

zene and the solution filtered hot. From the filtrate the product crystallized in fine, microscopic crystals of claret-brown color in the mass. It was further purified by recrystallizing from a 1:1 mixture of benzene and acetone. The pure substance melts at 263°. By employing the development method of application the dye may be made to color silk an écreu and wool a Brazil-red.

*Analysis.* Subs., 0.0205: AgBr, 0.0146. Calc. for  $C_{22}H_{20}O_2N_4Br_2$  (532): Br, 30.08. Found: 30.01.

**2,4-(Bis-5-bromo-2-*p*-xylylazo) $\alpha$ -naphthol**,  $[(CH_3)_2C_6H_2BrN_2]_2C_{10}H_6OH$ .—This dye was prepared in the same way as were those described above. The product was purified by boiling it in a large quantity of alcohol, filtering the solution while hot and allowing the filtrate to cool. The crystals separating from the cold solution are of indefinite shape, very dark brown to black when viewed in the mass and melt at 222–223°. When applied by the development method, this dye colors silk a Mars-orange and wool a claret-brown.

*Analysis.* Subs., 0.0325: AgBr, 0.0216. Calc. for  $C_{26}H_{22}ON_4Br_2$  (566): Br, 28.23. Found: 28.28.

**1-(5-Bromo-2-*p*-xylylazo) $\beta$ -naphthol**,  $(CH_3)_2C_6H_2BrN_2C_{10}H_6OH$ .—One molecular equivalent of the hydrobromide was diazotized, made alkaline and treated with 1 molecular equivalent of  $\beta$ -naphthol in alkaline solution. Acidification produced a brilliant red precipitate, weighing 40% more than the hydrobromide taken. On recrystallizing from acetone it was obtained in very beautiful, long scarlet-red needles in felted masses. Applied as the other dyes above, this dye colors silk a light red and wool a Nopal-red.

*Analysis.* Subs., 0.0673: AgBr, 0.0360. Calc. for  $C_{15}H_{13}ON_2Br$  (355): Br, 22.51. Found: 22.76.

### Summary

1. Bromination of 2-aceto-amido-*p*-xylene yields a monobromo derivative in which the bromine is located at Position 5 as proved by the following series of reactions: 2-aceto-amido-bromo-*p*-xylene (new)  $\longrightarrow$  2-amino-bromo-*p*-xylene  $\longrightarrow$  2,5-dibromo-*p*-xylene  $\longrightarrow$  2,5-dibromoterephthalic acid  $\longrightarrow$  2,5-dibromo-diethylterephthalate.

2. The following new azo dyes were prepared: 2,4-(bis-5-bromo-2-*p*-xylylazo)phenol; 2,4-(bis-5-bromo-2-*p*-xylylazo)resorcinol; 2,4-(bis-5-bromo-2-*p*-xylylazo) $\alpha$ -naphthol; 1-(5-bromo-2-*p*-xylylazo) $\beta$ -naphthol.

CHAPEL HILL, NORTH CAROLINA

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### NEW BOOKS

**Beiträge zur Geschichte der Naturwissenschaften und der Technik.** (Contributions to the History of Science and Technology.) By Prof. Dr. EDMUND O. VON LIPP-MANN, Dr. Ing. E. H. at the Technischen Hochschule at Dresden, Director of the "Zuckerraffinerie Halle" at Halle A.S. 314 pp. 2 figs. Verlag von Julius Springer, 1923, Berlin. 16.5 cm.  $\times$  24.5 cm. \$1.60 paper, \$1.90 bound.

This last work by Professor Lippmann comprises a selection of miscellaneous papers upon the history of alchemy, chemistry and chemical technology which have been published during the past 10 years in the *Chemiker Zeitung*, *Zeitschrift für Angewandte Chemie* and other periodicals.

It was at the request of the numerous friends of his two previous volumes of "Essays and Addresses" (Abhandlungen und Vorträge) upon historical chemistry that the author has compiled this third collection of scattered articles.

