# CELLS WITHOUT TRANSFERENCE FOR pH DETERMINATION

Sir:

Although methods of routine pH-determination have developed rapidly during the last few years, cells with liquid junctions, abandoned in most research work long ago, are still in use. In order to eliminate this source of experimental and theoretical inconvenience Hamer<sup>1</sup> suggested cells of the type

## $H_2$ , $H^+X^-$ + NaCl, AgCl,Ag

The concentration of the sodium chloride added to the solution must, of course, be known and allowed for in calculating the hydrogen ion activity.

For the same purpose we had examined cells of the type

## H<sub>2</sub>, H<sup>+</sup>X<sup>-</sup> + TlBr(satd.), AgBr, Ag

before we had knowledge of Hamer's paper. The solubility of thallous bromide (0.00257 mole per1000 g. of water at  $30^{\circ}$ ) is high enough to secure a definite potential not influenced by common impurities. On the other hand, the solubility is so low that the activity of the hydrogen ion is practically not altered and the liquid junction potential between a solution containing no thallous bromide and a solution saturated with this salt may be neglected safely. Even this liquid junction might be avoided by saturating with thallous

(1) W. J. Hamer, Trans. Electrochem. Soc., 72, 45 (1937).

bromide that portion also of the solution which is in contact with the hydrogen electrode.

The applicability of this type of cell is restricted, of course, to solutions which do not form any precipitate when saturated with thallous bromide and do not contain thallous or bromide ions in an amount comparable with the solubility of this salt. In such a case, however, another reference electrode of similar kind may be used, for instance, some organic zinc salt in connection with zinc amalgam or silver sulfate with silver etc.

Applying the usual formula one may obtain from the e.m. f. the quantity  $a_{\rm H} \cdot (\gamma_{\rm Br} - /\gamma_{\rm Tl} +)^{1/2}$ which is in any case identical with the hydrogen ion activity as far as the principle of ionic strength is valid. In this respect too the method compares not unfavorably with others. This type of cells might prove the most convenient basis of *defining* the term "hydrogen ion activity," which is well known to be arbitrary to some extent.<sup>2</sup>

As we were compelled to interrupt our work on various methods of routine pH determination, we wish to offer this suggestion.

(2) D. I. Hitchcock [THIS JOURNAL, **58**, 856 (1936)] suggested a different definition of pH on the basis of cells without liquid junction and discussed another suggestion made by Scatchard. The general idea of single ionic activities, introduced by Lewis and Randall, has been exhaustively discussed by E. A. Guggenheim (J. Phys. Chem., **34**, 1758 (1930), and previous papers).

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# NEW BOOKS -

Methodik der Hormonforschung. (Methods of Hormone Investigation.) By Dr. Phil. Habil. CHRISTIAN BOM-SKOV. Ovar (Follikelhormone, Gelbkörperhormon), Hoden, Hypophysenvorderlappen. [Ovary (Follicular Hormone, Corpus Luteum Hormone), Testis, Anterior Pituitary.] Georg Thieme Verlag, Rossplatz 12, Leipzig C 1, Germany, 1939. xxix + 1016 pp. 274 figs. 18 × 27 cm. Price, RM. 89; bound, RM. 91.

The work under review forms a second instalment to the volume which bears the same title, noticed in these columns in September 1937 (p. 1771). In the author's view, the subjects here considered constitute the most modern and successful chapters of endocrinology. They are: estrogenic hormones (264 pages), hormones of corpus luteum (72 pages), androgenic hormones (202 pages), hypophyseal hormones (gonadotropic 280 pages, growthstimulating 41 pages, thyreotropic 61 pages, lactogenic 23 pages, diabetogenic 7 pages, others of doubtful existence 22 pages). Of these, only the sex hormones at present offer extensive possibilities for chemical consideration.

