1962 Short Course Program Progresses

Substantial progress in preparation of the program, Developments in Fat Chemistry, for the 1962 A.O.C.S. Short Course is reported by W. C. Ault, Program Chairman. In fact the program is nearly completed and will be published in the March issue of the Journal. Among those who will deliver lectures are such authorities in their respective fields as George S. Sasin, Professor of Chemistry, Drexel Institute of Technology; H. J. Harwod, Research Associate, Armour Industrial Chemical Company; R. O. Feuge, Southern Regional Research Laboratory; William M. Kraft, Heyden Newport Chemical Corporation; A. J. Stirton, Eastern Regional Research Laboratory; and John P. Friedrich, Northern Regional Research Laboratory.

The Short Course will be held July 9 to 11, 1962, at Lehigh University, Bethlehem, Pa.

• New Books

SURFACE ACTIVITY. The Physical Chemistry, Technical Applications, and Chemical Constitution of Synthetic Surface-Active Agents, by J. L. Moilliet, B. Collie, and W. Black, Imperial Chemical Industries, Ltd., second edition, (D. Van Nostrand Co., Inc., 120 Alexander Street, Princeton, N. J., 518 pp., 1961, $15.00).

The second edition of this excellent text and reference work has been completely revised and expanded from 379 pages in the first edition (1951) to the present 518 pages. The authors have continued to emphasize the importance of underlying principles as the following quotation from the preface illustrates.

"Perhaps the most significant developments have been in the physical chemistry of interfacial processes, and in the technical applications of surface-active materials, and this fact has seemed to us to re-emphasize the desirability of approaching the whole subject from the physico-chemical point of view, i.e., in terms of the unifying 'scientific discipline' of colloid science. Such an approach seems more than ever to offer the best basis for examining the applications of surface-active agents, and for trying to relate surface-active properties to the chemical structures of the agents themselves, especially as the technological scope of surface activity continues to expand. We have therefore adhered to the general plan of our first edition, and have found that the considerable amount of new material has fitted in quite readily."

The subject is presented in three parts: I. The Physical Chemistry of Surface-Active Agents and Interfacial Processes; II. Technical Applications of Synthetic Surface-Active Agents; III. The Chemical Constitution of Synthetic Surface-Active Agents.

Although the book is quite readable throughout, and is embellished with footnotes which certainly do not interfere with continuity but contribute a special insight, explanation or comment, there are many pages particularly in Part I which are mathematical and require close study. This adds to the value of the book and makes it a work of reference. In particular there is a thorough discussion of adsorption, the Gibbs adsorption isotherm, the phenomena of wetting and the significance of contact angle, micellar theory and critical micelle concentration, the nature of foam and emulsions, and the mechanism of detergency.

In Part II the underlying principles developed are used to explain and clarify the many applications of surface active agents. New developments discussed include radiotracer studies, the effect of detergents on sewage disposal, water repellency, the use of surface active agents in construction and road building, emulsion polymerization, sucrose ester nonionics, mixtures of cationic and nonionic detergents, phosphonium compounds, polysiloxanes and perfluoro compounds.

In Part III, the different chemical types of surfactants are surveyed, describing their properties by reference to the earlier sections of the book. Because lists of commercial products become quickly out of date and are periodically available elsewhere, such a compilation is not included.

The book is attractive, well-indexed, and only one error was noted: Figure 16 lacks a square root sign for the Concentration term on the abscissa. It is an excellent text and reference book of special interest to detergent chemists and all those who would more fully understand the physical and colloid chemistry of surface active agents.

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THE CONDENSED CHEMICAL DICTIONARY, 6th Edition, edited by Arthur and Elizabeth Rose. (Reinhold Publishing Corp., 1277 pages, 1961, $17.50). How does one review a dictionary? One way is to weigh it and if it has adequate bulk one can assume that it has adequate content. In this regard, The Condensed Chemical Dictionary comes through very well as it has both adequate weight and content. If it were any heavier, it would be difficult to handle as a single volume. From a reviewer's standpoint, the best way to scrutinize a work of this sort is to look up those items with which he is familiar. In this regard, also, this volume comes through successfully. Although some definitions and items which this writer looked for were either omitted or not too explicitly defined, the omissions were the exception. The Dictionary is particularly valuable in having a fairly complete listing of trade names, with a reasonable amount of information on the actual composition of those substances to which the trade names refer. Another way of evaluating a dictionary is to see how easy it is to read. The present volume uses large enough type with a copious sprinkling of bold face to make the items easy to discern. Other useful features in this book are a numerical list of manufacturers, an alphabetical list of them, Interstate Commerce Commission shipping regulations, and brief information on safety, particularly on warnings and labels. Every library should have a copy of this Dictionary.