The 36 contributions of the new volume show the same variety of interest and scholarly attention to detail that have always characterized the historical researches of Professor Lippmann. "Chemical Papyri of the Third Century" (2 papers), "Origin of the name *Caput Mortuum*," "First Occurrence of the Word Chemistry," "On the History of Alcohol and Distillation" (6 papers), "Use of Petroleum in the Middle Ages," "Chemical and Technological Contents of the Medieval Receipt Books of Heraklius, Theophilus Presbyter, and Vitalis de Furno" (3 papers), "Chemical and Technological References in Dante," "Petrarch upon Alchemy," "The Alchemists J. I. and I. Hollandus" (2 papers), "The Philosopher's Stone and Homunculus, Two Alchemistic Problems in Goethe's Faust," "A biographical Note upon Liebig," and "The Centenary of Robert Mayer" are selected from the various titles to show the diversity of subjects which are discussed.

As belonging to the author's special field of technology, the papers upon "The Medieval Sugar Industry" and "Sugar Monopolies of the Middle Ages" form important addenda to his well-known "History of Sugar" published in 1890. There are also comments upon several recently discovered letters of Achard (the first manufacturer of beet sugar), a paper upon "Goethe and Sugar Manufacture," an article upon "The History of the Vacuum Pan," and an address upon "The Development of the Sugar Industry in Germany between 1888 and 1913."

For the casual reader of historical chemistry we know of no recent work which provides more pleasant entertainment than this new volume of Professor Lippmann's collected papers; while for those more critically inclined the numerous explanatory footnotes and bibliographic references offer abundant opportunities for additional study.

The book is printed in clear Roman type and is provided with a good index of both names and subjects. It should find a place in the library of every chemist, whether teacher or technologist, who is interested in the cultural aspects of his science.

C. A. BROWNE

**Catalytic Action.** By K. GEORGE FALK, Harriman Research Laboratory, The Roosevelt Hospital, New York. The Chemical Catalog Company, Inc., 1 Madison Avenue, New York, U. S. A., 1922. 172 pp. 23.5 × 15.5 cm. Price \$2.50.

The enormous growth of so-called catalytic industrial operations during the present century has stimulated research in the field of the mechanism of catalysis and indeed of chemical action in general. Owing to the wide range of literature which investigators have to cover it is both important

and necessary that from time to time a serious attempt should be made by someone actively interested in the subject to summarize the work in at least its more important aspects. In this respect the monograph of Dr. K. G. Falk is doubly welcome in that it not only fills one of these gaps but it also presents the case in a very readable form with ample references.

The volume contains 8 chapters, the first 3 dealing with the phenomena, criteria and theories of catalytic action. Two chapters are devoted to a discussion of the energy relations and recent theories in chemical action, 2 to enzyme action and life processes, while the last chapter includes a discussion on contact catalysis.

Dr. Falk believes that the only tenable theory of catalytic action is the associative theory which was originally definitely advanced by H. E. Armstrong, and the argument in the whole volume is thrown onto this hypothesis. It is now generally admitted even by the protagonists of the radiation theory that when a catalyst G operates in the union of two substances A and B, a complex of the general type AC or BC is first formed, which then reacts to form the complex ABC, with subsequent decomposition. The stability of these intermediate compounds is also a criterion of the catalytic efficiency of C. The objection to the theory is that it is too vague, since it is in reality merely a restatement of the fact that chemical action is action by contact. We require to know the nature of the complex and why it is more reactive than the original substances in order to obtain some insight into the *modus operandi* of chemical action and to assist us in the choice of a catalyst that will permit a chemical action to proceed at a determined speed. The author gives an excellent resumé of Stieglitz's work on the hydrolytic decomposition of the imido esters in which definite proof is advanced that the positive ion formed by the complex imido ester  $H^+$  is much more reactive than the imido ester atom. It is possible that the transformation of a substance into a charged ion by reaction with either hydrogen or hydroxyl ion may generally increase its reactivity with ions of the opposite sign. An extension of this hypothesis would indicate that an ester would form a complex with either hydrogen or hydroxyl ions and thus serve as the nucleus of an amphoteric electrolyte, a point which might possibly be confirmed by migration experiments. There are, however, many other ways in which molecular reactivity may be produced.