As in the first volume, the author has performed his onerous task with conscientious thoroughness, and has prepared a survey notable for catholicity rather than critical selectivity. The compilation as a whole suffers at times from a certain lack of balance. For example, two whole pages are dedicated to a detailed description of Butenandt's procedure for the isolation of estrone from palm kernel oil, whereas reference to studies on the effects of sex hormones on the metabolism of cholesterol and of carbohydrate is dismissed in a few lines of literature citations, without a hint as to the nature of these effects.

Typographical errors are relatively scarce, but a few

stand out, particularly among the structural formulas of the androgens. In this connection the hope may be expressed that in future editions the systematic nomenclature of the steroids will be critically scrutinized for inconsistencies, and that the admirable stereochemical terminology proposed by Fieser<sup>1</sup> will be adopted.

However, in a work of this character, susceptibility to criticism of detail is inevitable, and investigators in the hormone field can only be grateful to the author for collecting in one place the wealth of detailed anatomical and physiological information otherwise obtainable only by wearisome search through a scattered literature. A smaller supplement is promised, which is to include "hormone-like" substances such as the anti-anemic principle of liver and the physiologically active compounds of the posterior lobe of the pituitary.

(1) Fieser, "A Supplement to The Chemistry of Natural Products Related to Phenanthrene," 1937, p. 398, Reinhold Publishing Corp., New York.

H. T. CLARKE

Ions, Electrons, and Ionizing Radiations. By JAMES ARNOLD CROWTHER, Sc.D., F.Inst.P., Professor of Physics in the University of Reading, Sometime Fellow of St. John's College, Cambridge. Seventh edition. Longmans, Green and Company, Inc., 114 Fifth Avenue, New York, N. Y., 1939. xi + 348 pp. 117 pp. 15 × 22.5 cm. Price, \$4.00.

The titles of the different chapters are as follows: I, Introduction; II, The Passage of a Current through an Ionized Gas; III, The Properties of the Gaseous Ions; IV, The Charge on an Ion; V, Ionization by Collision— The Spark Discharge; VI, The Phenomena of the Discharge Tube; VII, Cathode Rays and Positive Rays; VIII, Emission of Electricity by Hot Bodies; IX, Photo-Electricity; X, X-Rays; XI, The  $\alpha$ -Rays; XII, The  $\beta$ and  $\gamma$ -Radiations; XIII, Neutrons, Positrons, Cosmic Radiation; XIV, The Physics of the Nucleus; XV, The Structure of the Atom; XVI, Radioactive Changes; XVII, Radium and its Products.

While the section on cosmic rays and the chapter on the nucleus have been rewritten and very considerably enlarged, it is to be regretted that this procedure has not been used in connection with the other chapters. The result is that many important general references to more recent literature have been omitted, and in some cases statements in one section, copied from previous editions, have not been modified to agree with those made in another section, which are based on the results of more recent investigations. This criticism **applies** especially to statements about the value of *e*, the charge on the electron.

The Bohr-Sommerfeld model of the atom is discussed in some detail, but in spite of the fact that the experiments on electron diffraction are mentioned (rather briefly, and not in the same chapter) the author has dismissed the wave mechanical treatment of atomic structure as "beyond the scope of this volume." A discussion of the "electron cloud" model would have added considerably to the value of the book, especially since it can be done without the use of any difficult mathematics. Furthermore, such a discussion would have helped to clarify the remarks on the wave mechanics interpretation of nuclear phenomena given in Chapter XIV.

Since the book is frankly intended to be an elementary introduction to the field of atomic physics, the author is to be commended for his clear and concise description of the methods used in the determination of fundamental physical constants and of the experiments upon which are based our present concepts in atomic physics. However, it would seem to the reviewer that the whole presentation could have been improved considerably by a rearrangement of the material. For instance, the chapter on atomic structure would logically follow that on X-rays. Moreover, certain sections in some chapters could have been inserted, with much better effect, in other chapters.

