

NOTE.

The Diphenylamine Reaction.—In a recent paper,¹ E. M. Harvey has pointed out the various factors affecting this delicate "nitro" and "nitroso" reaction, among others calling attention to the important rôle played therein by the presence of a varying amount of water. My experience with the diphenylamine reaction in the course of a research² on pseudo-muscarine or "synthetic muscarine," *i. e.*, the nitrous acid ester of choline, fully substantiates the important influence attributed to the amount of water present. In testing the chloroplatinates there concerned, the following procedure consequently proved satisfactory and supports the contention. A small amount of the chloroplatinate is crushed and stirred into 10 drops of the reagent (diphenylamine in conc. sulfuric acid) contained in a small porcelain dish, and the mixture is then heated slightly and allowed to cool. Thereupon the mixture is stirred with a thin glass rod which has been moistened with water (but not dripping-wet), and this procedure repeated until the dark blue color of the reaction suddenly appears. It will be noted that the repetition of said stirring (*i. e.*, successive addition of minute amounts of water) after the color has appeared, will at times immediately cause the color to vanish. With this method there is but little danger of missing the concentration favorable for the reaction, but in tests with negative results it seems advisable to repeat several times before drawing conclusions.

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NEW BOOKS.

"Anleitung zum Nachweis, zur Trennung und Bestimmung der reinen und aus Glukosiden usw. erhaltenen Monosaccharide und Aldehydsäuren." By DR. A. W. VAN DER HAAR (Utrecht). Gebrüder Borntraeger, Berlin, 1920. xvi + 345 pp, 14 fig. 16.5 × 25.5 cm. M. 64.

Dr. van der Haar, well known for his researches upon saponins and other glucosides, gives in the present volume practical details for identifying, separating and estimating the various monosaccharides and aldehydic acids obtained in the investigation of glucosides, gums, hemicelluloses and other plant materials. In publishing these results of his laboratory experience, he has rendered the students of plant and sugar chemistry a most valuable and unique service. There are, to be sure, other excellent works upon the glucosides, such as the theoretical treatise by Armstrong and the descriptive account by Euler and Lundberg in Abderhalden's *Biochemisches Handlexikon*, but no laboratory book upon the glucosides has hitherto appeared which gives the student explicit information

¹ Harvey, *THIS JOURNAL*, 42, 1245 (1920).

² *Ibid.*, 42, 1670 (1920).

upon the methods or technique to be employed in special problems of analysis. It was to help supply this deficiency that Dr. van der Haar has written what he very modestly terms an introductory manual.

After a few preliminary pages in which he eliminates from consideration various hypothetical and lesser known saccharides, the author discusses in Chapter 1 the more important constants of the 10 substances with which he is most concerned, *viz.*, the 8 monosaccharides, arabinose, xylose, rhamnose, fucose, glucose, mannose, galactose and fructose and the 2 aldehyde derivatives glucuronic and galacturonic acids. In Chapter 2, brief general directions are given for identifying sugars. Chapter 3 gives a selection of the more important spectral and other qualitative methods for identifying pentoses, methyl-pentoses and aldehyde acids and also methods for their quantitative estimation. In Chapter 4 a similar selection of qualitative and quantitative methods for the hexoses is given. Chapter 5 gives the general principles for estimating sugars both when occurring alone and in admixture. Chapter 6 describes the formation and properties of the hydrazones and osazones of the sugars obtained by use of phenylhydrazine and its numerous substituted derivatives and also gives the respective value of each of these compounds as a means of identification. Chapter 7 describes methods for regenerating sugars from their hydrazones. Chapter 8 gives numerous illustrations of methods for analyzing sugars, examples being given for 28 different mixtures of 2 monosaccharides and for 17 different mixtures of 3 monosaccharides. Chapter 9 gives specific directions for the various processes to be employed in analyzing glucosides and similar compounds. Chapter 10 gives 3 practical illustrations of the methods for more complicated cases, *viz.*, the analysis of the hydrolytic products (1) of apricot gum, (2) of the saponin from chestnut seeds, and (3) of gum tragacanth.

The author's treatment of his subject is upon the whole very careful and exact, the descriptions and observations of methods being based upon his own laboratory experience. Descriptions are given in simple concise language, the advantages and limitations of the various processes being clearly indicated. While the directions are sufficient for advanced students, the book is unsuited for those who have not yet received a preliminary training in the fundamental polarimetric and chemical principles of sugar analysis. In a few cases the description of processes might have been amplified to advantage. In the account, for example, of Bertrand's method for identifying xylose (p. 58) the chemical formula of the double bromide and xylonate of cadmium and the value of a cadmium or bromine determination as a means of identification should have been mentioned in addition to the microscopic appearance of the crystals. Many chemists will, no doubt, prefer in special cases other methods of identification or determination than those described by the author. It must be remem-

bered, however, that Dr. van der Haar's aim has been to give simply his own experience with certain illustrative methods which, although widely selected, are not intended to cover the entire field. The student who has acquired the technique of the processes described in Dr. van der Haar's manual, will have no difficulty in finding his way to other methods and to other applications.