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THE THEORY OF CRYSTAL STRUCTURE ANALYSIS, by A. I. Kitaigorodskii (1957). Translated from the Russian by David and Katherine Harker. (Consultants Bureau Enterprises, Inc., New York, 1961; 275 pp., $12.50.) This is a timely review of current theories being developed internationally, and a presentation of the author's theory of relationships between structure amplitudes. It is based primarily on work completed since 1945 relating determination of structure to given intensity distribution patterns and giving the relation between structure and amplitudes of electron densities.

The first chapter is a summary of the mathematical basis for Kitaigorodskii's theory. It gives all equations originating from Fourier integrals and Fourier transforms, and simplified equations for use with spherically symmetric functions for the reduction of triple integrals. (The text deals almost exclusively with spherically symmetric functions.) The system of projection of coordinates and new system of coordinates as well as Fourier transforms and convolutions of Fourier transforms and functions are explained.

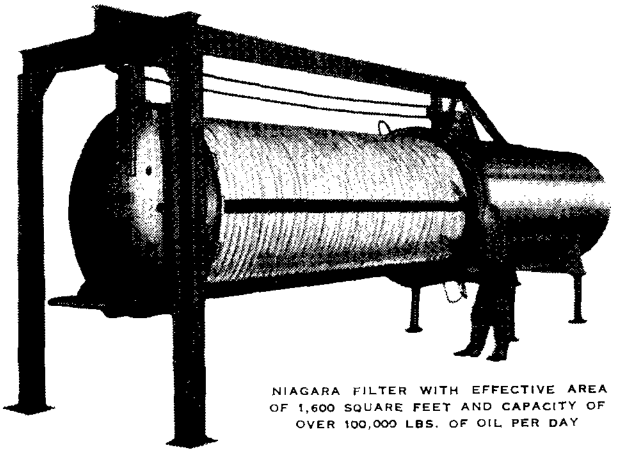
The second chapter is devoted to the theory of X-ray scattering by electrons, emphasizes that only the coherent part of scattered irradiation is of interest in structure analysis, explains that the structure of an object is determined by its scattering amplitude, and emphasizes that the mean square of the amplitude of the scattered wave determines the intensity which is measured experimentally. The amplitude intensity of scattering is defined as functions of position in reciprocal space and are functions of a vector, the length of which is determined by the magnitude of the scattering angle, and the direction of which depends on the orientation of the object with respect to the X-ray at instant of scattering. Conditions are set forth under which the scattering amplitude is the Fourier transform of the electron density of the scattering object. Experimentally, one gets the time average value of intensity and must derive ideas of structure from these values and not the instantaneous values. Equations are derived for relating experimental data of scattering with average electron densities and for the representation of the structural amplitude as the Fourier transform of the time average of the electron density. Kitaigorodskii gives a clear picture of the different stages of completion to which an X-ray crystal structure can be carried out beyond the simple determination of molecular symmetry by use of Fourier methods. It is emphasized that if one could compute the time average electron density at every point throughout the unit cell, and the maxima of density could be calculated, the structural problem would be solved, as the centers of the atoms reveal themselves as peaks related to their atomic numbers. Spherically symmetric atomic factors are used for structural computations since any structure, within experimental error, can be represented as a sum of spherically symmetric functions. Use is made of electron density projections. Up until about 1945, only the 2-dimensional electron projections were in use. With complex molecules, in order to establish the arrangement of atoms in space, it becomes necessary to extend a 3-dimensional projection which is most difficult to interpret.