The binding and printing of the book are fine, and with the exception of inconsistencies in numerical values, mentioned above, there are very few misprints or errors, as far as the reviewer could find.

SAUL DUSHMAN

Pharmacie Galénique. (Galenic Pharmacy.) By A. GORIS and A. LIOT. Volumes I-II. Masson et Cie., Éditeurs, 120 Boulevard Saint-Germain, Paris VI, France, 1939. xvi + 1917 pp. Illustrated. 17 × 25 cm. Price, fr. 390; bound, fr. 450.

The comprehensive scope of this work can best be realized from the chapter headings, which are:

- Vol. I. History of Pharmacy.
  - Medicaments, Aliments, Poisons, Selection and Preservation of Crude Drugs Composition of Vegetable Substances
  - Assay of Drugs and Pharmaceutical Preparations
  - Medicaments Prepared from Substances in their Natural State without any Previous Treatment Medicaments Obtained after Previous Treatment of the Crude Drugs
  - Medicaments Obtained by Division
  - **Operations Employing Heat**
  - **Operations Employing a Solvent**
- Vol. II. Medicaments obtained by Solution and Evaporation
  - Soluble Ferments
  - Organotherapy (Endocrine Glands)
  - Vaccinotherapy
  - Serotherapy
  - Bacteriotherapy (fermented milk, yeast, etc.)
  - Pharmaceutical Preparations Devised to Mask the Taste of the Medicaments Administered in Definite Dosage
  - Medicaments to be Applied to the Mucous Membrane
  - Medicaments for External Use
  - Dressings (for wounds)
  - Sterilization
  - Disinfection
  - Administration and Action of Medicaments, Incompatibilities
  - Alteration and Preservation of Medicaments

From the above chapter headings it is readily seen that these volumes include much more than Galenical Pharmacy which the title indicates. As stated in the preface, the authors have purposefully omitted bibliographies on the various subjects as the treatise is intended for students and pharmacists rather than the research worker.

The authors have drawn upon commercial pharmaceutical companies and hospitals for many of their illustrations of apparatus. Their illustrations (microscopic) of powdered vegetable drugs are excellent. The illustrations of the endocrine glands in color are also very good.

In general, the subject matter does not adhere as closely to the preparations of the Codex as seems to be the practice of most similar American texts in respect to the U. S. P. and N. F.

The presentation of the chemical relationship of various types of compounds is a very desirable feature. Thus the chemical similarity of the sex hormones, the chemical relation of vitamin A to carotene, the chemical formulas for the cardiac glycosides and the ergot alkaloids serve as examples. However, in the case of the last-named group of compounds, the discoverer of ergostetrine is given as John Hopkins instead of Marvin R. Thompson.

The discussion of the vitamins is excellent but may be criticized from the standpoint of not being entirely up-todate. Thus no mention is made of vitamin  $B_{\theta}$ , or the identity of the pellagra-preventative factor with nicotinic acid. Under vitamin D, the reader is given the impression that irradiated ergosterol is practically the only source of this vitamin. No mention is made of the various dehydro derivatives of cholesterol which are now definitely known to have marked antirachitic properties.

The reviewer feels that these volumes furnish an excellent text for students of pharmacy and a good reference for practicing pharmacists with the exception of at least one phase of the subject. *viz.*, the vitamins, in which they are not up-to-date.

F. W. HEYL

Gärungschemisches Praktikum. (Experimental Fermentation Chemistry.) Second edition. By Dr. CON-RAD BERNHAUER, Professor in the German University in Prague. Verlag von Julius Springer, Linkstrasse 22-24, Berlin W 9, Germany, 1939. xx + 317 pp. 40 figs. 14.5 × 22.5 cm. Price, RM. 15; bound, RM. 16.50.