That on association of the catalyst and reactant a molecular rearrangement may take place to give a decrease of free energy of the system is evidenced by citation of the work of Stieglitz and Derick but to include coupled and induced reactions, such as Traube's slow oxidations, in the same category would necessitate a somewhat wide extension of our present ideas on the subject. A study of the oxidation potentials of systems which can be transformed from a coupled to a catalytic reaction by alteration of

the hydrogen-ion concentration of the medium indicates an alternative method of investigation.

The author gives a brief but descriptive review of the various proposed atom structures before dealing with the varied problem of radiation and chemical change, in which the views of the various rivals are expressed impartially; the somewhat important criticisms and suggestions of Lindemann might have been included.

The chapters on enzyme action and life processes are extremely illuminating and present the interesting properties of such colloidal catalysts in a very readable form.

In the chapter on contact analysis the transition of the views of Bodenstein and Fink into the monomolecular film theory of Langmuir is given and a few examples of the varied types of decomposition that may be obtained with different catalysts. It might have been well to have extended the section on promoter action in catalysis, as this may in all probability provide an important method for investigation into two factors influencing surface action, namely, the effect of adsorption of reactants and products and the possible variation in the orientation and polarity of the adsorbed substance with the catalytic material.

Dr. Falk is to be congratulated on the production of an excellent monograph, which is both pleasantly and clearly printed.

ERIC K. RIDEAL

**The Formation of Colloids.** By THE SVEDBERG, Professor of Physical Chemistry in the University of Upsala. Monographs on the Physics and Chemistry of Colloids. D. Van Nostrand Company, 25 Park Place, New York, 1921. viii + 119 pp. 22 figs. 12.5 × 19 cm. Price \$2.00 net.

This is the first of a series of monographs that The Svedberg proposes to issue. It is his plan to keep the series up to date by new editions of such parts of the subject as develop with special rapidity.

As the author announces in the first monograph, he aims "to give a survey of the processes which cause the formation of colloids—or of heterogeneous systems with a relatively large boundary surface—especially with regard to the conditions that determine the degree of subdivision of the systems formed."

The formation of disperse systems in a vacuum, in gases, in liquids and in solids is presented in a scholarly manner. The discussion of formation in a vacuum is short but extremely interesting. As might be expected, the Bredig process of electric pulverization of metals with the oscillatory arc is discussed ably and at some length. The author favors the view that the sol is formed by condensation of metal gas and the sediment by dispersion of melted metal.

His distinction between volume condensation and surface condensation (p. 57) is interesting. In this connection he cites the striking fact that ul-

traviolet light converts an alcoholic solution of sulfur into a colloidal suspension by transforming the sulfur into another allotropic modification.

Among the best features of the monograph are the pages devoted to colloidal gold with their detailed equations and the excellent historical discussion of this particular colloid. Good, also, is the treatment of sulfur.

Peptization deserves fuller treatment. We find on p. 108 that "the so-called peptization processes are in general to be considered as reversible coagulations. They are not real dispersion processes, the degree of dispersion not being altered by the peptization, but only the mutual distances of the particles." The difference between peptization by solvent and by solute is not stressed. Under "Dispersion" the preparation of emulsions was merely touched upon but doubtless this will later become the subject of a complete monograph. The Plauson mill and the Premier mill are either too recent in development or too uncertain to be mentioned.

Colloid chemistry will be debtor to Svedberg for this series of monographs. He writes with authority.

HARRY N. HOLMES

**Organic Syntheses.** Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. II. JAMES BRYANT CONANT, Harvard University, Editor-in-Chief; ROGER ADAMS; HANS THACHER CLARKE; OLIVER KAMM. John Wiley and Sons, Inc., New York; Chapman and Hall, Limited, London, 1922. vii + 100 pp. 3 figs. 23.5 × 15 cm. Price \$1.50.

