Thus, in a typical experiment, 2.00 g. of *i*-cholesteryl methyl ether, m. p. 79.0–79.5°, was subjected to a one-half hour reflux period in absolute ethanol to which was added ethanolic *p*-toluenesulfonic acid (total volume of final solution 37 ml.) 0.001 *M* in excess of the slight potassium acetate impurity present in the *i*-methyl ether as usually prepared.[3] The acid was neutralized, the solvent was evaporated, and the organic material was taken up in hexane. Systematic separation of the products by chromatography with the aid of alumina gave rise to 1.09 g. of *i*-ethyl ether, m. p. 45.0–45.5° (reported[4] 47°), mixed m. p. with authentic material, 45.5–46.0°, $[\alpha]^{25}D$ (chloroform) +47.10° (1 dcm., c = 2.65) (reported[4] $[\alpha]^{20}D$ +49.78° (c = 1.607)), 0.18 g. of *i*-methyl ether, m. p. 78.5–79.5° and 0.48 g. of *n*-ethyl ether, m. p. 88.0–89.0°. Thus, under these conditions, the ethyl ether product was 68% *i*-ethyl. The latter ether is converted to *n*-ethyl at a very appreciable rate, but the results serve to indicate the initial conversion of *i*-methyl ether predominantly to *i*-ethyl.

The *i*-ethyl ether product was indistinguishable in melting point and optical rotation from authentic *i*-ethyl ether and has, therefore, the same configuration as that of the product of the first reaction of ion I with ethanol under the usual conditions of preparation of *i*-ethyl ether. As far as we are aware this represents the first demonstration of exchange at the 6-position of *i*-compounds and suggests that, with care, it can be general.

The present work strengthens the case for an intermediate ion I in certain forward and reverse *i*-sterol rearrangements. It supplies evidence neither for nor against some contribution of bimolecular type mechanisms, and these remain possibilities for some rearrangements.

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(3) Stoll, *Z. physiol. Chem.*, **207**, 147 (1932).

(4) Beynon, Heilbron and Spring, *J. Chem. Soc.*, 907 (1936).

(5) National Institute of Health Postdoctoral Fellow, 1947–1948.

NEW BOOKS

Biochemistry. Part I. FIAT Review of German Science, 1939–1946. Senior Author, RICHARD KUHN, Kaiser-Wilhelm-Institut für Medizinische Forschung, Heidelberg; Co-authors, H. FISCHER, H.-J. BIELIG, H. VON DOBENECK, D. JERCHEL, W. SIEDEL, M. STRELL, K. THOMAS, O. WARBURG AND G. WEITZEL, Published by Offices of Military Government for Germany, Field Information Agencies Technical, British, French, U. S. Printed under supervision of Dieterich'sche Verlagsbuchhandlung, Inhaber W. Klemm, Wiesbaden, Germany, 1947. 218 pp. Illustrated. 15 × 22.5 cm.

This volume, the first of a series of four devoted to biochemistry, consists of six review articles, respectively entitled: "**Fat and Fat Metabolism,**" by K. Thomas and G. Weitzel (51 pp.); "**Invert Soaps and Tetrazolium Salts,**" by D. Jerchel (7 pp.); "**Natural Pigments I,**" by H. J. Bielig (42 pp.); "**Natural Pigments II, Syntheses of Pyrroles and Bile Pigments,**" by H. Fischer and W. Siedel (19 pp.); "**Natural Pigments III, Syntheses of Porphyrins, Pentdyopent,**" by H. Fischer and H. v. Dobeneck (18 pp.); "**Natural Pigments IV, Chlorophyll,**" by H. Fischer and M. Strell (11 pp.). In addition, the book contains three original articles on carboxyhemoglobin and on the photochemical assimilation of carbon dioxide, by O. Warburg.

Much of the research work carried out during the war years was inevitably of a highly technical and utilitarian character, and in most instances the individual reports demand detailed study only by specialists. These review articles accordingly constitute a useful readers' guide for biochemists to whom the journals published in Germany in 1939 to 1946 are only now becoming available.

There are, however, several discussions of subjects of general interest. The section on fats and fat metabolism contains a stimulating account of fundamental work by Treibs (1942–1946) on the chemical reactions involved in the autoxidation of unsaturated fats, which must be carefully considered both by biochemists and by organic chemists. The same applies to the accounts of methods for the production of fatty acids from hydrocarbons and the studies of the metabolism and nutritional value of glycerides of these acids. The first section on natural pigments includes reviews, of more than ephemeral interest, of developments in the fields of carotenoids, flavines, pyrones and quinones. Of outstanding excellence are the reasoned discussions, by the late Hans Fischer and his associates, of the chemistry of porphyrins and other pigments related to pyrrole. The sections devoted to these topics resemble, in scope, articles in our own *Chemical Reviews*, and may well take a place in the permanent literature on the subject.