Basic equations are given for intensity of scattering from a spherical particle. The task becomes one of finding the electron density of an ideal crystal which approximates the time average electron density of the actual crystal under investigation. Then the scattering amplitude of the object as the Fourier transform of the function representing the electron density is found. The intensity as the Fourier transform of the self-convolution is then found. Experimentally, one first finds the values of the integrated intensities of spots which are then converted into moduli of the scattering amplitudes of the unit cell. After this, two methods of finding the time average electron density, which is needed before the structure can be established, are outlined. Kitaigorodskii explains briefly that methods of treating data obtained by a study of the intensities of the diffraction spots on electron and neutron patterns are almost identical to methods used with X-ray patterns and these intensities can therefore be used to compute functions which give the structure of the crystal.

By study of the Laue symmetry of an X-ray pattern, and with particular notice of the presence or absence of systematic extinctions of reflectances, one is able to classify a crystal into one of 122 X-ray groups.

In the third chapter, statistical rules for splitting an X-ray group into its component space groups are set forth. Specific examples are used to illustrate the application of the statistical theory. Although this statistical method is not applicable to all substances, it does increase considerably the possibility of establishing the symmetry of a crystal by X-ray methods.

The fourth chapter deals with the method of determining phases of structure amplitudes once the moduli of the amplitudes have been computed directly from experimentally measured intensities. Although the number of experimentally measured moduli of structure amplitudes is of the order of thousands for reflectances of different orders, this apparently insurmountable problem of determining phases can be solved, as the values of all moduli are determined by a relatively small number of atomic coordinates. Again, since the study is limited to those crystals having a center of symmetry, it becomes necessary to determine the sign of the amplitude only and not the phase angle. Determination of the former becomes less possible as the number of atoms in the unit cell increases and requires a knowledge of at least a small number of signs. Determination of all signs follows a chain mechanism, with each step depending upon the initial step of the analysis. The author presents several examples to elucidate the methods applied to space groups having one element of symmetry as well as to a few space groups having several elements of symmetry, thus giving the reader an opportunity to derive inequalities for space groups which might be of interest. Kitaigorodskii derives a general equation for connections between amplitudes, the indices of which are not necessarily related by symmetry. This general equation includes all inequalities based on Harker and Kasper's original work of applying Cauchy's inequality to obtain a series of correlations between amplitudes as well as all other currently proposed



correlations. Included is an outline of the procedural steps to be followed for a direct structural analysis.

In the fifth chapter, use of the Patterson Function for defining symmetry and structure of a crystal in the computation of the self-convolution of electron density from X-ray data is discussed. This analysis represents an aggregate of interatomic functions superimposed one upon another. Included is a table giving characteristics of P-function Space for 230 Fedorov Space groups of crystals, each of which has its origin of coordinates at the center of inversion.

The last chapter includes methods for obtaining agreement between measured and calculated structure amplitudes. Normal procedure of refinement consists of computing the position of peaks by Fourier methods, then using these peaks to calculate new phases. While a procedure is satisfactory for work of moderate accuracy, information of maximum accuracy can not be obtained from X-ray data by use of 1- or 2-dimensional projections, but a 3-dimensional Fourier summation must be used to identify all atoms. These resultant 3-dimensional electron equations have forms suitable to each of the 230 space groups. Computations of structure factors from mean electron densities are excessively complicated in certain 3-dimensional works, and mechanization of computations would therefore be desirable. Usually, the first set of atomic coordinate positions are in error, but are used to recalculate new signs or phases associated with structure amplitudes. Structure amplitudes calculated from the model and compared to corresponding amplitudes measured experimentally give criteria for accuracy of the model. The best model being the one with minimum reliability index, that is, one with the nearest convergence of observed and calculated amplitudes. Thus, the determination of phases is the main problem for the X-ray crystallographer, and once reliable phases are established, the true structure can be calculated. The magnitude of the mean electron density amplitude is the basic criterion for determining the solvability of the problem. If the mean density > 0.2, a large number of reliable connections between signs are set forth, and a first approximate series of electron densities are contracted. From the latter values, a more accurate structure is defined by any one of several statistical methods, and such a structural analysis can result in the determination of interatomic distances with an accuracy up to 0.05 angstrom unit.