The first volume of the "Organic Syntheses" was favorably reviewed in detail by E. P. Kohler.<sup>1</sup> The second volume now at hand reaffirms in the preface the purpose of this series: "The preparation of materials for research, always time-consuming and annoying, is made increasingly so by the inexactness of the published information which so often omits essential details. Because of this, much needless experimentation is necessary in order to obtain the results given in the published reports. As the additional information thus acquired is seldom published, duplication of such experiments occurs again and again,—a waste of time and material. It is hoped these difficulties may be remedied by the publication of this series of pamphlets. In other words, the authors hope to make this a clearing house for the exchange of information as to methods of preparation of some of the most needed organic chemical reagents."

As is well known, we owe to the Department of Chemistry of the University of Illinois the inception of the laudable purpose expressed in the above quotation. Four pamphlets under the title "Organic Chemical Reagents," edited by Roger Adams and co-workers, have been published by that University. The present new series of Organic Syntheses "aims to make available in a permanent form complete detailed directions for the preparation of various organic chemical reagents." In fact, nine out

<sup>1</sup> THIS JOURNAL, 43, 2702 (1921).

of the twenty-five preparations in Vol. II, of the "Organic Syntheses" are reproduced from the "Organic Chemical Reagents, II" with only slight changes.

The reliable nature of the laboratory directions for the various substances is vouched for by several investigators, and the names of the chemists who have studied the experiments is attached to each preparation, "so that further information concerning any obscure point can be obtained if any question arises in using these directions." The order of treatment is: (1) Procedure,—giving explicit directions for the preparation of the substance in 250g. to 2kg. lots; (2) Notes,—which explain why it is essential to observe the conditions laid down in the directions; (3) other methods of preparation, including a complete bibliography on the particular substance.

The preparation of the following organic chemicals is included in this volume: benzalacetophenone; benzyl benzoate; benzyl cyanide;  $\alpha,\gamma$ -dichloro-acetone; *p*-dimethylamino-benzaldehyde; ethyl oxalate; ethyl phenylacetate; glycerol  $\alpha,\gamma$ -dichlorohydrin; glycerol  $\alpha$ -monochlorohydrin; hydrazine sulfate; mesitylene; methyl red; *p*-nitrobenzoic acid; *p*-nitrobenzyl cyanide; *p*-nitrophenylacetic acid; nitroso- $\beta$ -naphthol; phenylacetic acid; phenylacetylene; phenylhydrazine; phthalimide; quinoline; quinone; sodium *p*-toluenesulfinate; 1,3,5-trinitrobenzene; 2,4,6-trinitrobenzoic acid.

The editors deserve the hearty support, as well as the thanks of the chemical profession. Let us hope that the issue of Vol. III will not be long delayed.

M. GOMBERG

**Qualitative Organic Analysis.** By OLIVER KAMM. 260 pp. John Wiley and Sons, Inc., New York, 1923. 15 × 23 cm. Price \$1.75.

This laboratory textbook is essentially the course in Qualitative Organic Analysis that has been given to his classes at the University of Illinois by Professor Kamm. A careful examination of its contents has convinced the reviewer that when used under a competent instructor it should prove an admirable and practical one. As the author remarks in his preface: "Qualitative Organic Analysis has not been taught generally because of the assumption on the part of the chemists that the multiplicity of organic compounds excludes the possibility of a systematic procedure. This is the opinion only of those who have not taught the subject; those who have had experience in presenting the work both in the classroom and laboratory realize that qualitative organic analysis is capable of logical and systematic treatment and that it is of fundamental importance in the training of the chemist in the organic field."

The work is specially arranged for a one semester course of 32 laboratory periods of 3 hours each, the first week being given to solubility tests

of known compounds, 5 weeks to the classification of known compounds, 6 weeks to the identification of 6 or 8 individual compounds, and 4 weeks to the examination of mixtures. The section of classified tables of compounds at the end of the book enables the student to apply the knowledge gained to a great diversity of substances, and the training in fundamental principles and methods given is so varied and well planned that the work as a whole deserves the highest commendation.