HANS T. CLARKE

Electrochemical Analysis with Graded Cathode Potential Control. By HARVEY DIEHL, Ph.D., Professor of Chemistry, Iowa State College, Ames, Iowa. Published by The G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio, 1948. vii + 56 pp. 15 × 23 cm. Price, bound copies, $1.00 each; paper back copies free on request.

Professor Diehl most appropriately has dedicated this booklet to the late Henry J. S. Sand, who, forty years ago, introduced the technique of controlling the cathode potential in electrolytic separations and electrogravimetric determination of metals. In spite of its obvious advantages the controlled potential method did not become generally popular because of the tedium associated with the manual control of the potential. Recently, however, potentiostats which automatically perform this

function have been described by Hickling (*Trans. Faraday Soc.*, **38**, 27 (1942)), Caldwell, Parker and Diehl (*Ind. Eng. Chem., Anal. Ed.*, **16**, 532 (1944)), and Lingane (*Ind. Eng. Chem., Anal. Ed.*, **17**, 332 (1945)), and consequently controlled potential methods are now beginning to receive the attention they deserve.

Following a brief résumé of fundamental principles underlying the controlled potential electrodeposition of metals, an improved model of the Caldwell, Parker and Diehl potentiostat is described in detail. This instrument comprises a conventional selenium rectifier and filter unit for supplying low voltage direct current to the electrolysis cell, a control circuit which includes a potentiometer, a vacuum tube amplifier which actuates a relay to control a motor-driven Variac autotransformer which powers the rectifier unit from the 110 v. a. c. line, and a vacuum tube voltmeter for measuring the potential of the working electrode against a reference electrode. When the cathode potential exceeds the value set on the potentiometer the motor is activated and turns down the Variac until the total e. m. f. applied to the cell is decreased sufficiently so that the cathode potential returns to the preset value. The instrument controls only in the direction of increasing cathode potential, and does not correct for a decrease of this potential below the preset value. Thus it serves to limit the potential of the working electrode but does not actually control it in the sense of maintaining the potential at a fixed value regardless of the direction of drift. In electrogravimetric determinations of metals using solid cathodes such uni-directional operation is usually adequate, but certain other applications of controlled potential electrolysis require an instrument which controls in both directions.

Various types of electrolysis cells are described. There are also brief sections on the Brown auxiliary electrode, on anodic reoxidation, and on polarization. In this latter section it is unfortunate that the author does not distinguish between polarization resulting from irreversible phenomena and the perfectly normal change in the potential of a working cathode caused by depletion of the concentration of metal ions at its surface.

The latter half of the booklet reviews the literature on the controlled potential electrogravimetric determination of silver, copper, bismuth, antimony, lead, tin, nickel and cadmium. A concluding section describes the Torrance procedures (*Anal.*, **62**, 719 (1937)) for the determination of antimony, copper, lead and tin in bearing metal, and the determination of copper, lead, tin and zinc in brass and bronze.

The booklet can be recommended to every analytical chemist interested in modern methods of metal analysis.

JAMES J. LINGANE

BOOKS RECEIVED

August 10, 1948–September 10, 1948

M. L. ANSON AND JOHN T. EDSALL. "Advances in Protein Chemistry." Academic Press, Inc., 125 East 23rd Street, New York, N. Y. 1948. 575 pp. $8.50.

C. E. H. BAWN. "The Chemistry of High Polymers." Interscience Publishers, Inc., 215 Fourth Avenue, New York 3, N. Y. 1948. 249 pp. $4.60.

H. R. BOLLIGER. "Allgemeine und anorganische Chemie." Wepf and Company, Verlag, Basel. 1948. 216 pp. 16 fr.

KARL K. DARROW. "Atomic Energy." John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1948. 80 pp. $2.00.

JOHN F. FLAGG. "Organic Reagents Used in Gravimetric and Volumetric Analysis. Chemical Analysis." Volume IV. Interscience Publishers, Inc., 215 Fourth Avenue, New York 3, N. Y. 1948. 300 pp. $6.00.

DONALD E. H. FREAR. "Chemistry of Insecticides, Fungicides and Herbicides." D. Van Nostrand Company, Inc. 250 Fourth Avenue, New York, N. Y. Copyright 1942, 1948. 417 pp. $6.00.

RAYMOND M. HANN AND NELSON K. RICHTMYER, Editors. "The Collected Papers of C. S. Hudson." Volume II. Academic Press, Inc., 125 East 23rd Street, New York, N. Y. 1948. 1694 pp. $15.00.

ERNEST HAMLIN HUNTRESS. "Organic Chlorine Compounds." John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1948. 1443 pp. $27.50.

ERLE B. PHELPS. "Public Health Engineering." Volume I. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1948. 655 pp. $7.50.

LUKE E. STEINER. "Introduction to Chemical Thermodynamics." (International Chemical Series.) McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 18, N. Y. 1948. 510 pp. $6.00.