As a helpful practical treatise upon a very difficult and special branch of sugar chemistry, the book deserves a wide recognition and is warmly recommended to all students of the subjects with which it deals.

C. A. BROWNE.

Text-book of Physical Chemistry. Revised and enlarged. By AZARIAH T. LINCOLN, PH.D., Professor of Physical Chemistry, Rensselaer Polytechnic Institute. D. C. Heath & Co., Boston, New York, Chicago, 1920. viii + 609 pp. 102 fig. 13.5 × 20 cm. Price \$3.80.

The first edition of this useful text-book, which appeared in 1918, was reviewed in *THIS JOURNAL*, **41**, 1475 (1919). The present (second) edition has been enlarged by the addition of 2 new chapters dealing, respectively, with electromotive force and with radioactivity, subjects which were conspicuously neglected in the former edition. No other changes have been made, beyond minor corrections, except in the appendix, which contains 2 more tables. The index has not been revised and does not cover the new chapters.

There are some things in the new portions which are open to criticism. The discussion of radioactivity loses in effectiveness by the absence of any mention of atomic structure, some knowledge of which is essential to enable the student to gain a clear conception of atomic numbers and of the chemical inter-relationships of the radioactive elements. The chapter on electromotive force is not free from misstatements, and at times the author seems to forget that he is writing for beginners. A conspicuous example of this is the last paragraph of the chapter, which will probably tax the powers of comprehension of even the advanced student.

On pp. 517 and 518 the symbol $+Q$ is defined and used to represent heat evolved, but a few lines beyond there is an abrupt change in usage, and heat evolved becomes $-Q$ in the same equation. The change is apparently intentional, but it is neither necessary nor logical.

Confusion between the algebraic sign of a term in a general equation and that which belongs to its numerical value in a given case occurs on p. 525, where the equation for the electromotive force of a concentration cell is stated in 2 different forms, to be used according as the negative or the positive ion has the greater speed. One of these expressions (the one preceding Equation 12) is obviously incorrect for the case under discussion. The statement on p. 522 concerning liquid junction potentials, to the effect that for 2 concentrations of the same salt the dilute solution

is always negative, must be a slip, for the author can hardly have overlooked the existence of innumerable neutral salts in which the positive ion is the faster.

On the whole the new portions of the book, though good in some respects, do not seem to the reviewer to reach the standard set by the earlier chapters.

R. G. VAN NAME.

Chemistry and Civilization. By ALLERTON CUSHMAN, A.M., Ph.D., Director Institute of Industrial Research, Inc., Washington, D. C. Ex-Lieut. Col. Ordnance Department, U. S. A. Richard G. Badger, Boston, 1920. 148 pp. 6 illustrations, 8¹/₄ x 5¹/₄". \$2.50 net.

This is a compilation of lectures delivered by Dr. Cushman under the Westbrook Foundations at the Wagner Free Institute of Science at Philadelphia. The book is designed for the cultivated layman, and it constitutes a very pleasant glimpse into the domain of chemistry. It does not pretend to be more than a cursory glance over chemistry in the past, in the service of man, in industry, in war, what it may do in the future, and some modern aspects of the subject. It is evident from the beginning that Dr. Cushman had a good time over it, and this good time he shares with his readers. He considers the historical aspect of the development of chemistry more thoroughly than is the usual habit of writers on popular science, and this feature, in his handling of the subject, has distinct merit and gives the book a quality which is unique among its kind. Usually publishers of books written for the general public have an almost superstitious fear of the history of science, and forget the romance that is connected with it.

It seems a great pity that whenever any of us touches on this point we have to glide over the contributions of the Arabs with only a few generalities. There's no use in blaming the author of the book under discussion in this connection, because it is all that any of us can do. It would be a grand thing to turn Georges Sarton loose in Southern Spain and in Northern Africa with all the needed means and facilities to rescue what remnants of history have been left unshattered by Christian wrath and Mussulman decay from the days when the Crescent enlightened the world. Most of us can merely say "Geber" and there we have to stop.

Rather more in the way of criticism is our comment on the note relating to Robert Boyle, which is good so far as it goes, and includes the well-known likeness with the grand wig. But we hardly think Boyle gets his deserts. With the exception of Agricola, who died when Boyle was 28, the chemists preceding him were frequently addicted to the practises of quackery, while most of the alchemists before them were engaged in efforts to get rich with that quality of expedition which seems to have especial charm for readers of the *Saturday Evening Post*. It was Boyle who made chemistry the profession of a gentleman, and we think he is

entitled to credit for his illumination and his integrity of purpose, even though he was too verbose to encourage even the diligent reader. Boyle set the pace for true research. As for Stahl, who is classed with Isaac Newton and Leibnitz and Boyle, we should be disposed to put him in a class by himself as the greatest of chemical cuttle-fish.

The reason why Benjamin Thompson left Rumford, at Concord, N. H., was then called, and offered his services to the British cause during the Revolution, is given by Dr. Cushman as due to the influence of the British Governor Wentworth, who made a Tory of him. It is a good story and well told, and we have no authorities at hand to prove the author in error. There are, however, conflicting reports to the effect that Thompson sought earnestly to get a commission in the Continental forces without avail, and the reasons why he failed are full of contradictions.