Introduction of new material and new references has made the second edition 68 pages longer than the first. The main portion of the book consists of fifty-six fermentation experiments on yeasts, bacteria, and molds. Methods for isolation and quantitative determination of fermentation products and intermediary compounds are given. Qualitative and quantitative experiments on the alcoholic, lactic, propionic, butyl, and cellulose fermentations are included. Oxidative fermentations by the acetobacter group and by the molds are well covered. Directions are given for the isolation and culture of many of the organisms used. The probable mechanism of each of the fermentations also is discussed. The literature references are pertinent and fairly complete.

An introduction, a chapter on methods, and an appendix deal with general chemical and bacteriological methods and with industrial aspects of fermentation.

While the book as a whole contains much more practical

information than any other work on fermentation of comparable size, it is, of course, not free from errors. Many of these obviously result from describing, as laboratory experiments, procedures which have been taken almost bodily from the literature and have not been tested as laboratory exercises. For example, on page 165 the directions for ether extraction of lactic acid say merely that 100 cc. of culture is to be extracted with ether. Only the wellinformed reader will know the pH, method, and time of extraction. In the experiment on the ethyl alcohol-acetone fermentation (page 204) the reader is told to determine ethyl alcohol by oxidation to acetic acid, but nowhere in the book is such a method described.

In addition there are many cases where improper procedures are specified. A few examples will be given from the experiment on the acetone-butyl alcohol fermentation (Experiment 29). Fermentation gases for analysis are collected over carbon dioxide-saturated water. Since the fermentation gas contains approximately 40% hydrogen, roughly 40% of this dissolved carbon dioxide will be carried out by the evolved gases. In Experiment 29a, this error would make the apparent volume of carbon dioxide produced about 35% too high.

Acetylmethylcarbinol is determined on a distillate which contains only 80% of the total quantity of this product. The statement is made that under the conditions of the acetone determination, acetylmethylcarbinol reacts with 16 atoms of iodine, whereas the correct value is 6 atoms. In the exercise on isopropyl alcohol formation, grain mash is used as a medium. The reviewer knows of no isopropyl alcohol-forming organism that will grow well on such a medium.

The book is a valuable addition to the literature of fermentation, and presents in convenient form a large number of procedures and numerous references which should be very useful to the fermentation chemist. The experimental procedures given are reliable in outline, but the reader is cautioned against applying them without first consulting the original literature.

M. J. JOHNSON

Micromethods of Quantitative Organic Elementary Analysis. By JOSEPH B. NIEDERL, Ph.D., Associate Professor of Chemistry, and VICTOR NIEDERL, Teaching Fellow, New York University, Washington Square College. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1938. xvi + 267 pp. 53 figs. 15.5 × 24 cm. Price, \$3.00.

The statement taken from the preface that "this book is primarily a laboratory manual for teaching and practicing the methods of quantitative organic microanalysis of pure organic compounds under ordinary laboratory conditions" makes clear the purpose of this book, and the following chapter headings will indicate its scope. The Microchemical Balance; Weighing on a Microchemical Balance; Miscellaneous Weighing Equipment; Miscellaneous Laboratory Utensils; Preparation and Weighing of a Sample for Analysis; Determination of Metals and Residues; Determination of Neutralization Equivalent; Volumetric Determination of Aminoid Nitrogen; Gasometric Determination of Nitrogen; Determination of Carbon and Hydrogen; Determination of Halogens; Determination of Sulfur; Determination of Phosphorus; Determination of Arsenic; The Determination of the Molecular Weight by (1) The Ebullioscopic Method (2) The Cryoscopic Method (3) The Vaporimetric Method and (4) The Osmotic Method; Determination of Alkoxy and Alkimide Groups; Determination of Acetyl Groups; Determination of Active Hydrogen; The Teaching of Quantitative Elementary Organic Microanalysis; Installation of a Laboratory for Organic Microanalysis; General Microchemical Literature and Calculations.

Organic microanalysts should be grateful to the authors for their inclusion and extension of the Nitrogen Reduction Table of Küster-Thiel. The measurement of nitrogen is often carried out above the temperature of  $24^\circ$ , the upper limit of the Küster-Thiel tables, consequently the extension of the table to  $36^\circ$  is particularly welcome.