Special emphasis is rightly given to the importance of the solubility of different classes of organic compounds for purposes of classification, separation and identification. Due attention is, however, also given to special methods for the determination of the chemical class to which a compound belongs by application of chemical tests to the small scale preparation of characteristic derivatives, to the determination of physical constants, and to the special technique of small scale preparations.

The book deserves a hearty welcome wherever organic chemistry is taught.

S. P. MULLIKEN

**The Chemistry of Urea. The Theory of its Constitution, and of the Origin and Mode of its Formation in Living Organisms.** By EMIL A. WERNER, Sc.D., Professor of Applied Chemistry in the University of Dublin. Longmans, Green and Company, 55 Fifth Avenue, New York; 39 Paternoster Row, London, E. C. 4; Toronto; Bombay, Calcutta and Madras; 1923. xii + 212 pp. 24.5 × 15.5 cm. Price \$4.75 net.

This volume is one of a series of monographs on biochemistry edited by R. H. A. Plimmer and F. G. Hopkins. The chemistry of urea is a subject of quite general interest and, hence, contributions to our knowledge of it will, indeed, be welcomed by many investigators.

The subjects listed in the table of contents of this monograph include the following: history of urea, mechanism of Wöhler's synthesis, constitution of cyanic acid, thermal decomposition of urea, decomposition of urea when heated in presence of acids and alkalis, interaction of urea and nitrous acid, mechanism of syntheses of urea from derivatives of carbonic acid, miscellaneous syntheses of urea, synthesis of urea from cyanamide, conditions necessary for the existence of true carbamides, properties of urea on the basis of the cyclic formula, occurrence of urea in nature, constitution of salts of ammonia and their relation to urea, and decomposition of urea in alkaline solution by hypochlorites and hypobromites.

The body of the material is presented in 15 chapters, the logical sequence of which is to be commended. A summary of methods for the detection and estimation of urea is presented in Appendix I. Appendix II gives the physicochemical constants of urea and also contains a short discussion of urea formation in its relation to nitrogen fixation. An extensive bibliography is appended which, though by no means complete, should be of assistance to those interested in this subject.

The material is presented from a much more restricted point of view than the title of the book and the chapter headings indicate, being limited essentially to a polemical discussion of the constitution of urea. As stated by the author in the preface, one of the main objects of the book is to refute the long-standing conception of the carbamide formula for urea, and to show that the cyclic formula proposed by himself disposes of disagreements between facts and theory in the chemistry of urea. The choice of material presented has been rather closely governed by this object and it is somewhat unfortunate that the fact is not more accurately reflected in the title of the work. The limited treatment of the subject is further indicated in the preface by the statement "the chemistry of substituted derivatives of urea is outside the scope of this work which is restricted to the consideration of the constitution of urea itself."

Since it is not the function of a single reviewer to pass upon the merits of the arguments which the author leaves to the judgment of all who are interested, it would be somewhat out of place to enter here into any detailed discussion. The book appears to be an excellent presentation of the views of the author but the reviewer believes that critical readers will fail to be convinced by the arguments offered in many instances. For example, those investigators who have had experience with the behavior of cyanamide in aqueous acid or alkaline solutions will certainly fail to agree with the author's impressions as set forth in Chapter IX, concerning the constitution of cyanamide, the mechanism of its polymerization and its relation to urea. The deductions as to the constitution of urea drawn from its relation to cyanamide are based on entirely erroneous information.

In the discussion of the subject "Urea and Nitrogen Fixation" the statement, "The fact that cyanamide is not directly hydrolyzed to urea, but requires a concentration of acid necessary to produce a salt of urea appears to be a serious drawback to the economic production of urea from this source," is likewise in error.

The book has a cardboard binding and the quality of the paper is rather poor, but the presswork is very good.

J. M. BRAHAM