In discussing the work of Pasteur, Dr. Cushman notes that in view of his animal experimentation, he would not be popular if he were living to-day. Imagining that he were alive and active, the author draws a vivid picture of the anti-vivisection ladies "warmed and adorned with the skins of animals that have been cruelly trapped and left to starve to death in their frigid habitats," crowding the corridors to demand in the name of humanity that Louis Pasteur be made to stop his work. The point is worth remembering.

In the discussion on sulfuric acid we are disappointed to find that the author has not soothed the distracted enquirer in regard to the pronunciation of pyrites. Chemists usually make the word sound something like pright ease, whereas metallurgists in increasing number refer to the product in words that are reminiscent of pie rights. We had hoped for an elucidation of this.

In the last chapter on "Modern Aspects of Chemistry" we miss the mention of Arrhenius in connection with dissociation; but we must bear in mind that almost the first requirement of a popular work is that it shall not have the qualities of a catalogue. The volume closes with an appendix on nitrogen supplies compiled by Lieutenant Commander Carleton H. Wright, under the instruction of the author.

The book is replete with little notes and turns that are worth remembering by those who have to lecture on chemistry to laymen or to beginners. For instance, in discussing radium emanation he says it is "like the ghost or astral body of radium itself," and that it "confers for a time the property of radioactivity on other bodies with which it comes in contact." His talk of Einstein's work is simple and direct, his description of the field of colloid chemistry is unusually clear, and his vision into the future is that of a thoughtful and scholarly man.

ELLWOOD HENDRICK.

Chemical Reactions. Their Theory and Mechanism. By K. GEORGE FALK, PH.D.,
Harriman Research Laboratory, The Roosevelt Hospital, New York. D. Van
Nostrand Co., New York. 211 pages. Price \$2.50 net.

This interesting book is an exposition of the electronic conception of valence as it has been applied by the author and Professor J. M. Nelson in numerous articles since 1909.

After a discussion of fundamentals, including evidence for the transfer of a definite quantity of electricity with a change of valence, the author takes up the chemistry of ammonium salts and analogous complexes, showing how his theory brings out most of the relationships discussed by Werner, without the use of any space-conception. The formation and decomposition of ammonium salts is the keynote of the book. From ammonium, the author passes to oxonium, and thence to "onium" salts in general, even including the organic halides as addition products of acids and olefines. The same idea determines his conception of catalysis, and the rôle of the solvent in chemical reactions. In each case there is first formed an addition-product, composed of all substances present, which (whatever its true structure) can be treated theoretically as an ammonium salt in simultaneous equilibrium with all its possible products of decomposition. Such a conception obviously makes it possible to view a surprisingly large number of reactions from a single point of view, though many readers will feel that it flattens the field by ignoring some essential differences. The 2 final chapters are devoted to oxidation and reduction, and also deal with the most difficult part of the subject, the determination of the direction of valence in organic compounds, and the subject of *electromerism*, to which the author still clings as a substitute for geometrical isomerism.

The perusal of the book can be heartily recommended to the conscientious and conservative teacher of organic chemistry who must continually speak of valence, and yet is pained when pressed for a definition. Such a chemist may well be unsatisfied with the traditional organic point of view, but he is unwilling to sacrifice any of its practical advantages, and while at heart he probably believes that it is electricity which binds atoms together, he is conscious that since the days of Berzelius all attempts to found upon this fact a working system helpful to the organic chemist have miserably failed him. Hence he waits with patient scepticism for the perfect electronic explanation "that should come."

It is safe to say that such a reader will lay down this book still unconvinced, but being accustomed to partial explanations, and knowing the helpfulness of many points of view, he will find it illuminating. Even in the treatment of the olefines (which he will regard as a relapse to the etherin theory) he will be pleasantly surprised at the amount of experimental evidence which the author can marshal to his support. Inevitably,

however, he will revolt at *electromerism*, which gives him more compounds than he wants, and furnishes no adequate means of distinguishing between them. Surely this is not a forward step. Walden's inversion and trans-addition exhibit the faults of our present structure theory on the dynamic side, but this is probably an inevitable weakness in all valence conceptions. Our hypothetical reader is sure to believe that molecular asymmetry is one of the most important facts in nature, and that the traditional views account with reasonable adequacy for the number and properties of isomers. If, therefore, he must now adopt some electronic conception of valence, he will be apt to look more favorably upon that of Lewis and Langmuir, which leaves these fundamentals essentially untouched.

In his preface, the author disclaims all intention of discussing the latter theory, or indeed space-conceptions of any kind. It is, therefore, hardly fair to criticise the limitations which he has set himself. Nevertheless, much of the book is, in spirit, an appeal to the organic chemist to forsake the space-conception for the electronic, and this can hardly be successful when the former is not discussed.

The book is agreeably written, the presentation being sober, thoughtful, and entirely free from that spirit of propaganda so common in books presenting an unorthodox point of view. Throughout its pages the author exhibits his wide and discriminating knowledge of the recent organic literature, a revelation which will be no surprise to his friends.

F. J. MOORE.