Expansion of automation of computations should give impetus to future research in the finding of geometric configurations of molecules and bring about changes or corrections in the author's theory.

The volume is recommended to those researchers well versed in the fields of single crystal structure and statistical analysis and for the library reference shelf. It is of limited value to the average organic chemist and to most oil chemists interested only in minimum information derived from X-ray data.

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Chemical Engineering Science, Volume XIV, January 1961. Pergamon Press, 396 pp., 1961, £7, approximately $17.25.) This is a paper bound book, 8 x 10 x 1 inches. It contains the thirty technical papers given at the three day Symposium in Amsterdam. Twelve sessions were held on the following topics: Introduction, Selectivity and Optimization, Reactions Involving Contact Between Gas and Liquid, Reactions Involving Contact Between Two Liquids, Distribution of Residence Time, Mathematical Techniques and Models, Reactions Involving Contact Between Fluid and Solid, Closing Session and Review. The papers are printed in the authors' native languages. Although the majority are in English, almost half are in French or German. A resume in all three languages is given for each article. Literature reference, discussion, and additional notes are included after the papers.

This is an excellent assembly of papers dealing with chemical reaction kinetics and applications to reactor design and operation. The papers present much laboratory data and experimental results. These are discussed from the theoretical and mathematical point of view. They are not concerned primarily with the pure science but with the applications to chemical engineering.

This publication should be of value to the chemical engineer who is concerned with chemical reactions. It should also be of value to the research chemist who is associated with the development of chemical reactions for plant operations.

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Handbook of Chemistry and Physics, 43rd Edition, edited by C. D. Hodgman, R. C. Weast and S. M. Selby. (The Chemical Rubber Company, 3467 pages, 1961, $12.00). As expected, this edition of the Handbook of Chemistry and Physics is a gold-mine of information. For many years this reviewer has found the preceding editions of immense value, and the present edition will be as useful as its predecessors. The five major sections are: Mathematical Tables, Properties and Physical Constants, General Chemical Tables, Heat and Hygrometry, and Quantities and Units. New tables of general use are: Color Code for Electrical Resistors, Lattice Energies of Alkali Halides, Sound Velocity in Water Above 212°F., and Van der Waals' Radii in Å. Tables of special interest to physical chemists include Magnetic Rotary Power, Magnetic Susceptibility of Elements and Inorganic Compounds, Dimagnetic Susceptibilities of Organic Compounds, Flame Spectra of the Elements. In addition to the extensive tables on the physical and chemical properties of thousands of organic and inorganic compounds, much information will be found in this book on industrial arts recipes, trade marks and trade names, and safety information. By the use of thin paper the publishers have managed to keep the size of this Handbook within reasonable proportions. It is unequivocally recommended for every technical worker in the field of chemistry and physics.

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Production Yearbook, Volume 14, R. D. Narain, Editor (Food and Agricultural Organization of the United Nations, Rome, Italy, 507 pp., 1960, $5.00).

The fourteenth edition of the Production Yearbook contains annual data on all important aspects of food and agriculture. The total of 180 tables includes figures on population, index numbers of agricultural production, crops, livestock numbers and products, food supply, means of production, prices, wages, and freight rates. A complete listing of data for 1959/1960, the latest revisions for 1956/1957 and 1957/1958, and the averages for the postwar period 1948/1949—1952/1953 is provided. Official figures were supplied by governments through questionnaires, and by government publications and reports to the United Nations and to the Food and Agricultural Organization. Data were also taken from reliable unofficial sources when official figures were not available. The tables and accompanying notes are printed in three languages, English, French, and Spanish.

While this publication is of most interest to those working in the field of agricultural economics, it is a useful reference manual for food and agricultural scientists in general.

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Castorseed and Its Products. Proceedings of the Seminar held August 11-12, 1960, at the Regional Research Laboratory, Hyderabad, India (Indian Central Oilseeds Committee, Hyderabad. 87 + x pp.)

A two-day conference on castorseed and its products was held in Hyderabad, India, in August 1960, under the auspices of the Council of Scientific and Industrial Research, India, to stimulate the castor industry. A cross section of interested personnel in India, educators, scientists, technologists and industrialists participated. This booklet is essentially a report of the minutes of that conference.