The present book, together with the English translation of the latest edition of Pregl, should do much to spread the use of microanalytical methods in organic chemical laboratories.

W. M. LAUER

## BOOKS RECEIVED

August 15, 1939 to September 15, 1939

- A. BEVTHIEN. "Laboratoriumsbuch f
  ür den Lebensmittelchemiker." Second edition. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 602 pp. RM. 28.50; bound, RM. 30.
- FRANK O. ELLENWOOD AND CHARLES O. MACKEY. "Vapor Charts and Special Tables for Turbine Calculations." John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 43 pp.
- L. ERHARD, Editor. "Blätter für Technikgeschichte." Sechtes Heft. Verlag von Julius Springer, Linkstrasse 22-24, Berlin W 9, Germany. 82 pp. RM. 4.
- CHARLOTTE A. FRANCIS AND EDNA C. MORSE. "Fundamentals of Chemistry and Applications." The Macmillan Company, 60 Fifth Avenue, New York, N. Y. 542 pp. \$3.00.
- GEORGE R. HARRISON, Editor. "Wave Length Tables." The Technology Press (M. I. T.): John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y. 429 pp. \$15.00.
- JAMES H. HIBBEN. "The Raman Effect and Its Chemical Applications." American Chemical Society Mono-

graph. Reinhold Publishing Corp., 330 West 42d St., New York, N. Y. 544 pp. \$11.00.

- F. H. MACDOUGALL. "Thermodynamics and Chemistry." Third edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 491 pp. \$5.00.
- THOMAS P. MCCUTCHEON, HARRY SELTZ AND J. C. WAR-NER. "General Chemistry. Theoretical and Descriptive." Third edition. D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, N. Y. 685 pp. \$3.75.
- CARL OPPENHEIMER. "Die Fermente und ihre Wirkungen." Supplement, Lieferung 11, and Bibliographie (1924–1938). W. Junk Verlag, Den Haag, Holland. 156 + 128 pp. Fl. 10 + 10.
- WILH. SCHLENK. "Ausführliches Lehrbuch der organischen Chemie." Vol. II. Verlag Franz Deuticke, Helferstorferstrasse 4, Wien I, Germany. 896 pp. RM. 30; bound, RM. 33.
- ALEXANDER SILVERMAN AND ABRAHAM L. ROBINSON. "Selective Experiments in General Chemistry." D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, N. Y. 310 pp. \$2.50.
- FOSTER DEE SNELL AND CORNELIA T. SNELL. "Chemicals of Commerce." D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, N. Y. 542 pp. \$5.00.
- MARY ELVIRA WEEKS. "The Discovery of the Elements." Fourth edition. Journal of Chemical Education, 20th and Northampton Sts., Easton, Pa. 470 pp. \$3.00.
- HARRY BOYER WEISER. "Colloid Chemistry. A Textbook." John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. 428 pp. \$4.00.
- G. H. WHITEFORD AND R. G. COFFIN. "Essentials of College Chemistry." Second edition. The C. V. Mosby Co., 3523 Pine Blvd., St. Louis, Mo. 534 pp.
- "Gmelins Handbuch der anorganischen Chemie, System-Nummer 59, Eisen." Teil C, Lieferung 2. Teil FII, Lieferung 2. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 35, Germany. 280 pp. RM. 33, 224 pp. RM. 27.
- "The Harvey Lectures." Series XXXIV. Delivered under the Auspices of the Harvey Society of New York, 1938-1939. The Williams and Wilkins Co., Mt. Royal and Guilford Aves., Baltimore, Md. 279 pp. \$4.00.
- "Standard Methods for the Sampling and Analyzing of Aluminum and Certain Aluminum Alloys." Aluminum Research Institute, 308 West Washington St., Chicago, III. 31 pp.