp.), olefins—solid, liquid and gaseous; Chapter II (66 pp.), alcohols, enols and phenols; Chapter III (22 pp.), mercaptans; Chapter IV (40 pp.), aldehydes and ketones; Chapter V (15 pp.), amines and amino compounds; Chapter VI (19 pp.), nitro, nitroso and cyano compounds, isocyanates and isothiocyanates; and Chapter VII (18 pp.), other groups, including acetyl, benzoyl, methoxyl, ethoxyl, propoxyl, butoxyl, methylimino, ethylimino, methyl and ethyl groups attached to sulfur, and methyl groups attached to carbon. Several, in some instances a half-dozen or more, alternative methods are given in full for each group, making it possible to select a procedure suitable for a particular group in a particular compound. The specialized methods used for the amino acids, the sugars and the sulfonamides have been omitted, because they often involve individual techniques.

The book is well documented with references to the original literature and concludes with subject and author indices. A feature of the subject index is that page numbers followed by (*r*) refer to particular compounds used as reagents, while those followed by (*p*) refer to the preparation of reagents or their solutions.

Dr. Wild's book will serve as a useful laboratory manual in advanced courses, and especially the research worker who needs to make organic analyses. The manual should fulfill the author's hope that it "will help to stimulate interest in this branch of chemistry, by presenting methods which are used for the estimation of organic compounds."

Printing, drawings (29 figures) and binding are good and the book appears to be free of typographical errors. This volume and its companion referred to above, will make a useful set on the bookshelf of all chemists who need to identify with certainty and to estimate accurately the quantity and/or purity of organic compounds.

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